Institute of Chemistry
Chemical Society of the Republic of Moldova

## International Conference

# ACHIEVEMENTS AND PERSPECTIVES OF MODERN CHEMISTRY

### dedicated to the 60th anniversary from the foundation of the Institute of Chemistry

# BOOK OF ABSTRACTS

October, 9-11 2019
Chisinau, Republic of Moldova

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**Note. The Authors of the Abstracts take the full responsibility for their content/originality.**

# WELCOME

*Dear Colleagues and Friends,*

*We are delighted to welcome you at the International Conference "ACHIEVEMENTS AND PERSPECTIVES OF MODERN CHEMISTRY" in Chisinau and we thank you for attending.*

*We celebrate this year the 60th anniversary from the foundation of the Institute of Chemistry. Starting from the foundation in 1959, the Institute of Chemistry became and still remains, the main centre of chemical research in the republic. During the years, the Institute of Chemistry passed through several structural and research-related reforms. Now the institute includes three scientific centers: the Centre of Physical and Inorganic Chemistry, the Centre of Ecological Chemistry and Environmental Protection and the Centre of Organic and Biological Chemistry.*

*The International Conference is the fifth in the series of conferences organized by the Institute of Chemistry with the generic title "ACHIEVEMENTS AND PERSPECTIVES OF MODERN CHEMISTRY". Bringing together scientists from all over the world with expertise in diverse area covering inorganic and physical chemistry, analytical and ecological chemistry, organic and bioorganic chemistry and not only, this conference is a unique opportunity to share the most recent results and also foster new collaborations between the participants.*

*We thank our distinguished guests from different countries for accepting our invitation to join our celebration, especially our key-speakers who readily accepted to give plenary lectures covering many aspects of chemistry.*

*Last but not least, we wish to thank all the sponsors and institutions for their enthusiastic and much appreciated support of the conference.*

*We hope that the program will stimulate enthusiastic discussions and we wish you a nice stay in Chisinau.*

*Professor Aculina ARICU*
*Director of the Institute of Chemistry,*
*The collective of the Institute of Chemistry*

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**L1**

# THE INSTITUTE OF CHEMISTRY AT 60 YEARS ANNIVERSARY. BRIEF HISTORY, ACHIEVEMENTS AND PERSPECTIVES

Aculina Aricu

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This communication reports about the arising and development of the scientific schools at the Institute of Chemistry that was founded in 1959. The dynamics of several structural and research-related reforms emerged along of the years within the institute are traced. The collaborations of our scientists with colleagues from abroad are also highlighted. Information related to the scientific schools achievements, their leaders and their guidance at our institute-is presented. The relationship of the institute with universities is presented, training of young researchers being underlined as well.

Relevant data concerning the latest main research results in the field of the chemistry of coordination compounds, fine organic synthesis, natural products chemistry, physicochemical analysis, quantum chemistry and ecological chemistry are presented. A detailed record of both fundamental and applied research is given:

- ✓ coordination compounds with various useful properties: polynuclear compounds as molecular magnets, catalysts for technological and biotechnological processes, agents for anticorrosive coating and protection of metals; plant growth stimulators and crop developers;
- ✓ porous transition metal coordination compounds based on mixed ligands and biphenyls containing carboxyl groups, and/or donor nitrogen atoms as potentials sorbents for small molecules;
- ✓ efficient methods for the synthesis of natural analogues of tetracyclic diterpenoids of *ent*-kauranic skeleton containing functional groups in cycles C and D, that include oxygenated and halogenated moieties;
- ✓ *β*-carboline derivatives produced from local vegetable raw materials and cyclic compounds with sulphur and nitrogen heteroatoms with enhanced activity against resistant forms of tuberculosis;
- ✓ hydro-solubilisation of natural polymers (tannins) by cleaving mechanisms resulting in the obtaining of biologically active compounds;
- ✓ optimization of activated carbons obtaining from vegetable by-products and their regeneration procedures;
- ✓ methodologies of investigation of industrial wastes treatment processes through thermodynamic optimization;
- ✓ environmental quality evaluation and elaboration of methodologies for toxic substances impact assessment onto natural waters, soils, sediments and agricultural products.

Perspectives of research development at the Institute of Chemistry will be emphasized.

**L2**

# HYDROGEN PEROXIDE AN OUTSTANDING AGENT IN ENVIRONMENT

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Hydrogen peroxide is a substance playing a key role in the appearance and maintenance of the life-supporting conditions on the Earth. Electron transfer processes between the reducers and oxidants are of major interest for natural, life, technology, food, pharmaceutics, agriculture etc.

Here we investigate the structure and redox proprieties of hydrogen peroxide molecule in model and real systems, trying to find answers to the questions: why this substance has the unique and specific dual reduction-oxidation properties?, how the electron structure of its molecule affects this substance reactions?, what role it plays in the catalytic redox processes occurring in natural environment and technological systems with the formation of intermediates, active radicals, complete and partial charge transfer complexes?, etc. We report the results of our multi-annual studies regarding this subject.

**L3**

# POLYMERS IN DRUG/GENE DELIVERY AND TISSUE ENGINEERING

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**L4**

# POROUS ORGANIC SOLIDS - CLATHRATE *VERSUS* ORGANIC ZEOLITE BEHAVIOUR

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The concept of clathrate compound [1] has been one of major discoveries in chemistry. Originally, it was concentrated on spatial fit between the host and guest components. Soon a physicochemical rationale for defining the stability conditions for clathrate formation was reported [2].

The term clathrate is in frequent use in contemporary scientific literature [3]. There are, however, many ambiguities concerning the appropriate use in different structural situations. At the 1st International Symposium on Clathrate Compounds and Molecular Inclusion Phenomena (Jachranka-Warsaw, 1980) Weber and Voegtle, have presented a proposal for more adequate nomenclature of inclusion compounds. They have suggested two main improvements: (a) structural one, defining more precisely the geometry of inclusion (cage, tubular etc.) and (b) interaction type guest-host, using ‘clathrate’ for systems without any chemical interactions and ‘complex’ for any other.

Taking into account frequent use of the term clathrate, intended mostly as description of mutual geometrical interaction between the components, an advanced nomenclature system would be welcome in order to precisely define the compounds, both structurally and from interaction point of view.

Geometric part of the problem seems rather straightforward (clear description of the host structure) but it may contain specific difficulties related to mutual relationship betwen the host and guest. The same host structure may be of cage type (guest species of adequate size and shape) or zeolite-type (small guest species) or, in some cases, tubular/layered for long chain or planar guest molecules.

Chemical interactions guest-host should conveniently be described in the compound’s name. The general term ‘complex’ is certainly adequate but may be replaced by more specific terms. The term ‘metallic’ would be appropriate for clathrate type structures having metallic type bonding of the guest species (Zintl phases), ‘hydrogen bonded’ for clathrates containing hydrogen bonds guest-host (in addition to the main clathrate type characteristics), covalent or coordination for respective ‘complex’ type clathrates, and ionic for inclusion compounds of, say, cationic species in t he anionic host (e.g. water/halogenide). Structures, called sometimes semi-clathrate, in which functional groups of the guest participate in the host framework, maybe ionic or neutral, depending on the nature of the guest.

In the present paper a novel nomenclature system will be presented and illustrated by respective examples. Evolution of the concept from ‘clathrate’through ‘organic zeolite’ to ‘Metal Organic Framework’ and ‘Covalent Organic Framework’, with the emphasis on the physicochemical properties as related to the crystal structure.

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**L5**

# $[MO_2O_2S_2]^{2+}$ AND $[MO_2O_4]^{2+}$ -BASED COORDINATION CHEMISTRY: FROM SYNTHESIS TO BIOLOGICAL APPLICATIONS

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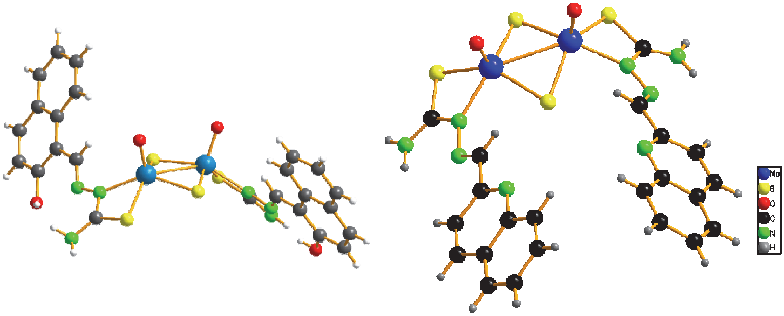
Molybdenum is a very important oligo-element which is involved in more than 50 enzymes. Therefore biological properties can be expected in many different domains as a function of the nature of the ligands coordinated to the Mo atoms. During this presentation, I will endeavor to illustrate the richness of the coordination chemistry we can develop with the small molecular clusters $[Mo^V{}_2O_2S_2]^{2+}$ and $[Mo^V{}_2O_4]^{2+}$ and the resulting biological properties we can get with these compounds.[1-3] A first part of this presentation will be focused on synthesis, characterizations (NMR, MALTI-TOF) and properties of coordination complexes obtained by combining thiosemicarbazone ligands with $[Mo^V{}_2O_2S_2]^{2+}$. A second part will be devoted to more classical coordination compounds obtained with $[Mo^V{}_2O_4]^{2+}$ which revealed very interesting and surprising properties for beekeeping.



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**L6**

# NANOSTRUCTURED MATERIALS FOR BIOMEDICAL APPLICATIONS

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Nanoparticles have unique physical and chemical properties and are ideal elements for creating nanostructured materials for using in medicine and pharmaceutics. The development of magnetic nanomaterials for use in medicine has been intensively developing for diagnosis of diseases, targeted delivery of biologically active compounds, etc. Magnetic nanoparticles (NP) of iron oxides or their composites with hydroxyapatite (HA) are used for the targeted delivery of biologically active compounds (BAC) and have a significant advantage over traditional methods of therapy, since the active substances immobilized on the nanocarrier are protected from chemical, enzymatic and immune degradation on the way to the target of therapy.

A one-stage method of the ultrasonic synthesis of nanocomposites (20-100 nm) with a core/coating structure has been developed. A feature of the proposed schemes for obtaining biocomposites is the presence of 2-arylaminopyrimidine derivatives in the medium of formation of the nanocarrier, which includes nanosized hydroxyapatite and magnetite (HA)$Fe_3O_4$ or ((HA)$Fe_3O_4$)PAD (PAD - polyaldehyde dextran). These nanocomposites can be uses as a system for target delivery of antitumor drugs.

Hollow and gel-containing multilayer microcapsules (protamine/pectin)$_n$ and (protamine/pectin-Ag)$_n$ have been obtained using layer-by-layer technique. The possibility of entrapment up to 50 wt.% imatinib methanesulfonate with efficiency of 85.0 ± 6.0% has been shown. The encapsulated form of imatinib allows prolongation its release in an acidic medium and phosphate-buffered saline for 3-5 hours; in physiological solution and an alkaline medium for 30 hours. Folic acid conjugated chitosan nanoparticles containing up to 49 wt.% imatinib methanesulfonate have been prepared by ionotropic gelation. It has been shown that the active ingredient prolonged releases for 5-6 hours in acidic medium, phosphate buffered saline and physiological solution. Entrapment of imatinib methanesulfonate into biopolymer microcapsules and nanoparticles leads to increase in its antitumor activity in comparison with free form up to 9 times.

**L7**

# HETEROMETALLIC RINGS AS BUILDING BLOCKS FOR SUPRAMOLECULAR ASSEMBLIES

Grigore A. Timco [a], Antonio Fernandez [a], Jesús Ferrando-Soria [a], Inigo J. Vitorica Yrezabal [a],
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Around a decade ago it was proposed that molecular magnets could be used as qubits for quantum information processing [1, 2].

The most studied targets involve preparation of two level systems as possible qubits – either $S = 1/2$ molecules or by using the ground $m_J$ doublets of a lanthanide centre [2].

We are pursuing chemistry to link together heterometallic rings to make large supramolecular structures that bring together multiple such potential qubits [3, 4]. We have shown that we can make supramolecular assemblies of hybrid organic-inorganic [*n*]-rotaxanes where the components of hybrid organic-inorganic rotaxane are the heterometallic octanuclear metallic wheels based on chromium(III) fluoride-carboxylate bridged $[Cr_7M^{II}F_8(O_2C^tBu)_{16}]^-$ rings and the axle is an organic thread which act also as a template for formation of the heterometallic ring about this axle. This route has allowed us to make hybrid organic–inorganic [*2*]- and [*3*]-rotaxanes. Using functionalised 'stoppers' on the axles we can produce hybrid organic–inorganic [*2*]- and [*3*]-rotaxanes that can act as ligands. Then these polymetallic rotaxane-ligands can be used as building blocks (modules) for construction of various supramoleculal assemblies [5].

Routes too much larger structures will also be described which involve heterometallic rings acting as ligands or as parts of hybrid [*n*]-rotaxanes.

Recently we have examined creating hybrid organic-inorganic rotaxanes featuring a new type of metallic wheels based on titanium(IV) oxo-carboxylate bridged $[Ti_7M^{III}O_8(O_2C^tBu)_{16}]^-$ rings [6].

We will also discuss building complex diamagnetic molecules as hosts for our multiple qubit arrays.

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**L8**

# POLYENE MACROLIDE ANTIBOTIC DERIVATIVES: DESIGN, SYNTHESIS, BIOLOGICAL ACTIVITY, OVERCOMING DRUG RESISTANCE, AND PROSPECTS FOR USE IN MEDICAL PRACTICE

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Fungal infections continue to rise because of environmental pollution, increased radiation background, irrational use of broad-spectrum antibiotics, extensive use of cytostatics and immunosuppressants, and several other factors. Invasive mycoses are becoming more problematical for medical practice because of the rising population of immunocompromised patients. Polyene macrolide antibiotics (PMA) such as amphotericin B, nystatin, pimaricin, levorin, candicidin, and others are widely used in medical mycology for treatment of both surface and deep mycoses. However, PMA used in antifungal therapy do not fully meet the needs of physicians because of their limited efficacy due to their low water solubility, high toxicity, and emergence of resistant species of pathogenic fungi. Hence, the search for novel PMA derivatives with improved medical and biological properties is a very urgent target.

In this report, we summarized our investigations on synthesis of various semi-synthetic PMA derivatives that were prepared by chemical modification. It was found that chemical modification, in particular phosphorylation, allows preparing highly efficient PMA derivatives with low toxicity and extended spectrum of biological activity. Biological studies have shown that synthesized semi-synthetic PMA derivatives possessed high antifungal activity against different species of pathogenic fungi and were 3-6 times less toxic than the starting antibiotics.

The additional virological tests have demonstrated that semi-synthetic derivatives of levorin, nystatin, amphotericin B, mycoheptin, and lucensomycin exhibited high antiviral activity against DNA-containing vaccinia virus and RNA-containing oncogenic Rous sarcoma virus and type A and B influenza viruses. The results obtained for hydrophosphoryl derivatives of PMA, concerning their antiviral action against the RNA-containing Rous sarcoma virus, were especially interesting because these experimental data were proposed as a retrovirus model suitable for screening and studying of anti-AIDS drugs.

It was established that the obtained semi-synthetic PMA derivatives were effective against many resistant strains of pathogenic fungi. Thus, dialkyl(diaryl)amidophosphate derivatives of amphotericin B and 3-N-α-dialkoxy(diphenoxy)phosphonate derivatives of pimaricin indicated high antifungal activity against several resistant strains of pathogenic fungi such as *Candida albicans*, *Aspergillus fumigatus*, and *Cryptococcus neoformans*, which cause opportunistic fungal infections occurring in AIDS patients.

In present report, a special attention is paid to an evaluation of structure-activity relationships for synthesized semi-synthetic PMA derivatives. Possible mechanisms of action of these new powerful antimycotics on pathogenic fungi are considered. The prospects of application in medical practice of most effective PMA derivatives (lead compounds), prepared by us, will be discussed.

**L9**

# QUANTITATIVE APPROACH TO THE ASSESSMENT OF ANTHROPOGENIC IMPACT ON THE ENVIRONMENT

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Every year scientists are increasingly involved in the scientific debate on anthropogenic influences and their consequences in relation to climate, the preservation of the ozone layer, increasing greenhouse gas concentrations etc. Often these discussions turn into political disputes, although all these issues are purely physico-chemical and needs to be addressed to methods, primarily of chemical kinetics.

Without exception, all natural ecosystems have been formed for millions of years, and those that have survived to date, undoubtedly have a solid reserve of stability and behave on the principle of homeostat. Any external influence causes an oppositely directed response of the system. The question of the ability of natural systems to self-repair is reduced to the quantitative assessment of two main parameters: (1) the "buffer capacity" of the environment and its comparison with the scale of the disaster; (2) the characteristic times of the attack and its neutralization.

The report examines examples of accumulation and loss of radiocarbon, stratospheric ozone and the potential impact of greenhouse gases on "global warming".

## L10

# DESIGN AND SYNTHESIS OF NEW THIAZOLIDINONE AS WELL AS NATURAL PRODUCT DERIVATIVES AS ANTIMICROBIAL AGENTS

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Despite the rapid progress of science, the treatment of infectious diseases the need for the design of novel antimicrobial agents is even greater for the treatment of infections of hospitalized patients, undergoing organ transplants, anticancer chemotherapy and for patients with and also due to the increased number of pathogenic microorganisms with multiple resistance to drugs.

Heterocycles are capable of binding to receptors with high affinity. During our project on the synthesis of compounds with potent biological action, was testified that many thiazole derivatives act as antimicrobial agents. The antibacterial activity in vitro of synthesized compounds, was determined against human pathogenic bacteria by using the microdilution method. The following Gram-negative bacteria were used: Escherichia coli, Pseudomonas aeruginosa, Salmonella typhimurium, Enterobacter cloacae (human isolate) and the following Gram-positive bacteria: Listeria monocytogenes, Bacillus cereus (clinical isolate), Micrococcus flavus, and Staphylococcus aureus. As reference drugs were used ampicillin and streptomycin.

For the evaluation of the antifungal activity, the following fungi were used: Aspergillus ochraceus, Aspergillus fumigatus, Aspergillus niger, Aspergillus versicolor, Aspergillus flavus, Penicillium funiculosum, Penicillium ochrochloron, Trichoderma viride, Candida albicans and Fusarium sporotrichloides. As reference drugs were used ketoconazole and bifonazole.

In order to evaluate mechanism of action docking studies were performed.

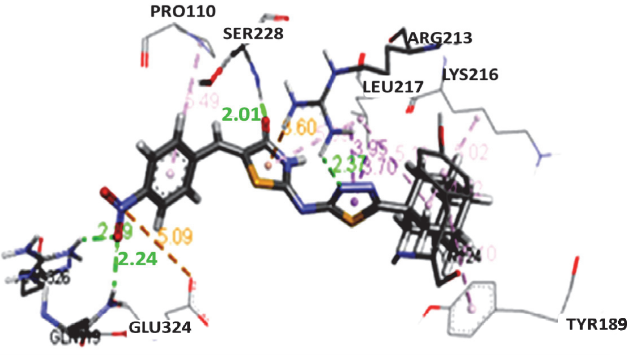

**Figure.** Docking pose of thiazolidinone derivative in *E.coli* Mur B

**L11**

# MONOHETEROATOMIC AZAHETEROCYCLES: MEDICINAL CHEMISTRY APPLICATIONS

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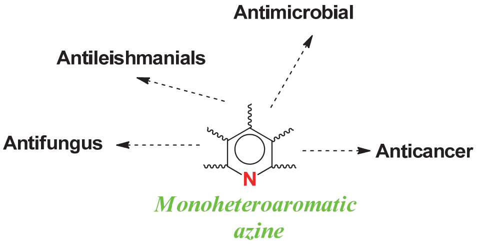
Azaheterocyclic derivatives, particularly monoheteroaromatic azine, were reported as valuable scaffolds in medicinal chemistry, showing variously biological activities such as antiviral and anticancer, antimicrobials, antifungus, anti-inflammatory, antihypertensive, diuretics, antithrombics, anticoagulants, antidepressant, anxiolytics, anticonvulsant, analgesic, etc.

As part of our ongoing research in the field of azaheterocycles derivatives, we present herein some core results obtained by our group in the field of monoheteroaromatic azine, especially pyridine, quinoline and fused quinoline, phenantroline, etc. focused on their medicinal chemistry applications as anticancers, antimicrobials, antifungus and antileishmanials.



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**L12**

# CHEMISTRY AND APPLICATIONS OF NEW STEROIDS: PROMISING PROSPECTS FOR AGRICULTURE AND BIOMEDICINE

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Steroids are a class of physiologically important natural substances which have intrigued researchers for about 200 years. Although being quite well investigated in some respects, they are still a subject of interest for many research groups and industrial companies especially because of their great potential for medicine and agriculture. In the recent decades, steroid research got new powerful stimuli owing to new important discoveries: discovery of steroid hormones in plants (brassinosteroids or BS) and their effects in humans, finding a high anticancer efficacy of new nitrogen-heterocycle-containing steroids active as inhibitors of CYP17A1, reconsideration of the vitamins D role as multifunctional vitally important agents responsible for many processes in a human body.

Studies on chemical synthesis of new physiologically active steroids have been a subject of interest in our Laboratory of Steroid Chemistry quite for a long time, and all the findings mentioned above (as well as some others) influenced our research activities in the recent period. Synthetic studies in brassinosteroid area were among the major directions. They gave us an access to the most important representatives of natural BS and producing technologies for some of them that formed a basis of BS-use in agriculture. At the same time, some problems still needed to be solved. Thus, BS are still rather uneasy available and expensive natural compounds as well as their modified derivatives, which are necessary very often for physiological and mechanistic studies, analytical needs, etc. Very important and mostly unsolved problems relate to a complex character of BS-bioactivity dependence from different conditions and very thin tuning the result by a combination of factors, changes in which can lead not only to desirable but also to opposite effects even for the same species. The third set of problems closely related to practical aspects of BS has their unusually low effective doses as a major reason. In fact, there are no other active ingredients neither in agriculture, nor among medications that act in such small doses as BS do. For some cases this means that existing approaches cannot be applied for necessary BS-studies like it takes place, for example, in studies of their pharmacokinetics in humans. All mentioned above indicates the necessity of further development of synthetic, biological and analytical branches in brassinosteroid research to get them closer to real understanding the physiological machinery in plants and humans and to wide practical use.

Along with studies in BS-area, other directions such as the synthesis of new heterocycle-containing anticancer steroids, anabolics' metabolites, vitamin D derivatives, haptens and conjugates were developed during recent 2-3 years as well. These directions including the data on chemical synthesis, analytical, bio-medical and applied aspects of new obtained steroids will be discussed.

**L13**

# HYDROPHILICITY TUNING AND SHAPING OF MOFS FOR WATER SORPTION IN HEAT TRANSFORMATION APPLICATIONS

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Water-stable MOFs with suitable water uptake capacity are gaining attention for reversible cycling water sorption in order to achieve low temperature heat transformation applications in adsorption heat pumps (AHPs), following our first report [1]. AHPs may be alternatives or supplements to conventional compression systems operating with high input of electricity. By using low grade heat as the driving energy, AHPs can significantly help to minimize electricity consumption. AHPs are based on the evaporation and consecutive adsorption of coolant liquids, preferably water (Figure 1a). The process is driven and controlled by the microporosity and hydrophilicity. Yet, the specific temperature boundaries for evaporation, desorption, heat rejection temperature from the adsorbent and the condenser for a desired cycling water sorption application necessitate the tailoring of the adsorbent in terms of hydrophilicity/hydrophobicity for optimized working conditions, which we have addressed here with a mixed-linker concept of MOF-160/CAU-10-H (Figure 1b) [2]. Further, for applications of MOFs one of the biggest current issues is to find effective methods to shape these microcrystalline, powdery materials into manageable forms such as monoliths, pellets or surface coatings with sufficient mechanical and chemical stability, maximal bulk density etc. under preservation of the crucial MOF porosity properties. We have approached this task successfully with MOF@polymer in different binder composites under retention of MOF porosity and hydrophilicity (Figure 1c,d) [3].

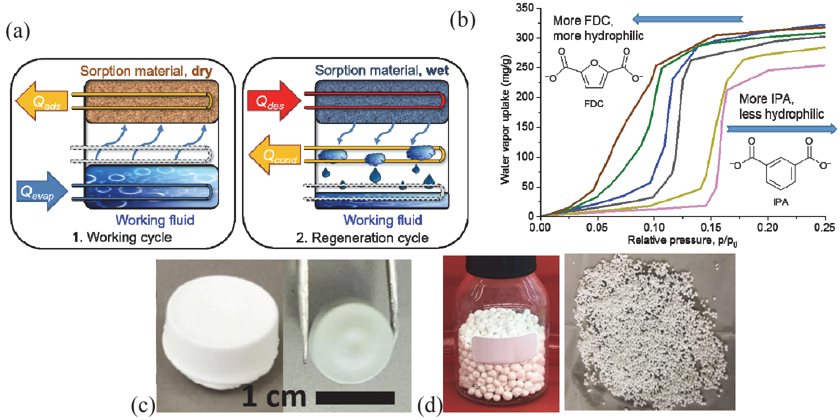

**Figure 1.** (a) Schematic illustration of the principle of adsorption heat pumps with the useful/needed enthalpies. (b) Hydrophilicity tuning through the transition of a mixed-linker Al-based MOF from MIL-160 to CAU-10-H. (c) Shaping of MOFs with polymers into mechanically stable monoliths and (d) shaping of MOFs into robust 1-2 mm diameter grains under retention of MOF porosity.

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**L14**

# TIME-REVERSAL SYMMETRY IN COORDINATION CHEMISTRY

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The time-reversal symmetry is one of the main symmetries in nature. The Hamiltonian $\boldsymbol{H}$ of the system is invariant under the time-reversal operator $\boldsymbol{T}$ introduced in quantum mechanics in 1932 [1]. In particular, there is a supplementary degeneracy of energy levels of a system containing odd numbers of electrons (Kramers degeneracy) as a consequence of the time-reversal symmetry.

It is shown that in coordination compounds with clusters, containing odd numbers of paramagnetic ions with a half-integer spin, there exist not only the Kramers degeneracy of energy levels, but also structural distortions caused by the existence of the time-reversal symmetry. It is due to the specific structure of the corresponding four-color point groups of magnetic symmetry, which do not contain rotation axes of third and fifth orders. We have proved that instability of spin populations occurs in corners of a triangle of isotropic antiferromagnetically coupled ions with respect to weak structural distortions, when the time-reversal symmetry is violated in trihomonuclear Kramers clusters.

We have also proved the theorem [2], according to which the change of the sign of the exchange interaction constant in magnetic binuclear clusters is equivalent to an isomorphic substitution of one of the cluster's ions by an ion (denoted as "time-reversed ion"), whose wave functions are time-reversed with respect to the wave functions of the unsubstituted ion. Based on this theorem, a method of synthesis of binuclear coordination compounds with predictable magnetic properties is proposed. This method consists of presenting the operator $\boldsymbol{T}$ as a product $\boldsymbol{T}_1\boldsymbol{T}_2$, where $\boldsymbol{T}_1$ and $\boldsymbol{T}_2$ are operators of "incomplete" time-reversal ($\boldsymbol{T}_1\boldsymbol{H}\boldsymbol{T}_1^{-1} = -\boldsymbol{H}$, $\boldsymbol{T}_2\boldsymbol{H}\boldsymbol{T}_2^{-1} = -\boldsymbol{H}$), unlike $\boldsymbol{T}_1\boldsymbol{T}_2$, which is the operator of complete time-reversal ($\boldsymbol{T}_1\boldsymbol{T}_2\boldsymbol{H}\boldsymbol{T}_2^{-1}\boldsymbol{T}_1^{-1} = \boldsymbol{H}$). The only symmetry operation, under which the Hamiltonian remain invariant, is "the operator $\boldsymbol{T}_1$ (or $\boldsymbol{T}_2$) + isomorphic substitution of one of the dimer's ion by the time-reversed one". In particular, if the operator $\boldsymbol{H}$ describes the intradimer exchange interaction between paramagnetic ions with electron spins $S_1 = S_2 = 1/2$, then a change of its sign is equivalent to an inversion of the singlet ($S = 0$) and triplet ($S = 1$) spin levels. The isomorphic substitution of one of the binuclear cluster ions by the time reversed ion leads to the same result. One of these transformations violates the time-reversal symmetry, while the other restores this symmetry. As a result, a transformation occurs of the antiferromagnetic exchange interaction dimer into a ferromagnetic exchange interaction one.

The above theoretical predictions are confirmed by experimental data concerning binuclear coordination compounds containing Copper(II)-Copper(II) and Copper(II)-Oxovanadium(II) dimers.

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**L15**

# PENTAGONAL BIPYRAMID COMPLEXES: A JOURNEY FROM MAGNETIC ANISOTROPY TO MOLECULAR MAGNETS

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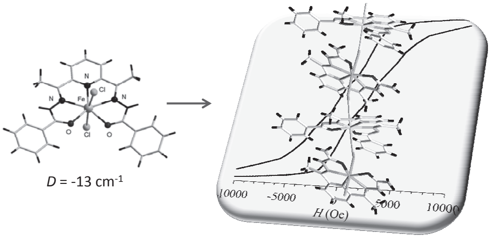
The energy barrier for magnetization reversal of a molecular magnet (i.e. SMM or SCM) is intimately related to the zero-field splitting characteristics ($D$) of its individual building units. However, it is still challenging for chemists to control the actual magnetic anisotropy of the complexes, all the more so when they get involved in the construction of heterometallic magnets.

We will discuss our approach using heptacoordinates 3d metal with pentagonal bipyramid geometry (Figure). In this environment $Fe^{II}$ and $Ni^{II}$ complexes are characterized by significant Ising-type anisotropy (i.e. $D$ ~-15 $cm^{-1}$) [1] and may even behave as single-center nanomagnets [2]. Taking advantage of their exchangeable apical positions, heteronuclear compounds were obtained and indeed found to exhibit slow magnetic relaxation [3]. We aimed also at optimizing two other parameters of importance in nanomagnets, namely the co-alignment of the axis of anisotropy and reduced inter-molecular interactions. This resulted in a CrFe single chain magnet characterized by an energy gap for the magnetization reversal of $\Delta/k_B = 113$ K [4].



$D = -13\ cm^{-1}$

$\Delta/k_B = 113$ K

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**L16**

# NANOSTRUCTURED COMPOSITE MATERIALS FOR ENVIRONMENTAL REMEDIATION FROM MERCURY AND ARSENIC

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Arsenic and mercury are among the top five substances most hazardous to human health affecting millions of people worldwide. The main and probably only approach is to reduce their emissions into the environment and eliminate human exposure to contaminated water, food and other environmental and occupational hazards. A number of technologies for removing As and Hg from water, waste and contaminated land have been developed. Among them, novel selective adsorbents have shown high potential for deep and efficient decontamination of aqueous environment. Nanoporous activated carbon (AC) has shown significant adsorption capacity for both As and Hg species. despite being a non-selective adsorbent. However, AC is considered to be an expensive material even if it is made of agricultural by-products and novel adsorbents are being developed to achieve this goal. The adsorption efficiency of candidate materials for deep decontamination of water has been enhanced by using nanoparticulate adsorbents designed with high selectivity towards Hg or As. We have demonstrated high selectivity of composite adsorbents containing silica or fly ash as a matrix with immobilised silver nanoparticles (NPs) towards inorganic Hg. Nanosilver reacts with Hg forming an amalgam; size-controlled Ag NPs (of 11nm to 45nm size) immobilised on silica surface rapidly and effectively removed mercury from aqueous solution, with 1g of Ag capable of treating > 10,000 m$^3$ of contaminated water (at environmentally-realistic ppb levels of Hg(II)). To solve the problem of high flow resistance of filtration devices packed with micro-/ nanoparticles, we explored two main routes: (i) make 3-D composites of supermacroporous (over 1 μm) polymer hydrogels with embedded target micro- and nanoparticles or entirely carbon 3D structures such as carbon aerogels. Metal nanoparticle-polymer/hydrogel composites were produced by the embedding of reactive nanoparticles into porous gel scaffolds, in particular hydrogels or cryogels. The latter are macroporous gels produced by the polymerisation of water-soluble monomers under freezing temperatures, which are easy to manufacture, and offer controllable permeability, high mechanical strength, chemical stability and shape recovery. Haematite and magnetite nanoparticles embedded in the cryopolymer walls surrounding the macropores were used as adsorbents to remove As(III) from simulated environmental waters, and showed that despite physical embedding of the nanoparticles into the polymer, high nanoparticle reactivity was retained due to short diffusion pathways. Rapid and effective sorption of As(III) was achieved across a wide pH range, even in the presence of competing ions. Highly porous metal–organic frameworks (MOFs) have formed a new, novel and effective addition to technologies for capturing hazardous metal ion pollutants. The structure and functionality of MOFs can be modified to target particular contaminant types and groups. It has been shown that the As(III) uptake by a MIL-100(Fe) MOF (consisting of a porous carbon matrix bearing zero-valent iron magnetic core coated with an Fe-oxide layer and iron carbide) was 3- to 10-times higher than other adsorbent materials, such as graphite/graphite oxide, activated carbon, and pyrolytic carbon.

## L17

# TERPENENOIDS FROM THE HAINAN SOFT CORALS: STRUCTURE, ABSOLUTE STEREOCHEMISTRY AND BIOLOGICAL ACTIVITIES

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Soft corals are marine benthic invertebrates widely distributed in the coral reefs of the world oceans. Of them, the animals belonging to the genera *Sarcophyton, Lobophytum, Sinularia* (phylum Cnidaria, class Anthozoa, subclass Octocorallia, order Alcyonaceae, family Alcyoniidae) are very prolific and are the intense research subjects for marine natural product chemists.

Literature checking revealed that these Cnidaria animals can produce different structural classes of secondary metabolites exhibiting various interesting biological activities ranging from antifouling, anti-inflammatory to cytotoxic activities. Among the metabolites reported, cembrane-type diterpenes are the most frequently encountered. Recently, quite a lot of cembrane-derived metabolites possessing rare and/or unprecedented frameworks were reported. Moreover, biscembranoids, characterized by the complex and highly oxygeneted macrocyclic frameworks, which are formally synthesized from two different cembranoid units via a probable [4+2] Diels-Alder cyclic addition, are unique and typical natural products from soft corals of the genus *Sarcophyton.* Due to the flexible nature of the macrocyclic cembranoids accompanying with the highly diverse substitution patterns, it has been being a challenging task for their structural determination, in particular, the absolute stereochemistry, by natural product chemists.

In this presentation, the latest chemical studies and promising bioactivity of some isolates from the corals of above mentioned three genera collected from South China Sea will be reported. All work has been performed in close collaboration with marine biologists and with pharmacologists.

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**L18**

# HIGH–PERFORMANCE OF GAS HYDRATES CONFINED IN NANOPOROUS SOLIDS FOR $CH_4$ AND $CO_2$ STORAGE

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The discovery of sediments deep under sea and in the permafrost containing methane molecules in the form of gas hydrate has opened a wide range of potential applications for energy storage. Gas hydrates are crystalline inclusion compounds that are formed when small guest molecules contact water in specific pressure and temperature conditions (below 10ºC, above 3.5 MPa) [1]. In the specific case of methane (the main component of natural gas), sI hydrates can store one molecule of methane for every six molecules of water, i.e. a maximum of 180 volumes (STP) per volume. Hence, artificial methane hydrates can be anticipated as a feasible alternative for storage and transportation of natural gas at much lower cost and safer than the current technologies, e.g. liquid natural gas and compressed natural gas.

Despite the promising performance of gas hydrates, their nucleation and growth is an interfacial phenomena associated with very slow kinetics. However, recent studies from our research group have shown that activated carbons with a widely developed porous structure and a proper surface chemistry can be promote the nucleate and growth of gas hydrates (methane) under milder conditions than nature (2ºC and 4-6 MPa), with faster kinetics (within minutes) and with a stoichiometry that mimics natural hydrates [2]. Similar experiments using MOFs have shown that besides the porous structure, the surface chemistry (hydrophobic/hydrophilic character) is of paramount importance to define the water-framework interactions, and consequently, the water-to-hydrate yield [3].

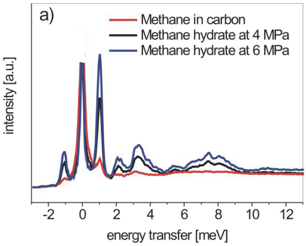

**Figure.** INS spectra of methane on dry and wet activated carbon [2].

**Acknowledgements.** This work was supported by MINECO (Project MAT2016-80285-P) and GV (Project PROMETEOII/2014/004).

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**L19**

# EXPLOITATION OF SECONDARY RAW MATERIALS: APPLICATION OF INNOVATIVE PROCESSES FOR VALORIZATION OF MINING WASTES

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The use as secondary raw materials (RMs) from marginal resources as industrial wastes, such as the WEEE (Waste Electronic Electrical Equipment) and the mining wastes, is of strategic importance for European industrial production, for economic and environmental reasons, due to their high concentration on valuable metals [1].

The availability of RMs is fundamental for the economy of the European countries and essential for maintaining and improving the standard of living of citizens. European Union (EU) is almost completely dependent by RMs. Several external countries have dominant supplies of RMs, mainly USA, Brazil and China.

Ensuring access to certain RMs, is becoming a growing concern in the EU and around the world. RMs (i.e. gold, silver, copper, zinc, manganese and nickel) and critical raw materials (CRMs) (i.e. platinum, indium, cobalt, vanadium, magnesium, antimony, niobium and rare hearts such as scandium, yttrium and lantanoids), are essential for many industrial activities, for the application of emerging modern technologies and for the environment [2]. It is therefore important the development of environmentally friendly processes, to achieve RMs and CRMs of economic interest, by exploitation of the secondary RMs.

The advancement of innovative bio-hydrometallurgical integrated circuit experimentally developed, compared with the conventional processes, is given by the lowest environmental impact and energy consumption and by the greater degree of purity of the valuable metals obtained: these sustainable technologies have been applied to the treatment and exploitation of mining tailings.

Gold extraction by thiosulphate leaching represents an example of the application of these new processes: Au extraction of 80% was experimentally obtained after leaching, under ambient conditions of temperature; moreover, the overall process achieved about 70% Au recovery, this being in line with the conventional cyanidation process. These results are very encouraging, considering that this is a commercially innovative process, applied to a low gold content ore (from 1 to 3 g/t). The optimization of process parameters and operating conditions-should permit the best results in terms of process yields to be achieved.

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**L20**

# *AB INITIO* INVESTIGATION OF MAGNETIZATION BLOCKING IN SINGLE-MOLECULE MAGNETS

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The magnetic anisotropy of complexes with strong spin-orbit coupling effects started to be successfully investigated in the recent years by state-of-the-art *ab initio* methods [1,2]. The blocking of magnetization in these complexes is found to depend crucially on the smallness of transversal Zeeman interaction or intrinsic tunneling gaps on the metal ions, i.e., on their *magnetic axiality*. The examples include single- and polynuclear Ln complexes, as well as mixed lanthanide - transition metal (TM) compounds.

In this presentation, the recent achievements in the theoretical study of blocking of magnetization in strongly anisotropic magnetic complexes will be overviewed. First, complexes involving one single lanthanide ion will be considered, for which the quantum tunneling of magnetization and the activated regime of magnetic relaxation will be discussed. In the second part, polynuclear lanthanide complexes will be described for which the interplay between the anisotropy of individual ions and the exchange interaction between them will be emphasized. Finally, the mixed 4f-3d complexes will be considered for which we will demonstrate the existence of two relaxation regimes, of intra-ionic and of exchange-blocking origin [3,4].

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**O1**

# MODIFICATION OF NATURAL ANALCIME

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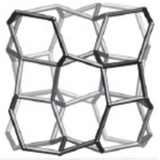
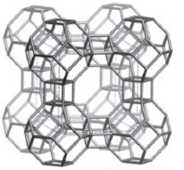


Analcime is usually referred among the commonly used natural zeolites, but its application is limited due to peculiarities of crystal structure. The possibilities of analcime modification are not well understood, and the purpose of our report is to demonstrate the new data on the results of the acid treatment of natural analcime samples from the Chachubeti (A-Cha) and Gelati (A-Gel) manifestations, Eastern and Western Georgia, respectively.

Acid treatment of the grinded samples (0.063-0.1 mm) at a solid:liquid ratio of 1:10 was carried out in aqueous HCl solutions of different concentration at a controlled temperature. Fast and significant removal of aluminum from the analcime crystalline structure occurs at low concentration of the acid, but high degree of dealumination (Si/Al>7) is unattainable even after protracted treatment in high-concentrated acid solutions. Removal of aluminum at acid concentration over 0.5 N can be expressed in terms of the relative aluminum content $C(N)=0.42(2)[1+1.38(7)\exp(-0.20(2)\cdot N)]$. The process of acid mediated dealumination in analcime is of a general nature, but removal of alkali and alkaline earth cations is specific for samples of different origin. X-ray diffraction patterns and IR-spectra of treated samples show partial decomposition of zeolite crystal structure, but the main peaks and IR-bands, especially structure-sensitive oscillations are remained even after treatment in 10N solution. The water adsorption capacity of micropores increases from ~2 to ~7 mmol/g for samples treated in diluted solutions (0.1-1.0 N), but decreases to 7 mmol/g at higher concentrations. Total benzene adsorption capacity after acidic treatment gradually increases with the increase of the acid concentration (from 0.4 to 1.3 mmol/g for A-Cha, and from 0.5 to 1.7 mmol/g for A-Gel). Pore size distribution curves of treated samples show a developed system of mesopores with sizes up to 200 nm and with total volume up to 0.05 cm$^3$/g. Thus, acid treatment allows to obtain micro-mesoporous adsorbents with a fairly high capacity. Preliminary thermal treatment at 300-700ºC makes analcime more resistant to acid, mesopores have low specific volume and narrow distribution of sizes up to 60-100 nm.



Preliminary acid treatment of natural analcime gives possibility to prepare commercially valuable Linde Type A (LTA) zeolite by simple hydrothermal crystallization. Processing of raw in target material also includes steps of suspension of treated analcime, gel formation and its aging followed by crystallization at temperatures up to 90ºC. The reaction mixture of $3.4Na_2O:Al_2O_3:1.1SiO_2$ results in product $0.92Na_2O\cdot Al_2O_3\cdot 2.04SiO_2\cdot 3.00H_2O$, characterized by the X-ray powder diffraction pattern and IR spectrum typical for the LTA framework (crystal chemical formula $|Na_{12}(H_2O)_{27}|_8[Al_{12}Si_{12}O_{48}]_8$-**LTA**), but the amount of water molecules in a synthetic zeolite is different from the number in the ideal LTA structure. According to experimental data, hydrated materials are produced by analcime recrystallization at low temperatures, hydrothermal crystallization at high temperatures (>80ºC) results in dehydration; lowering acidity of reaction mixture results in creation of LTA structure with high aluminum content (Si/Al≈1), rapid crystallization generates nanoscale crystals and aggregates, while slow crystallization at comparatively low temperatures gives micrometric crystallites.

**O2**

# HYBRID PHOTOPOLYMERIZED NANOCOMPOSITES USED AS PHOTOCATALYSTS FOR ORGANIC POLLUTANT DEGRADATION

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Metal nanoparticles have attracted considerable scientific attention due to their interesting characteristics and enhanced physical and chemical properties as compared to the conventional bulk materials, reason for that they are widely employed in various application such as catalysis, sensors, biomedicine, optoelectronics or solar cells manufacturing. Their quality of absorbing light in a large domain of the solar spectrum (visible and UV light) is intensively exploited in the design of efficient photocatalytic materials active in sunlight, and have already been tested for a variety of reactions, from mineralization of organic pollutants to fine organic reactions. Good candidates for this application are semiconductor materials (e.g. $TiO_2$, ZnO, $CeO_2$) and noble metal nanoparticles (NPs) (Au, Ag). The selection of the polymer substrates for the immobilization of the active catalyst particles is motivated by several advantages displayed by them, such as: environmental stability, chemical inertness and resistance to ultraviolet radiations, mechanical stability, low prices and easy availability. Additionally, the use of polymer nanocomposites as photocatalysts offers the possibility of a facile separation and reuse of the materials, eliminating thus the post-treatment separation processes and implicitly reducing the costs of the procedure.

From our point of view, the most convenient technique to prepare polymer-NPs materials with catalytic properties is the photocuring technology (photopolymerization/ photocrosslinking of a mixture of acrylic monomers and premade NPs or NPs precursors) because is very simple, non-invasive and does not require expensive devices, finally resulting flexible free-standing polymer films. Our group focused on the development of new catalysts based on $TiO_2$ [1-3], ZnO [4] or noble metal (Ag, Au) NPs [5] immobilized in a photocrosslinked matrix, which were further tested in photodecomposition of some model pollutants such as phenol derivatives or organic dyes. The performed studies were mainly targeted on the preparation, photocatalytic activity, strategies directed toward the increase of photocatalytic efficiency under visible-light and reuse of the hybrid polymer catalysts.

## Acknowledgement

This work was supported by a grant of Ministry of Research and Innovation, CNCSIS-UEFISCDI, project number PN-III-P1-1.1-TE-2016-1390 (34/02.05.2018), within PNCDI III.

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**O3**

# QUANTUM CHEMISTRY IN REPUBLIC OF MOLDOVA – POSSIBILITIES AND PERSPECTIVES

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A brief overview of the main achievements of the Computational Chemistry Group of the Laboratory of Quantum Chemistry of the Institute of Chemistry over the last 10 years is outlined. First of all, some progress was made in the development of the theory ofJahn-Teller effect (JTE) and pseudo JTE (PJTE), which was the main scientific theme of the laboratory for many years since its organization at the Institute of Chemistry. A new approach to handle instabilities and structural changes in molecular systems due to their interaction with another molecular systems or with a solid is worked out based on an approximate evaluation of the JT and PJT effects in systems with fractional charges that occur due to orbital charge transfers. Applications to specific coordination compounds demonstrate the predictive power of the theory and its efficiency in rationalization of the experimental data (see, for example, [1-3]).

Over the last five years, a new method has also been developed to analyze the influence of changes in the PJTE in molecular systems by means of external perturbations (such as excitation, oxidation, reduction, chemical substitution) on the subsequent change in their geometry and related properties. The method provides some clues to manipulate the structure and properties of molecular system [4-8].

Based on quantum-chemical calculations, the mechanisms of a number of chemical reactions have been clarified,among them are: decomposition of hydrogen peroxide catalyzed by Fenton's reagent, and manganese mono- and binuclear complexes [9,10], chemical activation and hydrogenation of white phosphorus in reaction with rhodium trihydride complex [11], accelerateddecomposition of fungicides on the wet $TiO_2$ surface under solar irradiation [12], *etc.* Some progress has also been made in a comparative study of the antioxidant activity of dihydroxyfumaric acid and its derivatives in the reaction with the stable radical DPPH* [13]. Moreover, the role of additives (such as $TiO_2$) in enhancing the antioxidant properties of organic compounds has been clarified.

As part of the study “structure-properties”, for a number of organic liquids the regression equations for the “structure-surface tension” relationships were developed, which allow us to bind this macromolecular parameter of liquids with the parameters of their electronic structure, which in turn can be estimated using quantum chemical calculations [14,15].

The perspectives for the development of this branch of physical chemistry in our country are also discussed.

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**O4**

# MIXED-VALENT TRINUCLEARCOBALT COMPLEXES WITH *N,N'*-BIS(2-HYDROXY-3,5-DIMETHYLBENZYL)-*N,N'*-DIMETHYL-1,2-ETHANEDIAMINE

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*N,N'*-bis(2-hydroxy-3,5-dimethyl)-*N,N'*-dimethyl-1,2-ethanediamine($H_2$hdde) is an interesting tetradentate ligand with an $N_2O_2$donor set, affording oligonuclear systems such as $[Mn_3(Hdde)_2(CH_3COO)_2(CH_3O)_2]$[1], $[Ni_4(hdde)_2(CH_3COO)_4]$ [2], $[Ni_6(hdde)_3(OH)_4(NO_3)_2(H_2O)_2]$[2], and $[Ni_7(hdde)_3(OH)_6(dmac)_3](ClO_4)_2$(dmac = *N,N'*-dimethylacetamide) [3] complexes. This might be due to the non-planar geometry of the $H_2$hdde ligand [4]. There have been considerable interests incobalt complexes, because cobalt ion becomes paramagnetic and diamagnetic properties depending on the oxidation state. In this study, we studied synthesis of cobalt complexes with $H_2$hdde ligand.The isolated complexes were characterized by elemental analyses, IR and UV-Vis spectra, and single-crystal X-ray structure analysis, elucidating the chemical formula of$[Co_3(hdde)_2(CH_3COO)_2(OH)_2]$ as shown in Figure. We report here the synthesis, crystal structures, and magnetic properties of these mixed-valent $Co^{II}Co^{III}$complexes together with other complexes.

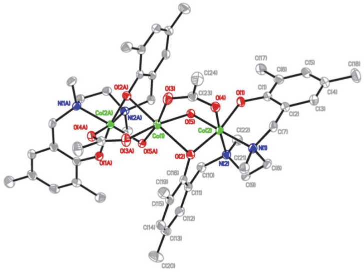

**Figure**. The crystal structure of $[Co_3(hdde)_2(CH_3COO)_2(OH)_2]$.

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**O5**

# PHOTOCATALYTIC PERFORMANCE OF POLYMERIC HYBRID COATINGS CONTAINING ZnO NANOPARTICLES

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Intensive studies were recently focused on the synthesis of hybrid materials, composed of both inorganic and organic elements, displaying remarkable and enhanced properties compared to unfilled resins, characteristics that may trigger their applicability in sensors, photocatalysis, environmental purification, solar cells or antibacterial materials [1-3]. However, polymer/nanoparticle composites could present issues regarding immiscibility between the two phases and consequently, to uniform distribution of nanoparticles within the polymer network. These drawbacks could be overpassed, on one hand, by the UV light rapid photopolymerization of acrylate/methacrylate multifunctional monomers and oligomers. This represents an environmentally friendly approach which allows the formation of polymer networks through a fast transformation of the liquid monomers/oligomers into thin films, with novel and tunable physical, chemical and mechanical properties. On the other hand, another viable strategy is the functionalization of preformed nanoparticles with organic molecules, providing thus an enhanced compatibility between phases and a better dispersion into host polymeric networks.

In the field of photocatalysis, ZnO became one of the leading candidate because of its unique characteristics, such as high catalytic activity, optical sensitivity, universal biocompatibility, and high chemical stability, reason for that has been successfully applied in catalysis [3], water treatment technology [4], cosmetics [5], etc. However, the use of ZnO nanoparticles in photocatalytic process under visible-light is limited by its large energy gap ($E_g$= 3.37 eV), reason for that doping with noble metal nanoparticles (Au, Ag, Pt, Pd) seems to be a convenient alternative and has gained significant scientific interest. Taking in consideration all these aspects, the present paper will describe the functionalization of ZnO nanoparticles with silane derivative and immobilization into polymeric matrices in tandem with the *in situ* photogeneration of noble metal nanoparticles, aiming the improvement of the photocatalytic activity in visible light. The chemical and morphological characterization of final composites will be also performed, in tandem with the evaluation of the photocatalytic activity and reusability of the proposed hybrid composite coatings.

**Acknowledgements**. This work was supported by a grant of Ministry of Research and Innovation, CNCSIS-UEFISCDI, project number PN-III-P1-1.1-TE-2016-1390 (34/02.05.2018), within PNCDI III.

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**O6**

# STATUS AND PROSPECTS OF METALFERRITES IN ENVIRONMENTAL CATALYSIS AND ADSORPTION

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The general formula for metal ferrites is given as $M^{2+}Fe^{3+}{}_2O_4$, with M (i.e., $Mg^{2+}$, $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, and $Cu^{2+}$). These are a class of compounds characterized by high stability, developed surface, small particle size, and excellent magnetic characteristics. Those characterizations determine their prospects for catalysts in Fenton-like reactions. The better efficiency of metal ferrites as compared to iron oxides is mainly due to the formation of $^{\bullet}OH$ radicals where the participation of $Fe^{3+}$ ions is augmented by $M^{2+}$ ions. It is important to note that in addition to catalytic properties, metal ferrites are also used as potential adsorbents [1].

This study describes the results of magnesium ferrite nanoparticles application for efficient catalytic degradation of organic dyes and pharmaceutical compounds and heavy metal ions adsorption. It was shown that magnesium ferrite can serve asan effective material for catalytic and adsorption treatment of multi-component aqueous solutions containing organic pollutants and toxic metal ions [2, 3]. The main results divided into following sections:

(i) High level of efficiency of $MgFe_2O_4$ Fenton-like catalyst under visible light was shown. The effect of transition metals sorption on catalytic activity was studied. For all catalyst's mineralization of ibuprofen and methylene blue up to 98% in 30 min was achieved. $MgFe_2O_4$ fully retained the initial activity after 4 cycles of organic pollutants degradation. A catalytic mechanism in metal-loaded $MgFe_2O_4/H_2O_2$ systems was proposed.

(ii) $MgFe_2O_4$ nanoparticles as a magnetic sorbent was synthesised by glycine-nitrate method. The prepared sorbent showed high adsorption capacity ($2.30 mmol.g^{-1}$) for $Co^{2+}$. The sorption equilibrium was achieved very quickly within 20–60 min. Firstly $MgCl_2$ solution was proposed for $MgFe_2O_4$ sorbent regeneration. $MgFe_2O_4$ sorbent can be efficiently used in adsorption-desorption cycles.

(iii) Firstly, the unusual behavior during $MgFe_2O_4$ regeneration after methylene blue adsorption was established. It was shown that the concentration of desorbed MB was much less than what had been previously adsorbed and did not correlate with regeneration efficiency. The possible mechanism of $MgFe_2O_4$ regeneration by $OH_3^+$ and $Mg^{2+}$ was proposed. The great role of specific adsorption and the super-equivalent adsorption of $Mg^{2+}$ ions was shown. The observed phenomena of $MgFe_2O_4$ regeneration using $Mg^{2+}$ ions must be taken into account in the theory and practice of adsorption.

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**O7**

# GAS PHASE ISOPRENE CHEMISTRY
# PRODUCTS, KINETIC AND MECHANISTIC INVESTIGATIONS

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Volatile organic compounds (VOCs) are emitted to the atmosphere from biogenic and anthropogenic sources. The reactivity of VOCs toward atmospheric relevant oxidizing species results in an appreciable contribution to photooxidants and secondary organic aerosols (SOA) formation. Direct emissions of VOCs as well as their chemical degradation products are associated with effects on climate and human health [1].

Isoprene comprises half of total non-methane volatile organic carbon emitted to the atmosphere by the biosphere. The gas phase chemical degradation mechanism of isoprene is very complex and despite years of research studies is still poorly understood. Ozonolysis of isoprene releases mainly primary carbonyl products, methacrolein, methyl vinyl ketone and formaldehyde but also $HO_x$ radicals *via* the Criegee mechanism. Determination of OH and peroxy radicals ($HO_2$) from isoprene ozonolysis is of the utmost importance especially for the low $NO_x$ environment specific for remote area.

Investigations on the ozonolysis of isoprene over a large range of temperature, relevant for atmospheric conditions, will be presented in this study. Temperature dependent formation yields were determined using two OH radicals scavengers (CO and cyclohexane to scavenge >97% OH radicals). The results are compared with those yields estimated from a gas phase chemical degradation model based on the Master Chemical Mechanism (MCM). The study investigated the formation yields of methacrolein (MACR), methyl vinyl ketone (MVK), formadehyde, OH and $HO_2$ radicals over the range 263–343K using HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry) chamber from Leeds, UK, employing FTIR (Fourier Transform infrared spectroscopy) and GC-FID (gas chromatography flame ionisation detector) for isoprene, MACR, MVK and formaldehyde (only by FTIR) detection and FAGE (Fluorescence Assay by Gas Expansion) for the detection of OH and $HO_2$.

Most important products from isoprene ozonolysis are $HO_x$ radicals. $HO_2$ yields measured using FAGE instrument are obtained at low $RO_2$ interference contribution (< 5%). OH radical formation yields determined at room temperature were obtained using three different methods:i) kinetic method - pseudo first order kinetic experiments in the presence and absence of an OH scavenger; ii) tracer method - following the tracer concentration decay and iii) direct measurement - determination using FAGE-HIRAC instrument and fitting the OH temporal profile.

These results will be highlighted in accordance with the latest findings on isoprene chemistry.

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**O8**

# IMPROVING PHYSICAL AND CHEMICAL PROPERTIES OF INDUSTRIAL GLASSWARE BY DEALKALIZATION WITH GASEOUS REAGENTS

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The efficiency of glass utilization significantly decreases due to its low mechanical strength and bad thermal stability, losses during the stages of production, transportation and storage amounting to 5 %. Different methods for improving the mechanical and thermal properties and chemical resistance of industrial glassware have been developed. A substantial drawback of most methods is the necessity to change the glassware manufacturing technology.

The aim of the undertaken experiments was to investigate the influence of thermochemical treatment by gaseous reagents on the physical and chemical properties of industrial glassware.

Objects of investigation werevarious types of industrial glassware: containers (bottles, jars and flasks) of transparent colorless glass, bottles and flasks of green glass, sheet glass samples, ampoules made from medical glass, insulators made from alcali-free glass, illuminating glassware made from transparent colorless and milk glasses, laboratory and assorted glassware etc. Sulfur oxide, nitrogen oxides, carbon oxide, hydrogen fluoride and chloride, difluorodichloromethane, difluorochloromethane and mixtures of these gases were used for the chemical treatment of glassware.

Experiments were held in laboratory and industrial conditions. In laboratory glass samples have been subjected to treatment by gaseous reagents in the following regimes: temperature – between 300 and 600 $^0$C, duration – between 1 s and 2 h, quantity of gaseous reagent introduced into the reacting vessel - between 0.01 and 1.00 mol.

Thermochemical treatment by gaseous reagentsin laboratory experiments increases water resistance of industrial glasses by 5-8 times, acid resistance - by 6-7 times, alkali resistance - by 20-30 %, central symmetrical flexural strength - by 50-70 %, impact strength - by 30-50 %, thermal stability and microhardness - by 10-15 %.

The main regimes of hollow glassware thermochemical treatment by gaseous reagents on processing lines are the following: temperature - between 450 and 900 $^0$C, volume of gaseous reagent per one unit of glassware - between 0.05 and 10.0 mL, duration - between 1 s and 30 min. Glassware was treated by gaseous reagentsin different places: final blowing of containers, conveyor for transportation of glassware towards annealing and lehr. The reagents were fed into the glassware mainly in gaseous state and in the form of solutions and solid substances.

The mechanical strength of jars, bottles and flasks is characterized by resistance to internal hydrostatic pressure. Additionally, jars were tested for resistance of compressive force in the directions of vertical axis to the body and the resistance of compressive force in directions perpendicular to the body walls.

Subjected to thermochemical treatment, chemical stability of glass increases by tenfold, the mechanical strength - by 15-25 %, the microhardness and thermal stability - by 10-15 %.

The experiment helped to develop optimal regimes of thermochemical treatment of industrial glassware subjected to gaseous reagents in laboratory and industrial conditions.

**O9**

# APPLICATIONS OF GRAPHENE OXIDE IN WASTEWATER TREATMENT

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Water pollution is one of the most important worldwide environmental concern. More than 80% of sewage in developing countries is discharged untreated, polluting rivers, lakes and coastal areas. The clothing industry is the second largest polluter in the world, and alsotremendous consumer of water, dyes and various processing chemicals that are used during the textile processing.Graphene oxide-based composites (GO) are potentially applicable in environmental applications. Due their two-dimensional plane and one-atom thickness, GOoffer superior specific surface area for elimination of numerous substances, including heavy metal ions ($Cd^{2+}$, $Pd^{2+}$, $Hg^{2+}$, $Cr^{6+}$, $As^{3+}$, *etc.*), synthetic or natural organic molecules (dyes), pharmaceuticals (antibiotics), agriculture molecules (pesticides), biomolecules (proteins, DNA, etc.) or mixtures (oil/petrol) [1]. Recent studies have reported electrochemical oxidation, photocatalysis, adsorption, and sonocatalytic as effective techniques for the treatment of assorted wastewaters.

The objective of this study was to employ GO for the surface coating of the stainless steel (SS) using electrophoretic deposition technique. The new GO-SS electrode was used for electrochemical oxidation of commercial textile dye Reactive Black 5. Oxidants were obtained during the process directly at the electrode surface or indirectly from chemical compounds in the treated water [2]. The initial dye compounds were degraded to smaller and more polar compounds (aldehydes, carboxylic acids, inorganic compounds, carbon dioxide, water and minimal amount of secondary pollutants).The surface deposition of the stainless steel electrode by GO will provide more active surface area for adsorbing chargers and thus, will increase efficiency of electrochemical oxidation in wastewater treatment.The large specific surface area and abundant functional groups make GO a strong candidate for wastewater treatment.

**Keywords:** wastewater treatment, graphene oxide, electrophoretic deposition, electrochemical oxidation

## Acknowledgements

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**O10**

# POLYFUNCTIONAL INHIBITORS BASED ON SOME 3d METAL COORDINATION COMPOUNDS WITH SUBSTITUTED SALICYLIDENE- AND PICOLIDENE-4-ALLYL-S-ALKYLISOTHIOSEMICARBAZIDES

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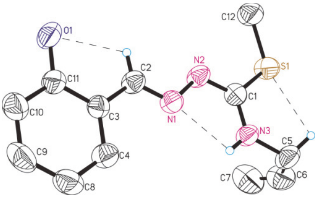
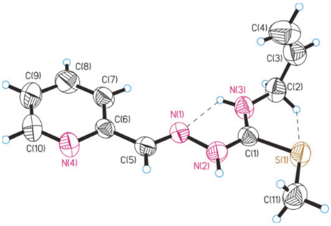
Thiosemicarbazones and their metal complexes attract constant scientific interest due to their antibacterial, antifungal and antitumor activities. In the recent years, a number of thiosemicarbazone derivatives have been synthesized and their biological activities were evaluated. Therefore, it is of interest to study the influence of thiosemicarbazide's alkylation on the composition, structure and properties of transition metal complexes with these ligands. Isothiosemicarbazones have shown different coordination modes and are a potentially biologically active class of ligands because, compared with thiosemicarbazones,the alkylated sulphur atom remains uncoordinated at complexation in many cases with the exception of complexes of platinum metals.



2-hydroxybenzaldehyde-
4-allyl-S-methylisothiosemicarbazone



2-formylpyridine 4-allyl-S-
methylisothiosemicarbazone

The aim of this work is to find the conditions of synthesis and to determine the structure and biological properties of substituted salicylidene- and picolidene-4-allyl-*S*-alkylisothiosemicarbazides.

The structure and purity of the synthesized isothiosemicarbazones were confirmed using $^{1}$H, $^{13}$C NMR spectroscopy and also X-ray analysis. All peaks in the spectra of isothiosemicarbazones are double. It indicates the presence of tautomeric forms of isothiosemicarbazone in solution.Coordination compounds were obtained as a result of interaction between corresponding 3d metal salt and isothiosemicarbazone or by interaction of acetates of 3d metals and hydroiodide, hydrobromide or hydrochloride of corresponding isothiosemicarbazone.

The *in vitro* antiproliferative activity of the isothiosemicarbazone and complexes was screened on human leukaemia HL-60, cervical cancer HeLa, pancreatic adenocarcinoma BxPC-3 and muscle rhabdomyosarcoma RD cells and normal MDCK cells. Some of the synthesized coordination compounds showed promising antiproliferative activity and low toxicity.

**Acknowledgements**. This work was fulfilled with the financial support of the Institutional Project **15.817.02.24F**.

## O11

# NOVEL THIOSEMICARBAZONE ACETAMIDE DERIVATIVES AND THEIR COPPER COMPLEXES: SYNTHESIS, CHARACTERIZATION AND POTENTIAL BIOLOGICAL ACTIVITY

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Thiosemicarbazones derived from 2-formylpyridine and their metal complexes exhibit awide range of biological applications. Nevertheless, the literature contains examples of biologically important bidentate thiosemicarbazones: p-acetamidobenzaldehyde thiosemicarbazone, known as thiacetazone, is employed in the treatment of tuberculosis [1]. There are some reports on the studies of 4-phenyl 2-formylpyridine thiosemicarbazones and their metal complexes with antioxidant properties that surpass 33 times better than Trolox [2]. Using the procedures previously described for synthesizing thiosemicarbazones and their metal complexes as well as measuring their antifungal activity. The group of researchers [3] have tested coordination compounds of copper (II) with 4-allylthiosemicarbazone of 2-acetylpyridine and showing an antifungal activity 133 times better than Fluconazole. Based on published data suggesting that the acetanilide and pyridin-2-yl fragments present biological properties. Aims of this work are synthesis of new ligands that will contain 4-phenylacetamido-3-thiosemicarbazones derived from 2-formylpyridine.

The tridentate ligands containing derived from 2-formylpyridine thiosemicarbazones were synthesized and characterized by $^{1}$H, $^{13}$C-NMR, FTIR spectroscopy. On the basis of the ligands and copper salts obtained ten coordination compounds, characterized by FTIR spectroscopy. Coordination compounds could look potential biological activity for antimicrobial, antifungal and antioxidant properties.

**Acknowledgments.** This work was fulfilled with the financial support of the State Project 18.80.07.17A/PS.

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**O12**

# ANTIMICROBIAL ACTIVITY OF SEA BUCKTHORN POWDER AGAINST FOUR PATHOGENIC BACTERIA STRAINS

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Plants present a source of natural antimicrobial agents. Plant bioactive molecules can interact with organisms in their environment and can act against pathogenic microorganisms.

In this present study, sea buckthorn powder was investigated against four pathogenic bacteria strains: *Bacillus subtilis* ATCC 6633, *Staphylococcus aureus* ATCC 25923, *Escherichia coli* ATCC 25922 and *Klebsiella pneumonia* ATCC 13883. The chemical composition and antiradical activity of the hydroalcoholic and liposoluble sea buckthorn extracts were investigated. The hydroalcoholic extract of sea buckthorn contained polyphenols 9.34±0.65 mg GAE/g, tannins 27.72±1.25 mg TAE/g and the antiradical activity was 93.65±2.17 % of inhibited DPPH. The liposoluble extract of sea buckthorn has contained β-carotene 7.20±0.32 mg/L, lycopene 7.37±0.18 mg/L and the antiradical activity was 68.07 ± 3.72% of inhibited DPPH.

The sea buckthorn powder showed an antimicrobial activity pronounced against *Staphylococcus aureus* and *Bacillus subtilis*. In the case of *Escherichia coli* and *Klebsiella pneumoniae* antimicrobial activity of plant powder was low. The sea buckthorn powder showed the inhibitory activity against pathogenic bacteria strains in the following series: *Staphylococcus aureus>Bacillus subtilis>Escherichia coli>Klebsiella pneumonia.* This phenomenon is explained by the fact that *Staphylococcus aureus* and *Bacillus subtilis* are Gram-positive bacteria and *Escherichia coli* and *Klebsiella pneumoniae* - Gram-negative bacteria. Thus, Gram-positive bacteria are more sensitive to the action of sea buckthorn powder than Gram-negative bacteria. It was found that a 1.0% addition of sea buckthorn powder reduced the risk of appearance of ropiness in wheat flour bread caused by *Bacillus subtilis*.

The investigated sea buckthorn powder has shown promising antimicrobial potential against pathogenic microorganisms and can be used in the food industry.

## Acknowledgments

This work was benefited from support through the 18.51.07.01A/PS State project "Decreasing raw material and food products contamination with pathogenic microorganisms".

**O13**

# NEUTRON ACTIVATION ANALYSIS IN THE ENVIRONMENTAL STUDIES: MOLDOVA CASE STUDY

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Neutron activation analysis is a high sensitive analytical technique used in the environmental studies for the determination elements in a wide range of concentrations. The principles of instrumental neutron activation analysis are discussed and the advantages of this technique in analysis of environmental objects are shown. Examples of studies performed on the radioanalytical complex REGATA at the IBR-2 reactor (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna) in collaboration with scientific centres from the Republic of Moldova are summarized.

**O14**

# STRATEGIES FOR CLASSIFICATION AND REUSE OF IRON AND MANGANESE MINING WASTES

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Mining and mineral-processing wastes represent one of the world's largest chronic waste concerns. A number of environmental problems are associated with the disposal of these wastes, including ecological losses, downstream contamination and pronounced landscape transformation.

In recent years, difficulties to access raw materials (RMs) have led to progressive resource depletion, increase in metals price and environmental pressures. The recovery of critical raw materials (CRMs) from low-grade ore, steel works by-products and industrial wastes has become an important issue and a global challenge for present and future economy.

Due to the continuous need for mining activities to collect RMs to sustain our economy, the recycling and reuse of mining and mineral-processing wastes should be pursued through appropriate innovative management strategies aimed at minimizing the environmental impacts and preserving human health. Furthermore, it is generally difficult to assign a universal method to reuse all kinds of mining and mineral-processing wastes; hence, the choice of possible recycling, reprocessing and reuse strategies should be case-specific.

Aim of this paper is to evaluate integrated multidisciplinary strategy for the characterization and analysis of mining waste, its possible recycling and re-use and strategies for CRMs recovery.

Proposed strategies have been applied to wastes produced in the Fe-Mn mine in Bichakundi (near Joda West, Odisha-India). In the first phase, *in situ* sampling campaigns have been carried out; mining wastes have been thoroughly characterized by X-Ray Powder Diffraction (XRPD), X-Ray Fluorescence (XRF) and spectral signatures analysis and the acquired mineralogical, chemical and spectral information have been used to create a map of mining waste deposits by means of the new multispectral satellite Sentinel-2A classification. The use of Fe-Mn rich wastes in arsenic removal and phosphorus recovery from water will be discussed. Furthermore, the potential metals uptake from contaminated soils and their possible recovery from incinerated/lyophilized biomass by hydrometallurgical methods is evaluated also according to preliminary phyto-myco-remediation tests carried out using *Helianthus annuus* (i.e., sunflower) and *Rhizophagus intraradices.*

**O15**

# WATER AND WASTEWATER TREATMENT: CURRENT PROCESSES APPLIED FOR SOLIDS REMOVAL

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A huge part of contaminants in natural water resources and also in different wastewaters is associated with solids, and thus important removals of polluting species are expected to be achieved by simple and advanced solid/water (S/W) or solid/wastewater (S/WW) separation in adequate operating conditions. Often the effluents from different industries or different natural polluted water resources contain 40-70% of total COD associated with suspended solids (in colloidal and settable forms), and also other contaminants such as metals, bacteria and viruses (size range of 0.01-10 μm), organic micropollutants (PCBs, PAH) are associated with particulate matter due to their adsorption, agglomeration and incorporation onto solid matrices. Incorporation of S/W or S/WW separation processes prior to advanced chemical or biological treatment such as microscreening, primary sedimentation, direct mechanical filtration, or chemical coagulation-flocculation associated with solids separation, flotation, activated carbon adsorption or membrane processes has improved the performance of treatment steps and increased treatment capacity in advanced chemical or biological units. Consequently, the presentation of the most used S/W and S/WW separation equipments, processes and operations in different treatment systems, overall efficiency and cost is of great importance in this work. All S/W or S/WW separations may be used in any step of a sewage treatment system, but the type of raw sewage limits each S/W or S/WW separation associated with the adopted cleaning regime. Moreover, the water and wastewater services are able to offer efficient products and equipments for the complete water and wastewater treatment sector and worldwide market: (*i*) very fine screens; (*ii*) clarifiers, filtration installations (sand-based or multilayers-based filtration); (*iii*) membrane bioreactors to separate fibrous materials and reduce the COD/BOD ratio of treated discharges in receiving watercourse; (*iv*) grit separation of digestible organic materials and other mineral materials; (*v*) sludge treatment (screening-thickening-dewatering-drying from one source). For further improvements, precipitation and coagulation agents are also added, all having a solids’ agglomeration effect. Thus, dissolved and very fine particles from wastewater are converted into ease separable agglomerates to enable filtreable solids to be reduced by up to 95%, COD/BOD by 65% and phosphorus by 60%.

In addition, the case study of five different S/WW separation processes applied in a textile wastewater treatment plant (a private cotton manufacturing company) is evaluated in terms of solids and organics removal efficiencies and also risk control of residuals in the treated textile effluent and natural aquatic receptor.

**O16**

# THE ROLE AND PLACE OF ACTIVE CARBONS IN ENSURING ENVIRONMENTAL SAFETY

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Progressive environmental pollution has made environmental safety an important component of national security as a whole. Today, almost the entire planet and especially areas with high population are exposed to serious environmental threats, the main of which are radiation contamination of territories, soil suppression by acid rain, soil contamination with chemicals and pesticides, oil spills on land and sea, and the destruction of the atmosphere.

Due to their physico-chemical properties, active carbons (AC) are unique and ideal sorption materials that allow solving a wide range of issues related to ensuring chemical and biological safety of humans, the environment and infrastructure [1].

A particularly significant threat to the biosphere is the reduction of soil fertility and even a complete depletion of farmland as a result of human activities. Today, only 6% of the total land area is suitable for agriculture. Given that at the end of the XXI century the population will reach 10 billion, according to some estimations, the protection and rehabilitation of soils should be of prime focus. The essence of the carbon-sorption detoxification of soil contaminated with pesticides is the introduction of AC into the soil, in the form of grains or powder with a micropore volume of 0.20–0.30 $cm^3/g$ and subsequent incorporation into a depth of 10–15 cm, followed by sowing of a given crop. This technology allows to obtain environmentally friendly crop production and increase crop yield on polluted soils by 20-80%.

In order to supply cities and large populated areas with quality potable water, surface water supply sources need to be treated, and here active coal is required, as well. Currently, JSC TopProm has fully completed the development of a technology for producing a unique AC based on anthracite. Anthracite from the Gorlovskoye field of Kuzbass was taken as the raw material. After crushing the pieces of anthracite, the desired fraction of 1–3 mm was sieved, and further subjected to activation with water vapour at a temperature of 870°C to a burnout value of 15%. The results of the research have shown that the adsorption properties of DAS per unit volume are at the level of the best world analogue GSN 830, derived from coconut shell.

The role of active carbons in ensuring the safety of man as the main object of the biosphere is also worth mentioning. An effective way to efficiently neutralize the negative impact of a number of environmental factors on a human being is to develop AC for body detoxification, providing conditions for the internal ecological purity, characteristic of a healthy individual - endoecology.

Early organization of new AC productions will give a powerful impetus to environmental protection and the creation of a higher life quality for people.

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**O17**

# EVALUATION OF METHYLENE BLUE INTERACTION WITH HUMAN SERUM ALBUMIN AND POLY(ACRYLIC ACID): COMPUTATIONAL STUDIES AND EXPERIMENTAL VALIDATION

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Contaminated waters with synthetic dyes pose health hazards; thereby, it is essential to unveil toxicological actions of such xenobiotics [1] and to optimize the existing processes for dyes removal. In the first part of this study, the interaction mechanism of methylene blue (MB) to human serum albumin (HSA) was elucidated by molecular modelling and spectroscopy techniques. This study was undertaken aiming to disclose molecular interaction insights useful to conceive the toxicological action of the dye. Outcomes of the molecular docking simulation suggested that the main active binding site for MB was pinpointed in the domain II of HSA and, the complex formation was favoured by hydrophobic contacts [2]. The fluorescence and circular dichroism spectroscopic techniques confirmed the real interaction between MB-molecule and HSA-macromolecule. The second part of this work dealt with removal of MB dye from aqueous solutions by complexation-ultrafiltration using poly(acrilic acid) (PAA) as chelating agent. The complexation-ultrafiltration process was modelled and optimized using response surface methodology and desirability function approach. The optimal conditions established in this study implied a polymer to dye ratio equal to $r$=2.10 and pH 6.52. Under these optimal conditions the maximum rejection efficiency (99.12%) was observed. Additionally, the molecular docking simulation shed light on the interaction mechanism between MB dye and PAA oligomer (Figure).

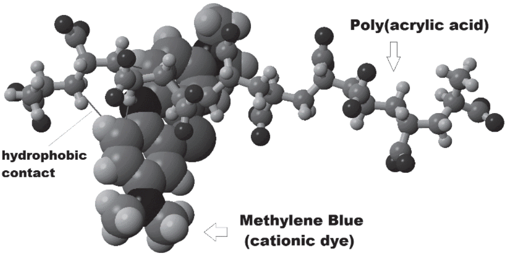

**Figure.** Docking pose of MB-PAA complex showing the interaction at molecular level.

**Acknowledgment**
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**O18**

# SEQUENTAL EXTRACTION OF VALUABLE PRODUCTS FROM CITRUS AND APPLE WASTES

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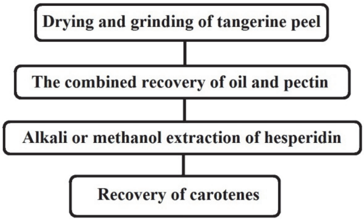
Agro-industrial wastes are the cause of environmental pollution and lead to significant problems. On the other hand, they are a rich source of commodity products – oils, flavour, natural pigments, antioxidants, etc. Modern concept focuses on complete utilization of agricultural wastes and use of eco-friendly separation technique requiring standard equipment for industrial application. Recently, we proposed a scheme for the extraction of products from the tangerine peel including steps of extraction of oil by supercritical carbon dioxide (SC-$CO_2$), acetone-modified SC-$CO_2$ extraction of carotenes, and methanol-modified SC-$CO_2$ extraction of flavanones, culminating in the recovery of hesperidin from extract and pectin from dry residue [1]. The scheme provided high yields of target products, but for a number of SMEs it turned out to be too difficult due to the use of the SC-$CO_2$ technology.



Alternative conventional low cost extraction procedure for extraction of the same bioactive compounds from citrus peel was developed.

Pectin is extracted simultaneously with the distillation of the oil. Citric acid was added for maintaining pH=1.5. Both alkali and methanol extraction method were used for recovery of hesperidin. Disadvantage of this scheme is low yield of carotenes in comparison to sequential SC-$CO_2$ extraction.

Sequential scheme of ultrasound-assisted extraction (UAE) was developed for recovery of phenolic compounds, triterpenoids (ursolic and oleanolic acids – predominant triterpenoids of apple peel) and pectin from apple pomace.

It was found that highly polar and non-polar solvents are not effective in extracting of flavonols, the acetone is the most selective providing high yield of product, therefore it was used as a solvent for recovery of phenolic compounds during UAE. Optimal conditions are: the ratio of liquid/material 10:1, ambient temperature, 22 kHz, 1h extraction time. Both methanol and ethanol extraction methods result in high yield of ursolic and oleanolic acids, but methanol is a more toxic solvent. Therefore, 96% ethanol was selected as an extraction solvent. Optimal conditions were: the ratio of liquid/material 10:1, temperature 40-45$^{o}$C, 22 kHz, 1h extraction time. Optimal operative conditions for recovery of pectin are pH=1.5, extraction time – 1h, the temperature – 80$^{o}$C. Extraction of these highly bioactive compounds from apple pomace is considered the most reasonable way of utilization.

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**O19**

# THE STUDY OF TOXIC SUBSTANCES IN LOW DANUBE REGION OF REPUBLIC OF MOLDOVA

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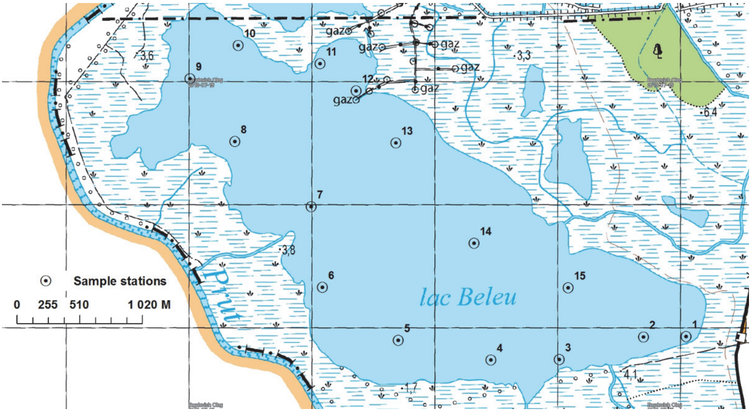
The wetland area of Low Prut River is a part of Danube Delta and Wetland system. The aim of this study is a characteristic of the environmental status of Beleu Lake, natural reserve of Republic of Moldova. The analysis of POPs, PAHs substances and heavy metals in water and sediment samples was made. The sampling was made at the beginning of June in the period of high water level in Danube and Prut rivers. Water and sediment samples were taken from all lake area including and petrol mining enterprise (Figure). The analysis was made by Gas Chromatography and AAS methods in accredited laboratory. The total PAHs value in water samples was detected from <0.001 to 0.117 μg/L. The total PAHs value in sediment samples was in the interval from 0.022 – 0.900 mg/kg. The total POPs concentration in water samples is ranged from <0.001 to 0.053 μg/L. The total POPs concentration in sediment samples is in the interval from 0.030 to 1.448 mg/kg. 20 % of sediment samples have a total POPs value more that 0.10 mg/kg. The chlororganic pesticides and PCBs are principal pollutants. Heavy metals concentration is on the background levels. The conclusion is - natural lake Beleu is under strong anthropogenic impact from different pollution sources including POPs polluted sites from past pesticide storages. The specific sediment monitoring is required for the more correct assessment of the status of this water body.



**O20**

# SPIRULINA PLATENSIS AS RENEWABLE SORBENT FOR COPPER-CONTAINING EFFLUENTS TREATMENT

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The growth of *Spirulina platensis* biomass in synthetic copper-containing effluents with different chemical composition in order to obtain renewable biosorbent was studied. Metal uptake by biomass was traced using neutron activation analysis. Biomass survival ability was strongly dependent on metal ions concentration and chemical composition of the effluents. At higher metal ions concentrations (Cu -10mg/L, Fe-5mg/L, Ni – 2mg/L and Zn- 2mg/L) biomass was able to grow only for one cycle, while reducing metal concentration (up to Cu – 2.5mg/L, Fe-1.25mg/L, Ni – 0.5mg/L and Zn- 0.5mg/L) the number of cycles increased. The effect of metals ions on biomass productivity and its main components content: proteins, carbohydrates, lipids, phycobilins and $\beta$-carotene was assessed. The decrease of productivity as well as proteins, phycobilins and β-carotene in varying degrees was noticed in all studied systems. Content of carbohydrates decreased at high metal ions concentration in all studied systems, while their increase was observed with reduction of metal concentration. Lipids were less affected by presence of metal ions in the cultivation medium. *Spirulina platensis* can be considered as renewable biosorbent for diluted effluents or wastewater post-treatment.

**Acknowledgments**
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**O21**

# METHOD OF INFORMATIVE MARKER SCALE AND LOW TEMPERATURE NITROGEN ADSORPTION IN ASSESSING THE ADSORPTIVE PROPERTIES OF ACTIVATED CARBONS FOR MEDICAL USE

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Three types of medical granulated activated carbon (AC) with increased porosity (3 samples of each): SCN (derived from N-containing synthetic polymers, Ukraine), K-814 (derived from coconut shell, Silcarbon, Germany), BAC (derived from petroleum pitch, Kureha, Japan) were obtained by the method of steam activation in fluidized bed of the laboratory furnace. Nine samples were evaluated using low temperature nitrogen adsorption and compared with direct sorption capacity measurement method for markers of the main groups of toxic substances: freely soluble compounds with small and medium molecular weight (creatinine-Creat., methylene blue-MB, vitamin B12), protein-bound toxins (unconjugated bilirubin-Bil.) and carrier protein of hydrophobic compounds (human serum albumin -HSA). Scale of this type, representing practically important groups of substances to be removed by AC, can be called informative marker scale (IMS).

**Table1.** Low temperature nitrogen adsorption parameters and quantity of markers adsorbed by 1 g of AC after 2 hours of mild shaking

| | | $\gamma$, g/cm$^3$ | $S_{BET}$, m$^2$/g | $V_S$, cm$^3$/g | $V_{micro}$, cm$^3$/g | $V_{meso}$, cm$^3$/g | MB, mg | Creat., mg | B12, mg | Bil., mg | HSA, g |
|---|---|---|---|---|---|---|---|---|---|---|---|
| SCN | 1 | 0.43 | 1224 | 1.004 | 0.451 | 0.553 | 201 | 65 | 82.3 | 3.81 | 0.083 |
| | 2 | 0.28 | 2105 | 1.862 | 0.861 | 1.001 | 340 | 69.1 | 123.6 | 4.87 | 0.131 |
| | 3 | 0.135 | 2886 | 4.663 | 0.784 | **3.879** | 596 | 92.8 | 239.2 | **20.73** | 1.2 |
| K814 | 4 | 0.44 | 1178 | 0.533 | 0.439 | 0.094 | 33.7 | 48.7 | 1.9 | 0 | 0 |
| | 5 | 0.29 | 2001 | 0.983 | 0.776 | 0.207 | 245.2 | 79 | 58.1 | 0.64 | 0 |
| | 6 | 0.185 | 2788 | 1.775 | 1.218 | 0.557 | 412.5 | 83.5 | 129.0 | 3.19 | 0.098 |
| BAC | 7 | 0.54 | 1606 | 0.731 | 0.644 | 0.087 | 85.7 | 47.5 | 6.5 | 2.7 | 0.137 |
| | 8 | 0.28 | 2859 | 1.745 | 1.433 | 0.312 | 352 | 67.3 | 96.2 | 3.59 | 0.259 |
| | 9 | 0.12 | 2457 | 4.703 | 0.707 | **3.996** | 538 | 92.9 | 162.9 | **5.54** | 0.600 |

In Table 1, along with the summary of IMS, the results of nitrogen adsorption are presented, namely: $S_{BET}$, $V_s$, $V_{micropores}$, $V_{mesopores}$. All 3 types of sorbents during activation demonstrate the growth of the IMS and nitrogen adsorption parameters. Moreover, the sorption characteristics of SCN and BAC-MU (synthetic AC) surpass those of K 814 AC made from coconut shell. At the same time, the porometric indices do not always correlate with the values of the IMS. For example, samples 3 and 9 in the table with a significant similarity in porometric indices $S_{BET}$, $V_s$, $V_{micropores}$, $V_{mesopores}$ show almost 4 times the difference in the adsorption of unconjugated bilirubin from albumin solution. This result indicates a certain advantage of the informative marker scale (IMS) method in comparison with those of low temperature nitrogen adsorption in assessing the adsorptive properties of activated carbons for medical use.

**O22**

# THE ANALYSIS OF GROUNDWATER QUALITY IN MONITORING NETWORK OF REPUBLIC OF MOLDOVA

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The delineation and characterization of Groundwater Bodies (GWB) is an important for the development of Integrated Water Management according to EU Water Framework Directive. The aim of this study is an analysis of groundwater quality in the groundwater monitoring network for the characteristic of delineated groundwater bodies. Major ions, dissolved metals and organic micro-pollutants were analyzed for this purpose in 23 samples taken from 8 GWBs. Metals were analyzed by AAS technology and included Fe, Mn, Al, As, Pb, Cd, Cr, Cu, Ni, Zn. Organic micro-pollutants included POPs, BTEX, PAHs, and pesticides. The list of pesticides included: Liufenuron, Trifluralin, Dimetoat, Diazinon, Clorotalonil, Fenitrotion, Malation, Clorpirifos, Triadimefon, Tiametoxam, Cyprodinil, Penconazol, Triadimenol, Procimidon, Endosulfan, Flutriafol, Krezoximmetil, Ciproconazol, Propiconazol, Tebuconazol, Bifentrin, Fenoxycarb, Tetradifon, Fosalon, lambda-Cihalotrin, Permetrin, Piridaben, Cipermetrin, Esfenvalerat, Fluvalinat-tau, Fenvalerat, Difenoconazol, Deltametrin, Azoxstrobin, Dimetomorf. GWB MDDBSGWQ120 is characterized by heterogeneous chemical composition. No samples that meet the requirements of the normative document for this GWB. But in the case of the absence of other water source this GWB can be used for the water supply in the south part of country. This GWB is sensitive to anthropogenic impact. Samples for GWB MDPRTGWQ130 correspond to normative documents besides of nitrate concentration due to the anthropogenic impact. GWBs MDDPBGWD310, MDDPBGWD420 are characterized by the good water quality and all parameters are in admissible interval. GWB MDDPBGWD620 has a high sodium and chloride content. The different types of the groundwater are indicated for all samples of this GWB. GWB MDDPBGWD730 is characterized by slightly alkaline type and high sodium value. GWB MDPRTGWD740 is characterized by slightly alkaline type, high sodium value, and high mineralization. GWB MDPRTGWD820 has a high concentration of sodium, sulphate ion. One sample has a high nitrate concentration. All samples have different types of water. Only three metals have a higher concentration in several samples: Fe, Mn, Al. All this elements have a natural origin. Thus we can conclude that groundwater quality parameters are formed basically under natural factors. Organic micro-pollutants as POPs, pesticides, and BTEX group were indicated on the level below of admissible value or on the detection limits. Only two samples have a relative high value of PAHs substances for GWBs MDDBSGWQ120 MDDPBGWD620. This case can be explained by the artificial pollution from anthropogenic impact. The conclusion is that delineated GWBs are different by the chemical composition. The groundwater quality is changed from north to south part of the Republic of Moldova and depends of climatic and geological conditions.

**O23**

# THE STATUS OF THE INVENTORY OF SHORT-LIVED CLIMATE POLLUTANTS IN MOLDOVA

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The inventory of short-lived climate pollutants (SLCPs) such as black carbon (BC), methane ($CH_4$), ground-level ozone, hydrofluorocarbons (HFCs) is an important task under the Supporting National Action and Planning Initiative (SNAP) of the Climate and Clean Air Coalition. The SLCPs are responsible for up to 45% of global warming and have a strong impact on climate change and human health. The rising of the global temperature affects the soil aridity, agriculture and ecosystems productivity, intensifying the heat waves. These effects are emphasized in Moldova. Evidently, SLCPs affect public health. Since SLCPs contribute to ambient levels of ozone and PM2.5 are directly associated with cardiovascular and respiratory diseases, including heart disease, pulmonary disease, respiratory infections, and lung cancer. The SLCPs emissions thus contribute significantly to the more than 7 million premature deaths annually linked to air pollution.

The project “Institutional strengthening support to scale up action on short-lived climate pollutants in Moldova” started on February 2019 with the aim of inventory of the SLCPs under the coordination of the Ministry of Agriculture, Regional Development and Environment, and the support of the United Nations Environment Programme (UNEP), and Climate and Clean Air Coalition (CCAC). The project is hosted by the Institute of Chemistry ensuring the investigations, researches and coordination of key actors’ actions for reducing the air pollution, especially, the SLCPs by further promoting the proposals for policy development and measures to reduce air pollution at the national level. It also aims to increase the ability of the government to participate more actively in the different activities and in the decision-making processes of the UNEP and CCAC.

The emissions inventory is done via the European Monitoring and Evaluation Programme (EMEP) for monitoring and evaluation of the long-range transmission of air pollutants (guidebook 2016). The projections of emissions will be done using the Long-range Energy Alternatives Planning (LEAP) - Integrated Benefits Calculator (IBC) as the integrated planning tool which helps to assess greenhouse gases, short-lived climate pollutants (SLCPs) and EMEP emissions, building mitigation scenarios and monitoring the climate, health and crops benefits.

**O24**

# PROMPT-GAMMA ACTIVATION ANALYSIS – NON-DESTRUCTIVE ANALYSIS TECHNIQUE

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An experimental setup for determining the elemental composition of materials by Prompt Gamma-ray thermal Neutron Activation analysis (PGNAA) is under developing at Frank Laboratory of Neutron Physics (FLNP) 11b channel IBR-2 reactor of the Joint Institute for Nuclear Research (JINR) in Dubna, Russian Federation.

11b channel is equipped with mirror neutron guide which brings from reactor IBR-2 into experimental room thermal neutrons with the mean energy of ~ 0,025 eV. For registering the prompt gamma-rays from the interaction of the neutrons with sample nuclei we used high purity germanium gamma detector (HPGe) which has high energy resolutions and 80% relative efficiency of gamma-rays registration. The gamma-detector was protected with cadmium covered lead shielding.

A set of measurements was performed for determination of the hydrogen content in the nano diamond sample. Some preliminary results are reported.

**O24**

# POLYMER-BASED COMPOSITES FOR HEAVY METAL IONS

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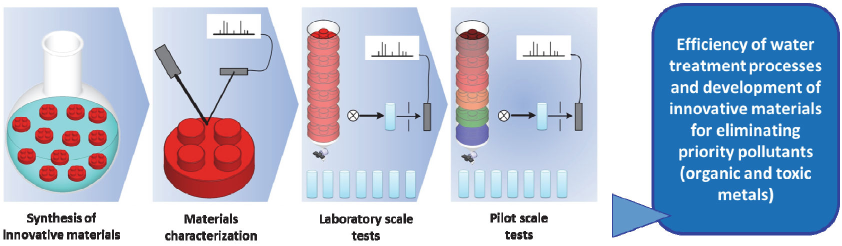
The current concept of sustainable development applied in solving society's problems requires both the use of ecological materials for water, air and soil depollution and their green chemistry. In this context, the use of renewable materials in the structure of polymeric sorbents has been imposed in recent years. Synthetic and natural polymers are increasingly being used in building materials with high performance structures. The combination of the two categories of polymers can lead to materials that possess both chemical stability and resistance to extreme pH and temperature values specific to synthetic compounds as well as special characteristics of natural polymers (bioadhesiveness, biodegradability, biocompatibility) with increased capacity sorption and improved mechanical properties. This study proposes the development of new solutions that are based on individual or combined unit processes for sequential / simultaneous elimination of priority pollutants (organic and toxic metals). For this purpose, innovative polymeric materials or composites are designed with properties (porosity, shape, size, sorption, selectivity) adapted to the characteristics of treated waters (types and concentrations of pollutants).



The study brings novelties and important contributions to advanced water treatment. The proposed technological solutions at the laboratory scale will be tested on the pilot plant. The adaptation and exploitation of a pilot plant for the testing of the selected technological solutions at the laboratory scale is the key link for the technological transfer to the industrial scale for this study.

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## O26

# THE USE OF SOME NON-CONVENTIONAL METHODS IN CHEMISTRY OF BICYCLOHOMOFARNESENIC METHYL ESTERS

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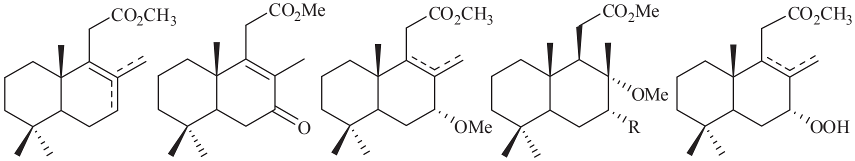
The non-conventional methods of synthesis belong to green chemistry and offer many advantages. The microwave and ultrasound irradiation, as well as electrochemical and photochemical transformations often lead to desired results through nonspecific mechanisms, reduces the cost, increase yields and exclude the use of reagents, or the formation of toxic reaction products.

Since being obtained by the Stoll method from commercially available (+)-sclareolide [1], esters **1-3** have been noted as an important starting material for the synthesis of new compounds or natural analogues from the homodrimanic or drimanic series [2-4]. The disadvantage of this method, however, lies in the too long duration of the transesterification-dehydration reaction (96h).



**1-3** ($\Delta^{7-8}$, $\Delta^{8-9}$, $\Delta^{8-17}$) **4** **5**, **6** ($\Delta^{8-17}$, $\Delta^{8-9}$) **7** R = H; **8** R = OMe **9-10** ($\Delta^{8-17}$, $\Delta^{8-9}$)

**Figure.** Bicyclohomofarnesenic methyl esters **1-3** and products of their electrochemical and photochemical transformations **4-8**.

Using microwave irradiation (MeOH, $H_2SO_4$, MW, 15'), we managed to obtain compounds **1-3**, in just 15 minutes, with the same yield and co-ratio of the products.

Further, an exhaustive study of the anodic oxidation reaction of esters **1-3** ($LiClO_4$, MeOH, ê, 6h) was performed. Additionally to previously reported compounds **4** and **5** [5], a series of minor compounds **6-8** were isolated from the reaction mixture and characterized (Figure 1).

The sensitized photooxidation of esters **1-3** mixture (DCM, TPP, hν, 7h) lead to new isomeric hydroperoxydes **9** and **10**. In continuation, by means of standard methods, these compounds were converted in corresponding alcohols and acetates.

The structures of all synthetized compounds were fully confirmed by spectral methods of analysis.

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**O27**

# POLYMERIC SUPRAMOLECULAR NUCLEIC ACIDS DELIVERY SYSTEMS: DYNAMIC COMBINATORIAL LIBRARIES

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Nucleic acids delivery (gene therapy) has the unique potential to provide therapies for many incurable to date diseases [1-3]. The main problems in the gene therapy, however, are associated with poor transfection efficiency, cytotoxicity, immune response, drug loading and targeting delivery as well as ethical concerns and commercialization [1-3]. Therefore, in the last decades numerous of transporters for nucleic acids (vectors) were developed. Based on their design and properties, viral vectors currents show the best results in effective gene delivery. Alternatively, all other approaches are based on non-viral gene delivery systems, which try to mimic the efficiency of viral vectors by artificial means [4]. Our main strategy is based on building and self-generation of multifunctional nanostructures from commercially available or “easy to prepare” units, which will further self-assembled in complex, tuneable and multifunctional materials, suitable for specific targeted gene delivery and by this to overcome some existing issues [5-8]. On the other hand, nucleic acids and target cells are highly variable and therefore, rational design is limited to a relatively small number of components and a high number of synthetic steps, thus exploring dynamic chemistry and combinatorial approach for building nucleic acid vectors will provide a facile method to build large libraries of various compounds.

In this communication, an overview related to preparation of libraries of non-viral vectors, characterization and self-assembly properties, nucleic acid binding properties, cytotoxicity and transfection efficiency is presented [5-8]. Vectors were build from lipid moiety, biocompatible polymers (PEG) and nucleic acid binding sites (PEI), liked all together to a core connector molecule through reversible dynamic imine bonds. It has been shown that obtained libraries of vectors have a good cell viability and a better transfection efficiency when compared to precursors [5-8].

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**O28**

# SYNTHESIS AND BIOLOGIC PROPERTIES OF SOME N'-((3-ARYL-1-PHENYL-1H-PYRAZOL-4-YL)METHYLENE)ISONICOTINOHYDRAZIDES

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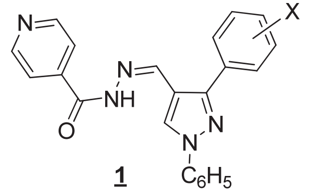
Pyrazole derivatives have found vigorous use as components of new bioactive substances, especially in the composition of some drugs. The pronounced biological activity of several pyrazole derivatives has spurred research into obtaining new compounds with additional heterocyclic structures. Of particular interest are pyrazole-4-carbaldehydes, which have a higher reactivity carbonyl group. In the present work as a condensing agent with isonicotinic acid hydrazide (isoniazid) - an effective medicine for the treatment of active tuberculosis, was proposed these aldehydes.



**1**

X = H, 4-Br, 4-Cl, 3-$NO_2$, 4-$NO_2$

3-Aryl-1-phenyl-1H-pyrazole-4-carbaldehydes were synthesized by the Vilsmeier-Haack reaction, from the ring substituted phenylhydrazones of the acetophenones and the Vilsmeier reagent. The synthesis method of pyrazolecarbaldehydes has been modified by using phosphorus pentachloride as a reagent for obtaining the Vilsmeier reagent. The 3-aryl-1-phenyl-1H-pyrazole-4-carbaldehydes obtained were condensed with isonicotinic acid hydrazide. The structure of obtained N'-((3-aryl-1-phenyl-1H-pyrazol-4-yl) methylene)- isonicotinohydrazides 1 was confirmed based on IR spectra, $^1$H-NMR and $^{13}$C-NMR.

Isonicotinohydrazides **1** were subjected to a virtual screening through the PASS (Prediction of Activity Spectra for Substation) program, the results of which showed that synthesized isonicotinohydrazines would exhibit antituberculous, antiviral and antimicrobial activity.

The antibacterial activity (bacteriostatic and bactericidal) under laboratory conditions of the substances **1** was investigated for the microorganisms: *Staphylococcus aureus, Staphylococcus epidermidis, Enteroccocus faecalis, Escherihia coli, Pseudomonas aeruginosa, Acinetobacter baumannii*.

The investigation results show that the 4-chloro derivative posses bacteriostatic activity for Gram-positive microorganism *Staphylococcus Aureus* at concentration of 75 µg/mL. Bacteriostatic and bactericidal action of substances **1** is at concentrations above 300 µM for all test bacterial cultures investigated.

**O29**

# HETEROCYCLIC IMINES WITH IONOCHROMIC BEHAVIOUR

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Imine-based compounds (also known as azomethine or Schiff bases) constitute an important class in coordination chemistry as their coordinating ability is widely reported. They find applications in analytical chemistry, food and dye industry, catalysis and in many biological areas. The attractive features of imines like facile synthesis coupled with synthetic tailorability, biodegradability, pronounced photophysical properties and ability to coordinate to metal ions tag azomethines as one of the most widely explored molecular chemosensors. Schiff bases can be used for heavy metal sensing, for removal of pollutant in the environment, as spectrophotometric and fluorimetric agents. Therefore, Schiff base complexes have attracted increasing attention in the area of ionic binding [1,2].

1,10-Phenanthroline is a chelating bidentate ligand for transition metal ions that has a significant influence incoordination chemistry and still continues to be a versatile starting material for organic, inorganic and supramolecular chemistry. 1,10-Phenanthroline is a rigid planar, hydrophobic, electron-poor heteroaromatic system, who is responsible for its coordination ability toward metal ions. Taking the advantages of these structural features 1,10-phenanthrolinederivatives and their metal complexes have been used as intercalating or groove binding agents for DNA and RNA, as building units for the construction of efficient luminescent materials and photo-switchable molecular devices [1,3,4].By combining animine-type structure of the phenanthroline heterocycle with other chromophoric rigid cores, either aromatic or heteroaromatic, it is expected to enhance the conjugation length and to facilitate an increase in electron transport.

Therefore, we report the synthesis and characterization of a series of conjugated phenanthroline-based imines incorporating different chromophoric units. Their recognitionability towards a series of transitional metals was studied by UV-vis spectroscopy and cyclic voltammetry measurements.

## Acknowledgements

This work was supported by a grant of Ministry of Research and Innovation, CNCS - UEFISCDI, code PN-III-P4-ID-PCE-2016-0708, no. 66/2017 within PNCDI III.

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**O30**

# NEW APROACHES TO POLYIMIDES WITH CHROMIC RESPONSE TO EXTERNAL STIMULI

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As one of the most interesting class of smart materials, chromic materials which show a colour change when exposed to an external stimulus are generally employed in high-tech applications being exploit the chromic effect induced by the stimulus, for instance in thermometry, electronics, ophthalmics, photonics, biomedicine, etc. The colour change, whether it is from white to black, from colourless to coloured or from one colour to another could be induced by heating (thermochromism), solvent quality change (solvatochromism), mechanical stress (mecanochromism), ions detection (ionochromism), electromagnetic radiation (photochromism), biological agents detection (biochromism) etc. [1].

More than half a century after the launch on the market of high performance polymers, aromatic polyimides are still a subject of intense research efforts, both in academic and application studies, due to the excellent combination of high thermal resistance and superior mechanical properties, long-term use and an advantageous synthetic pathway that makes them suitable for advanced technologies [2]. Due to these superior properties, the application field of polyimide has generally been enlarged from printed circuit boards and electrical insulation layers in microelectronics to functional layers of humidity sensors, shielding layers for sensor surfaces and novel platforms for thermal sensor devices, temperature sensor arrays, micro-hotplates integrated into gas sensors and biosensors [3]. Although these polymers exhibit interesting properties, addressing the polyimide materials design issue as to present interesting colour changes in response to an external stimulus and, based on them, sensing ability, is extremely challenging.

Based on these considerations, we report some of our attempts to develop polyimide materials with chromic response to external stimuli, such as pH, electrical potential, light radiation or metal ions. By using some tools provided by organic chemistry, the receptors were tailored with specific functionalities which allowed their easy incorporation into polyimide chains, as well as to endow these polymers with both inherent properties and recognition capability towards various surrounding stimuli.

## Acknowledgements

This work was supported by a grant of Ministry of Research and Innovation, CNCS - UEFISCDI, code PN-III-P4-ID-PCE-2016-0708, no. 66/2017 within PNCDI III.

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**O31**

# PET WASTES RECYCLING USING VARIOUS GLYCOLS AND METAL CONTAINING IONIC LIQUIDS

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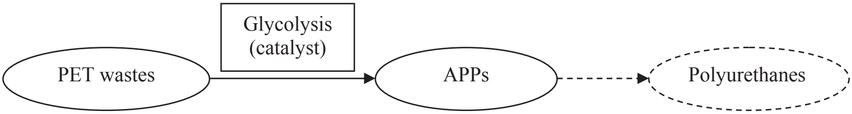
Poly(ethylene terephthalate), also known as PET, is one of the major postconsumer waste, being non-biodegradable [1]. Present methods for PET recycling are divided into physical methods and chemical methods. However, chemical recycling of PET is the most attractive and widely studied, due to the final product quality. Glycolysis is the simplest, oldest, and least capital-intensive process. Glycolysis is, usually, carried out using ethylene glycol to produce bis(2-hydroxyethyl)terephthalate and other PET glycolyzates, which can be used to manufacture unsaturated resins, polyurethane foams, copolyesters, acrylic coatings and hydrophobic dyes [2]. Being a transesterification reaction, the classical catalysts needed for PET glycolysis are inorganic salts (metal halides). The alternative to the metal-catalyzed glycolytic depolymerization is given by the organic superbases (TBD, DBU, DBN) and ionic liquids catalysts which are intensively studied lately [3].

In the present work, our aim is to perform PET wastes glycolysis reaction using other glycols than ethylene glycol, using as catalyst metal containing ionic liquids in order to obtain aromatic polyesterpolyols that can be used to manufacture polyurethane foams. The catalyst used are methylimidazolium salts with general formula $[Rmim]^+MX_3^-$.



**Acknowledgements**. The financial support from UEFISCDI, Complex Projects CDI, no 70PCCDI/2018 – MAUS is gratefully acknowledged.

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**O32**

# SYNTHESIS AND CHARACTERIZATION OF NEW DERIVATIVES CONTAINING AZO GROUP

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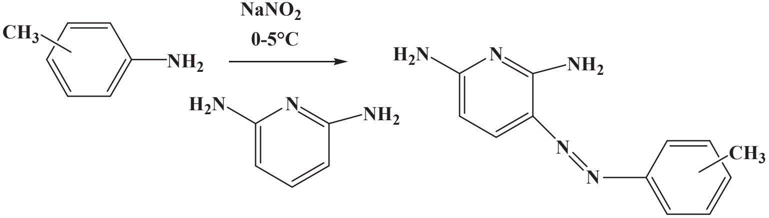
Considerable interest has been made in the development of materials that are optically responsive and have the potential to be useful in photonic technology. Organic materials based on the azobenzene moiety have received significant attention because of their photoresponsive properties that results from the *trans-cis-trans* isomerization of azo chromophores. Reversible transformation between more stable thermodynamically *trans*-azobenzene and less stable *cis*-azobenzene can be monitored by UV or visible light irradiation or thermally in the dark. The photoisomerization process can be followed by monitoring the intensity of the absorption band of the *trans*-isomers at around 350 nm while the *cis*-isomers show a less intense absorption band at longer wavelengths. In this way the light response becomes of special importance in order to control at will the molecule configuration. Reversible *trans-cis-trans* isomerization of the molecules causes structural changes resulting also in spectral changes. During *trans*- to -*cis* conversion, the intensity of the absorption band corresponding to the $n - \pi^*$ transition increases, while the $\pi - \pi^*$ band decreases [1]. Structural changes of the azobenzene are reflected in obtaining a stable dipole moment by the *cis*-isomer (3.0 D) and in the change in geometry caused by a reduction in the distance between carbon atoms in positions 4 and 4' from 9.0 Å for the *trans*-isomer to 5.5 Å for the *cis*-isomer [2,3].

The derivatives used in this study are new aromatic diamines containing azo group, namely *3-o–tolylazo-pyridine-2,6-diamine and 3-p–tolylazo-pyridine-2,6-diamine.* These diamines have been synthesized *via* the one-step diazonium coupling reaction of *ortho*- or *para*-toluidine diazonium chloride with 2,6-diaminopyridine, as shown in the Scheme. The obtained diamines were characterized by elemental analysis, FTIR, $^1$H NMR and UV-Vis spectroscopy. The isomerization behaviour was monitored following the changes in ultraviolet-visible absorption spectra.



**Scheme**. Synthesis of azo-derivatives

**Acknowledgements.** This work was supported by a grant of Ministry of Research and Innovation, CNCS-UEFISCDI, project number PN-III-P4-ID-PCE-2016-0708, within PNCDI III.

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## O33

# INTERACTION FEATURES OF 2-HYDORXY-JUGLONE WITH PERILLALDEHYDE

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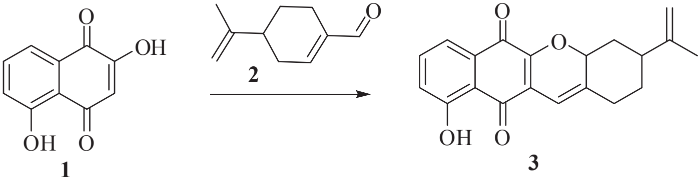
Juglone **1** is a naphthoquinone compound found in the plants of the *Fam. Juglandaceae*. Especially high amounts can be detected in the eastern black walnut (*Juglans nigra*) and common walnut (*Júglans régia*).

It is well known that juglone has a broad spectrum of biological activity, including antibacterial and antifungal properties [1]. Juglone is widely used in traditional medicine in the form of tincture, balsam, syrup, as general tonic, immunomodulatory, blood sugar regulatory, hipotensive and antiparasitic remedy. Juglone containing ointments are used as anti-inflammatory, antibacterial and antifungal remedies [2]. Anticancer properties have been also detected for juglone by some researchers [3].

The main objective of the present research was investigation of the reaction between 2-hydroxy-juglone **1** with perillaldehyde **2** with obtaining of an unusual new derivative of 1,4-naphthoquinone **3** (Scheme). Reaction has been performed in the presence of the Hantzsch ester as a reducing agent and L-proline as catalyst. The reaction mechanism included not only methylation but also 1,4-addition.



**Scheme.** The synthesis of compound **3**.

The product was separated with application of the column chromatography. The structure of the obtained compound was confirmed by application of different physico-chemical methods of analysis. The identity of the compounds has been established by various $^{1}H$-, $^{13}C$-NMR experiments including those bi-dimensional (COSY, HSQC, HMBC, NOE). Also the structure of **3** was confirmed by X-ray analysis.

**Acknowledgements.** The authors are grateful for the funding offered by the National Agency for Research and Development of the Republic of Moldova under the project 19.80012.80.07A.

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**O34**

# CHITOSAN – A VERSATILE PLATFORM FOR BIOMEDICAL APPLICATIONS.
## I. CHITOSAN-BASED MEDIA FOR CONTROLLED DELIVERY OF BIOACTIVE COMPOUNDS

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Chitosan, one of the most widely used natural polysaccharides, has been considered for biomedical applications due to its excellent biocompatibility, low toxicity, immune-stimulatory action and tissue repair capability. Aside these characteristics, there are other properties that influence its use as support for the delivery of various compounds with biologic activity (i.e., growth factors, drugs, nucleic acids) [1].

Thus, the molecular weight and degree of acetylation affect its solubility and its hydrophobic character, as it is insoluble in most organic solvents, but highly soluble in water under acidic conditions due to the protonation of the amine groups. Its susceptibility to degradation by lysozyme and chitinase, its mucoadhesive nature and the ability to temporarily open some epithelial tight junctions favour the delivery of drugs across well-organized epithelia (such as nasal, intestinal, ocular, buccal and lung). At the same time, the presence of the reactive functional groups on the macromolecular chain allows the chemical binding of drug molecules [2].

All these features make chitosan a highly convertible platform for such applications. Therefore, it is intensively studied and used in controlled delivery of bioactive compounds, whether it is employed as films, nano-/micro- capsules or particles, hydrogels, coatings or even as matrix to assembly bio(macro)molecules, cells, nanoparticles, etc. by chemical and/or physical bonds [3], as it will be presented herein.

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**O35**

# SYNTHESIS OF POLYFUNCTIONALIZED TERPENIC DERIVATIVES *VIA* RADICAL AND CATIONIC REACTIONS

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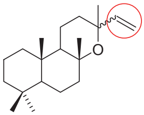
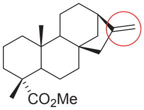
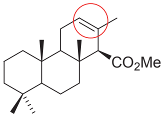
Assembling of new C-C and C-heteroatom bonds in natural products of potential biological activity can provide opportunities for broadening of molecular diversity, leading to new chemical space, in addition to trivial functional group transformations. We have initiated a program for modification of available terpenic scaffolds by free radical [1] and cationic [2, 3] processes and examples reported in this communication relate to labdanic **1**, *ent*-kauranic **2** and isocopalic **3** diterpenoids. They represent important groups of natural products with relevant properties and applications.



Manoyl oxides **1**



ent-Kaurenoic ester **2**



methyl ent-Isocopalate **3**

Manoyl oxides have been used to several radical reactions, such as hydroazidation, carboazidation, hydroalkynation and carboiodination. At the carboiodination reactions iodine migration was observed at the distal methyl from cycle A of substrate, involving 3 successive 1,5-HAT [4].

As with manoyl oxides, *ent*-kauranic derivatives were modified by radical reactions. Were synthesized five new azides, which were converted into amines, triazoles, amides, lactams and guanidine in very good yields. Many functional groups, for example: -$N_3$, -$SO_2Ph$, -$CF_3(CF_2)_n$, -$CF_3$ and etc., were introduced in structure of kaurane derivatives

Carboazidation of isocopalic ditepenoids with ethyl iodoacetate and phenylsulfonyl azide under DTBHN initiation conditions resulted in the formation of the azides in good yields. In that case, it was demonstrated that we can get good results not only with natural compounds having terminal double bond, but also with non-terminal such as methyl *ent*-isocopalate **3**.

In the result of the performed investigations, 85 new functionalized compounds have been synthesized. Preliminary biological activity studies revealed relevant cytotoxicity of some selected derivatives against several cancer cell lines.

**Acknowledgments.** The Swiss National Science Foundation (SNSF) is acknowledged for the scholarship offered and University of Bern for the opportunity to work in their laboratories.

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**O36**

# CHITOSAN – A VERSATILE PLATFORM FOR BIOMEDICAL APPLICATIONS. II. CHITOSAN-BASED SCAFFOLDS FOR TISSUE ENGINEERING

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Immunologic basis of the mechanisms of the graft rejection are not yet fully revealed, despite the scientific progress in the field, and regardless of the form of transplant, although it has been shown that allotransplantation elicited the lowest immune response [1,2]. Such shortcomings can be circumvented by using the pacient's own cells/tissue or biodegradable artificial materials. In the latter case, the selected materials must be able to promote the neighboring cells proliferation or to act as scaffolds where the transplanted cells will adhere, proliferate and specifically differentiate under local physiological conditions.

There is a wide variety of scaffolds made of polymeric biomaterials able to encapsulate cells, mitigate immune responses and regeneration of different types of tissue, or act as a barrier between tissues [3], and their key feature is the ability to interact with human living tissues while arousing no or minimal immune reaction. An in-depth insight of their biocompatibility may be achieved by understanding the fine bio-chemical and -physical mechanisms of the phenomena that occur during the interaction between the biomaterial and the living cells [4,5].

Among the naturally derived biomaterials (such as decellularized ECM, alginates, collagen, elastin, pullulan etc.), chitosan proved to be one of the most versatile natural biopolymers and its use in tissue engineering was motivated by the good biocompatibility, low cytotoxicity, and its ability to mediate the transfer of biologically active compounds or living cells between a scaffold and the host tissue. Chitosan-based *in situ* gels are already known as smart biomaterials in the regenerative medicine. The typical chitosan-based *in situ* gelling reaction systems and the corresponding mechanisms will be presented herein, as well as some of their special applications in tissue engineering.

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**O37**

# CATALYTIC $\beta$-C($sp^3$)–H SILYLATION OF ALCOHOLS

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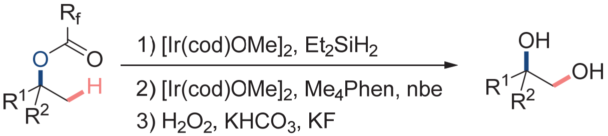
Advances in synthetic methodologies are essential to increase the share of natural products and their derivatives in modern drug discovery screening efforts. However, the derivatization of these molecules is challenging due to their complexity. One of the approaches to address this problem is to conduct site-selective C–H functionalization reactions. Among the possible C–H functionalization reactions, the borylation and silylation of C–H bonds are particularly valuable because of the potential of groups based on silicon and boron to undergo cross-coupling or oxidative functionalization reactions.



The hydroxyl group is the most commonly encountered functional group in natural compounds, making alcohol-directed C–H functionalization particularly important for the late-stage functionalization of complex molecules. We have developed an Ir-catalyzed functionalization of primary $\beta$-C($sp^3$)–H bonds of tertiary and secondary alcohols enabled by traceless directing groups. The targeted alcohol is transformed into a perfluorinated ester and then reduced with diethyl silane. This silyl acetal directs the C–H silylation reaction to obtain the six-membered dioxasilinanes. Tamao-Fleming oxidation of these oxasilolanes leads to the formation of 1,2-diols. The developed sequence was applied to a series of natural products derivatives containing hydroxyl groups.

## O38

# INNOVATIVE PROTOCOLS FOR THE SELECTIVE OXIDATION OF CELLULOSE

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Polysaccharides are ubiquitous natural occurring polymers widely used for a variety of biomedical applications including drug delivery and tissue regeneration. These polymers due to their biochemical similarity with human extracellular matrix components are readily recognized and accepted by the body. Natural polymers inherit numerous advantages including natural abundance, relative ease of isolation, and chemical modification to meet the varied technological requirements [1].

The most common processes involving chemical modification of cellulose include oxidation reaction [2-5]. Nitroxyl radicals, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or *N*-hydroxyphthalimide (NHPI) are one of the best and modern catalysts, having great performances in oxidation reaction (Figure) [6-7].

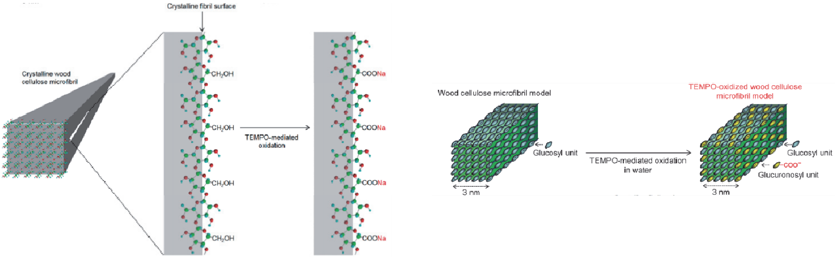

**Figure.** General schematisation of cellulose fibril oxidation performed by TEMPO radical

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

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## O39

# HIGHLY RESPONSIVE NEW AZO-BASED DIAMINES TOWARDS *TRANS-CIS* PHOTOISOMERIZATION

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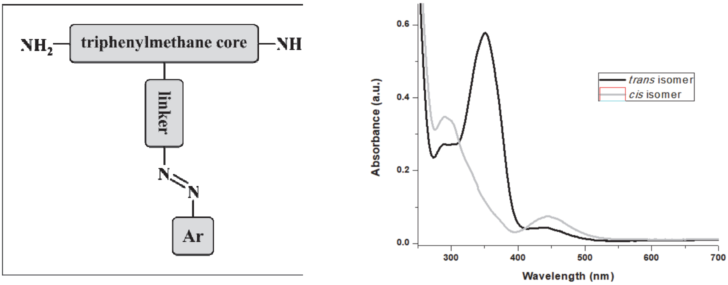
Azo-based compounds (including dyes, monomers, polymers, etc.) have been the topic of sustained research due to the emergence of new technological areas where they folded efficiently. During the past decades, this king of compounds, having different design concepts that can overcome the growing need of modern technologies, stand into the attention due to their easy structural modification. One of their attractive features is the possibility of changing the orientation of structural motifs due to the presence of azo group through *trans-cis* photoisomerization. This interesting property generated many technological applications due to their excellent photosensitivity. They were successfully implemented in applications such as high-density optical data storage, liquid-crystal devices, optical waveguides, and diffractive elements [1,2]. Taking all this into account, two azo-based diamines (Figure (a)), having as the main structural element the triphenylmethane core, have been developed for photo-optical applications.

Here we report the design, synthesis and *trans-cis* photoisomerization investigations of these novel aromatic diamines. The influence of the structural motif on the photoisomerization process has been thoroughly explored and comparedby UV-Vis (Figure (b)), $^{1}$H-NMR and electrochemistry investigations.



(a)

(b)

**Figure**. The structure of azo-based diamines **(a)** and evidence of photoisomerization **(b)**.

**Acknowledgements**

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**P1**

# CRYSTAL STRUCTURE OF BIS(LIDOCAINE) TETRATHIOCYANONICKELATE(II) DIHYDRATE

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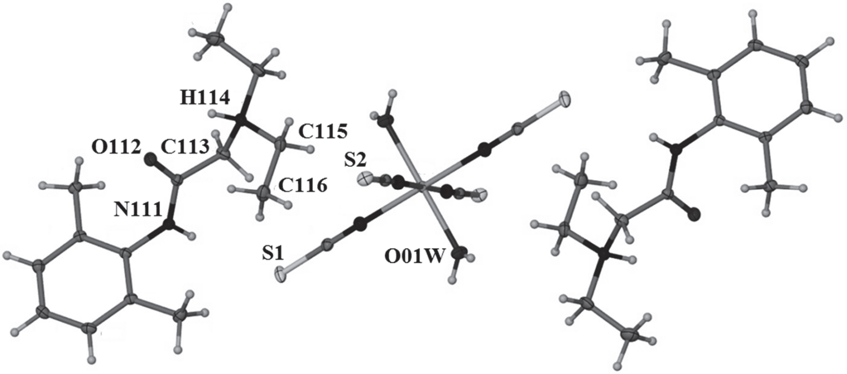
Lidocaine is a drug used as an anesthetic and for the treatment of chronic pain. Nickel(II) complex of lidocaine was prepared in water-methanol solution (pH=7) with 1:2:4 molar ratio of the nickel chloride, lidocaine, and potassium thiocyanate. Resulting bis(lidocaine) tetrathiocyanatonickelate(II) dihydrate, $(LidH)_2[Ni(NCS)_4]{\cdot}2H_2O$, crystallizes in the monoclinic space group $P2_1/c$ with $a$ = 18.3509(5), $b$ = 7.6532(2), $c$ = 14.9585(4) Å, β= 109.964(2)°, V=1974.57(9)Å$^3$, and $Z$ = 2 (Cambridge Crystallographic Data Centre 1859310). Coordination of the $Ni^{2+}$ ion with ligands generates octahedral anion $Ni[(NCS_4){\cdot}2H_2O]^{2-}$ with N-bonded thiocyanates, while two protonated cations $LidH^+$ remain in an outer coordination field.



The anion and cation are also associated by H-bonds: the sulphur atom S1 interacts with hydrogen atoms covalently bonded to the nitrogen N111 and carbon C113 atoms, and the atom S2 forms a H-bond with the atom C116. The atom H114 of protonated diethylamino-N-group forms a bifurcated H-bond with the carbonyl atom O112 and the sulphur atom S1$^{iv}$ of neighbouring unit cell, the carbon atom C115 forms a weak H-bond with O01W$^{i}$ of the water molecule in neighbouring unit cell, and hydrogen atoms of water molecule are included in hydrogen bonding between the oxygen atom O01W and the sulphur atoms S2$^{ii}$ and S2$^{iii}$ of the neighbouring unit cells (Symmetry codes: (i) −x+1,−y+1, −z+1; (ii) −x+1, y+1/2, −z+1/2; (iii) x, y+1, z; (iv) x, y−1, z).

**P2**

# WHEAT STARCH-PROTEIN INTERACTION: EFFECT OF SALT AND TEMPERATURE OBSERVED BY SMALL ANGLE NEUTRON SCATTERING

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*β*-Lactoglobulin is the major whey protein abundant in cow's milk. *β*-Lactoglobulin has been widely used in the food and pharmaceutical industries due to its rheological and structural characteristics (*e.g.* unfolding, aggregation and gelation properties) [1]. This protein is capable of binding various hydrophobic ligands, such as fatty acids and vitamins, carbohydrates, proteins and even inorganic elements [2]. At the present there is a gap with regard to the knowledge of *β*-lactoglobulin and polysaccharides interactions. Such an understanding of the impact of interactions between *β*-lactoglobulin and polysaccharides in food products and their biological functions will help to design food products with optimized nutritional properties.

The aim of this study was to investigate the effect of NaCl presence and temperature on wheat starch-protein interaction. With that purpose the mixture of *β*-lactoglobulin and wheat starch at a ratio of 1:1 in the presence and absence of 200 mM NaCl was subjected to thermal treatment in the interval of 20-65-25°C and investigated using small angle neutron scattering method.

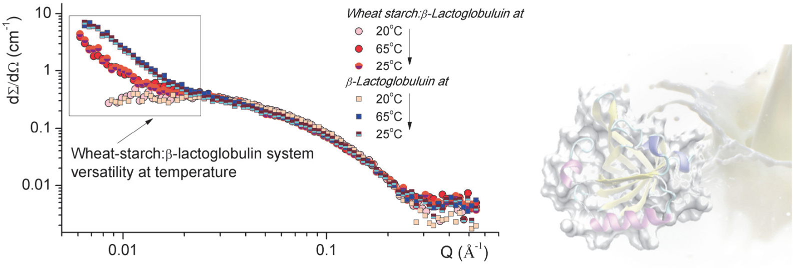

**Figure 1.** Solution neutron scattering results for wheat starch: *β*-lactoglobulin and *β*-lactoglobulin systems.

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**P3**

# THERMAL STABILITY AND MAGNETIC PROPERTIES ASSESSMENT OF Ni AND $Ni_{0.4}Cu_{0.6}$ CERIUM DOPED FERRITES

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Nanocrystalline ferrites are known to be used in different type of applications involving electronic, electrical, wastewater management industry and more recently, as sensible materials. The changes occurred in their electric and magnetic properties when are stressed by an external stimulus can or cannot recommend them as sensitive materials. Before testing the sensibility for a specific stimulus, detailed analyzes of materials must be carried out.

Four samples with nominal composition $NiFe_2O_4$, $NiFe_{1.90}Ce_{0.10}O_4$, $Ni_{0.4}Cu_{0.6}Fe_2O_4$ and $Ni_{0.4}Cu_{0.6}Fe_{1.90}Ce_{0.10}O_4$ were obtained by coprecipitation technique [1]. All samples were calcinated at 600°C for 6h in order to form the specific cubic type spinel phase with *Fd-3m* space group. The newly obtained ferrite powders were pressed into pellets using a 13 mm matrix and sintered at 950°C for 6h. Visible differences such as color and diameter changes were noticed between the samples, indicating porosity or structural modifications, like those occurred in copper cerium doped ferrites ($CuFe_{2-x}Ce_xO_4$) thermal treated at 600°C and 950°C [2]. X-ray analysis and Rietveld refinement technique were used to identify and calculate the quantity of phases present in samples. The results suggested the formation of cubic spinel ferrite as the main phase. For several samples, small quantities of secondary phases such as $\alpha$-$Fe_2O_3$, CuO and $CeO_2$ were identified. Magnetic values such as remanent magnetization ($M_r$), saturation magnetization ($M_s$) and coercivity ($H_c$) were determined by VSM (vibrating sample magnetometry) technique in an applied magnetic field of ±10 kOe. The *M-H* loops of all samples showed an ferrimagnetic behavior, typical for a soft magnetic material, even if the magnetic values raised after the 950°C thermal treatment.

The XRD results indicated a structural instability for cerium doped ferrites due to $CeO_2$ presence in both calcinated and sintered samples. For the $NiFe_{1.90}Ce_{0.10}O_4$ sample, the $CeO_2$ content rises from 1.30 wt% to 3.30 wt% after the 950°C treatment and for $Ni_{0.4}Cu_{0.6}Fe_{1.90}Ce_{0.10}O_4$ sample from 0.50 wt% to 2.90 wt%. This raise of $CeO_2$ phase demonstrate the mobility of $Ce^{3+}$ cations which are unable remain in a higher crystallinity degree spinel structure.

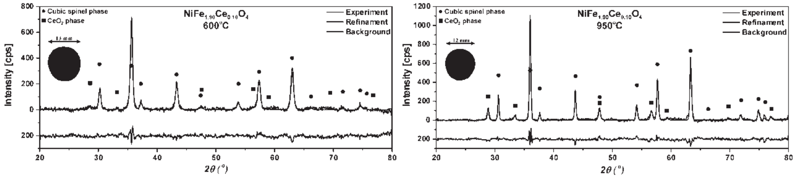

**Figure.** Rietveld refinement of $NiFe_{1.90}Ce_{0.10}O_4$ ferrite sample before and after the 950° thermal treatment.

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**P4**

# QUANTUM-CHEMICAL STUDY OF THE MECHANISM OF NEW DIMERIC COMPLEXES OF TRIVALENT CHROMIUM OBTAINING

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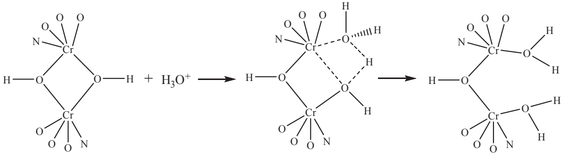
Synthesis of complex compounds with programmed properties with the use of "building blocks" has proven to be very effective, especially in obtaining of molecular magnets, MOFs or optical materials. In the works [1-3] it is shown that structure of such "building block" influence the magnetic properties of complexes with dimeric anions $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$and $[Cr_2(\mu\text{-}OH)(\mu\text{-}Ac)(nta)_2]^{2-}$.

In the present work a possible three-steps mechanism of reaction between the anion $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$(**I**) and isonicotinic acid resulting in formation of a new dimeric complex $[Cr_2(\mu\text{-}OH)(\mu\text{-}iNic)(nta)_2]^{2-}$(**II**) is proposed, on the base of DFT PBE calculations using the quantum-chemical program PRIRODA 06 [4].

**Step 1:** In aqueous solution the electrolytic dissociation of isonicotinic acidtakes place:

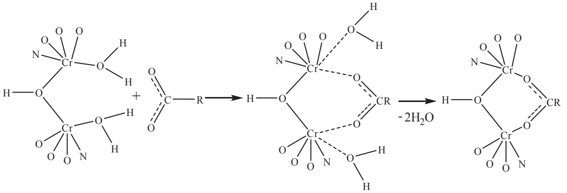
$$R\text{-}COOH + H_2O = RCOO^- + H_3O^+$$

**Step 2:** Interaction of hydronium cation with (**I**) leads to the Product 1 (**Prod1** in Fig. below). The energy barrier of this step is quite small (the calculated value is 3.39 kcal/mol).



| | **R** | **TS1** | **Prod1** |
|---|---|---|---|
| Relative energy | 0.00 | 3.39 kcal/mol | -11.61 kcal/mol |

**Step 3:** The obtained **Prod1** interacts with isonicotinic anion resulting in final complex (**II**).



| | **Prod1** | **TS2** | **Prod2** |
|---|---|---|---|
| Relative energy | 0.00 | 99.58 kcal/mol | 5.21 kcal/mol |

The energy barrier of this reaction is high enough (the calculated value is 99.58 kcal/mol in Fig. above), which is also confirmed by the conditions of synthesis (T and P).

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**P5**

# THEORETICAL STUDY OF KETO–ENOL TAUTOMERISM OF 2-METHYLPROP-1-EN-1-OL

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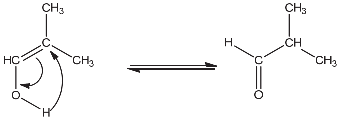
Keto-enol tautomerism refers to chemical equilibrium between a keto and an enol forms. It is usually assumed that the interconversion of the two forms involves a simple intramolecular proton transfer and the subsequent reorganization of the binding electrons leading to a double bond displacement (Eltekov-Erlenmeyer rule) [1].

In the present work, the possible intramolecular mechanism of tautomeric reaction between the unsaturated 2-methylprop-1-en-1-ol alcohol (**I**) and 2-methylpropanaldehyde (**II**) was studied according to Scheme below, by *ab initio* SCF-RHF calculations using the quantum-chemical program GAUSSIAN 09 [2] and the 6-31G basis set.



**III**

The transition state for the intramolecularproton transfer (**TS** in Fig. 1) was localized, and the intrinsic reaction coordinate (IRC) from (**I**) to (**II**) was calculated.Calculations have shown that **TS** is indeed a transition state with one imaginary frequency 2667,25*i* cm$^{-1}$.

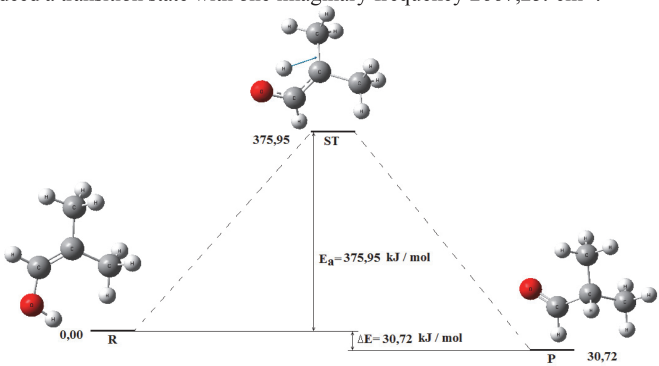


**Fig. 1.** Energy profile of reactionfrom 2-methylprop-1-en-1-ol to2-methylpropan aldehyde.

The calculated activation energy of this reaction is 375,95 kJ/mol. The isomerization process is exothermic with energy release of 30,72 kJ/mol. Thus, one can conclude that the keto isomer (2-methylpropan aldehyde)is more stable than corresponding enol form. However, the calculated energy barrier between the isomers is too high for the free interconversion between them, and in this case the process can be started only with the help of a catalyst.

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**P6**

# INHIBITING EFFECT OF HEXAMMINE-COBALT(III) TRICHLORIDE BIS(1,10-PHENANTHROLINE) ON TUMOR GROWTH IN GRAPEVINE

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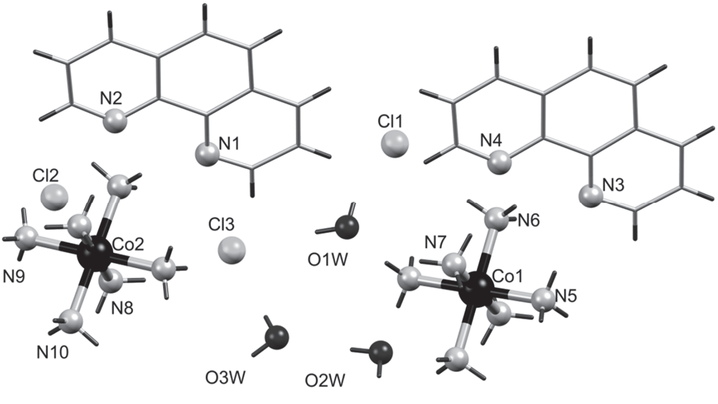
Bacterial cancer of the vine caused by oncogenic bacterium *Rhizobium vitis* is a harmful and widespread disease provoking the significant economic damage in viticulture industry. The lack of chemical substances against this grapevine disease has led to the fact that in the Republic of Moldova the disease still cannot be efficiently controlled and occurs in all areas of vine cultivation. In this regard, the development of new multicomponent compounds with antibacterial properties against oncogenic bacteria that cause the formation of tumors in plants is the most important challenge.

Cobalt(III) coordination compounds showed remarkable biological activities and have found applications as antiviral and antibacterial agents [1]. A new coordination compound with a formula $[Co(NH_3)_6]Cl_3 \cdot 2(phen) \cdot 3H_2O$ (**I**) (Figure) has been prepared from the reaction of hexaminnecobalt(III) chloride with 1,10-phenanthroline. The 3D framework formed in **1** is stabilized by both electrostatic interactions between cations and anions, and strong intermolecular N–H···O, N–H···N, N–H···Cl and O–H···O hydrogen bonds. The cobalt(III) complex **I** has been tested for activity against *Rhizobium* (Agrobacterium)*vitis* and showed the significant antibacterial activity compared with commercial antibiotics andinhibited tumor growth.



**Acknowledgments.** This work is supported by the Science and Technology Center in Ukraine and the National Agency for Research and Development of the Republic of Moldova (17.80013.8007.10/6245STCU).

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**P7**

# 1,3,5-TRIS(4-CARBOXYPHENYL)MESITYLENE – COBALT 2D NETWORKS: OPTIMIZING REACTION CONDITIONS

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Metal-organic frameworks (MOFs) are crystalline porous materials comprised of metal nodes or clusters, bridged together by organic linkers [1]. By carefully choosing the right metals, linkers and reaction conditions, MOFs can be fine-tuned, making them highly attractive for various applications, such as gas storage and separation [2], selective adsorption [3], heterogeneous catalysis [4], controlled drug release [5], or even biomimetic study of enzymes [6].

The present study focuses on preliminary results obtained by reacting 1,3,5-tris(4-carboxyphenyl)mesitylene ($H_3L$) with 4,4'-bipyridyl and cobalt nitrate in various conditions. It was found that slight variations in reaction conditions lead to different outcomes. Thus, by using a lower temperature, the predominant SBU appears to be a Co-Co paddlewheel cluster. Moreover, by using a smaller $H_3L$:4,4'-bipyridyl ratio, a linear trinuclear Co cluster was also observed. On the other hand, when the temperature used was higher, no paddlewheel motif was found. Instead, a dinuclear Co cluster, comprising one tetrahedral and one octahedral metal ion, was observed at a $H_3L$:4,4'-bipyridyl ratio of 1:1.

In all cases, mixtures of two or more products were obtained. Further research, meant to identify sets of conditions which will lead to single products, is underway.

**Acknowledgements.**This research was supported by the grant „Novel porous coordination polymers with organic linkers of variable size for gas storage" (POCPOLIG), ID P_37_707, MySMIS code 104810, funding contract 67/8.09.2016.

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**P8**

# VIBRONIC ORIGIN OF NONPLANARITY AND PUCKERED RING STRUCTURE OF TROPYLIUM TRICATION $(C_7H_7)^{3+}$

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Both the planar and pyramidal nuclear configurations of tropylium trication $(C_7H_7)^{3+}$ are the metastable ones, and there exists a stable off-ring structure with a lower total energy [1]. In the present study, we have revealed the origin of the structural features of this molecule based on a detailed study of its electronic structure and the Jahn-Teller Effect (JTE) and the Pseudo JTE (PJTE).

We start with two reference configurations, the planar structure of the $D_{7h}$ symmetry, and the pyramidal one of $C_{6v}$ symmetry. The planar $D_{7h}$ structure has a doubly degenerate ground electronic state $^1E_2'$ (the highest molecular orbital $e_1''$ is occupied by two electrons). Therefore, due to the JTE, it undergoes the in-plane distortions to the structure of $C_{2v}$ symmetry. The cross-section of the adiabatic potential energy surfaces (APES) along the $Q_{e2'}$ coordinate is shown in the Figure 1, part (a). In its turn, this configuration is unstable with respect to the out-of-plane distortion of $b_1$ symmetry due to the PJTE coupling of the ground $^1A_1$ and the excited $^1B_1$ electronic states (the PJTE $(^1A_1+^1B_1)\otimes b_1$ problem; part (b) in the Figure 1).

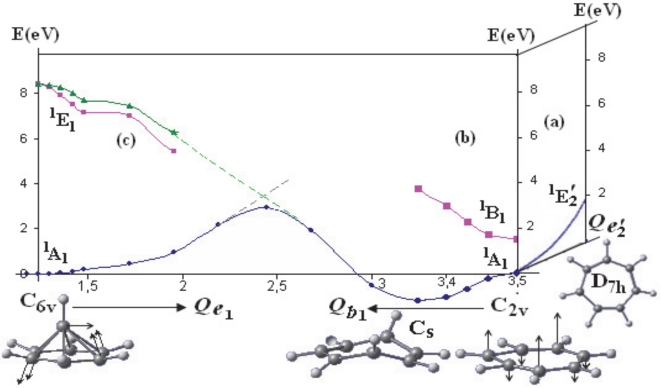

**Figure 1.** APESes of $(C_7H_7)^{3+}$ along the distortion coordinates $Q_{e1}$, $Q_{e2'}$, and $Q_{b1}$ in the planar and pyramidal configurations. They are the distances from the nonequivalent ($C_7$) carbon atom to the middle of the opposite C-C bond.

Transformation of the pyramidal ($C_{6v}$) structure into the equilibrium puckered ring structure takes place along the low-symmetry coordinate $Q_{e1}$. At $Q_{e1}=0$ the electronic ground state is $^1A_1$, and there is a double-degenerate excited $^1E_1$ state at 8.40 eV. Along the $Q_{e1}\neq 0$ the $C_{6v}$ symmetry is reduced to $C_s$, the $^1E_1$ doublet splits into the $^1A'$ and $^1A''$ states, and one of its components ($^1A'$) has an avoided crossing with the ground $^1A'$ state at $Q_{e1}$= 2.44Å (part (c) in the Figre 1). The global minimum at $Q_{e1}$=3.34 Å is a clear continuation of the split excited $^1E_1$ term and corresponds to the equilibrium puckered ring structure.

Thus, the metastability of the pyramidal configuration of tropylium trication molecule, and its equilibrium puckered ring structure are owing to the common action of the PJT coupling of the ground and excited electronic terms and the JT effect in the degenerate excited state.

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**P9**

# LANTHANIDE-BASED METAL ORGANIC FRAMEWORK. SYNTHESIS, STRUCTURE AND PROPERTIES

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Metal-organic frameworks (MOFs) are a class of new porous materials which have been intensively studied in the last decade [1]. These compounds provide diverse and easily modifiable structures so that their applications in diverse fields like gas storage [2], catalysis [3], molecular separation [4], optics [5] and drug delivery [6] are promising.

Herein, we report the synthesis, structure and properties of new lanthanides MOFs, obtained by using *1,3,5*-tris(*4*-carboxyphenyl)-*2,4,6*-trimetylbenzene($H_3L$) as a linker. X-ray crystallography reveals isostructural lanthanide MOFs, $Ln(L)(H_2O)_2$ (Ln = La, Ce, Nd), that are obtained from the solvotermal synthesis in DMF, ethanol and water as solvents. All three compounds are stable up to 450°C and exhibit permanent porosity, with BET surface areas around 400 $m^2$/g. Other properties (fluorescence, magnetism, etc.) are under investigation.

**Acknowledgements**.This research was supported by the grant „Novel porous coordination polymers with organic linkers of variable size for gas storage" (POCPOLIG), ID P_37_707, MySMIS code 104810, funding contract 67/8.09.2016.

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**P10**

# PHYSICO-CHEMICAL CHARACTERIZATION OF ROBUSTA COFFEE AND GROUNDS RESULTED FROM THEIR USE IN PROFESSIONAL COFFEE MACHINES

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Coffee is, without a doubt, the most wide-spread and well-known drink in the world. People all around the world have been drinking coffee, prepared by one way or another, for over 400 years. No day passes by without the majority of the inhabitants of this planet sipping from a steaming cup of coffee (400 billion cups of coffee are drunk every year all over the world). Robusta is a bitter coffee, with a high caffeine content, but lacking in the flavour and aroma of the Arabica varieties. Robusta is usually added to blends with Arabica, for economic purposes (lower priced coffee). In the traditional Italian espresso mixtures (especially *miscela napoletana*), Robusta is added at a minimum of 20% ratio to the Arabica content in order to raise the caffeine content of the coffee. The 100% Robusta coffee is not recommended for consumption, even though it can still be found on the market, including in Romania, especially in coffee bean blends intended for vending machines. The increase of the purchasing power and the elimination of the excise duty in 2016 have contributed to a significant increase in coffee consumption and to obtaining an increasing amount of coffee grounds that could be exploited [1-3]. The amount of coffee grounds generated each year is estimated to reach approximately six million tonnes [5]. This study aims to analyze the main physic-chemical characteristics of Robusta coffee and grounds resulted from their use in professional coffee machines in order to identify new possibilities for exploitation. The thermal characterization techniques applied for Robusta coffee grounds are TG/MS/FTIR and MCC. The morphological characterization of coffee grounds particles was carried out using Scanning Electron Microscopy (SEM). The experimental density measurement for espresso coffee was recorded using an Anton Paar DMA 4500 density meter. In order to evaluate the possibility of using left-over espresso coffee for beautifying and protecting wood, UV/Vis absorption spectra were recorded with the help of a Shimadzu spectrophotometer. Left-over Robusta coffee was applied on fir wood plates with the size: LxWxT = 120x30x5 mm, and was left to dry. A KRUSS Goniometer was used to measure the contact angle and an increase in value from 52° for the control sample to 85° for the left-over espresso (Robusta) coffee-treated plates was found.

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**P11**

# ELECTROCHEMICAL FORMATION OF NANOSTRUCTURAL FUNCTIONAL COATINGS FOR MICROELECTRONICS

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The work deals with the solution of the fundamental problem of the modern electroplating technology of functional materials by the controlled synthesis of metal silver and gold coatings with tailor-made properties for microelectronics.

The range of the stable process of functional deposition (minimal dynamic instability of the system) (the electrochemical resistance is $4RT/\alpha nFj_{lim}$ under polarization with current $j=0.4\div0.6j_{lim}$) where the most favourable energetic of preferential crystal face growth at the minimal work of surface formation is realized, has been determined; this allows one to obtain in any electrolyte deposits of electrolytic gold and silver whose physicochemical properties are stable. A new law governing electrochemical kinetics has been established: the discharge of different coordination silver (I) and gold (I) ions occurs by a common mechanism. A self-consistent parameter, which is the electrochemical resistance of a system, the nature of complex ion and electroactive complex (EAC) formation conditions, is proposed as a correlation parameter for the prediction of the functional properties of silver and gold coatings.

New engineering solutions have been found: alternative ways of replacing contact gold by alloys based on refractory metals with iron subgroup metals have been developed; a new selective method for the electrochemical regeneration of silver has been developed; electrolytes have been optimized (the electrolyte composition, the nature of EAC, the range of stable electrodeposition, electrolysis conditions have been justified); the problems of contact exchange, passivation of anodes, increasing the service life of buffer electrolytes have been solved; these electrolytes have been introduced in technologies for the deposition of conducting contact layer of gold, silver, tungsten and molybdenum alloys and competitive articles of micro- and nanoelectronics with considerable (up to 15%) reduction of rejected products [1-5].

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**P12**

# SYNTHESIS, CHARACTERIZATION, CRYSTAL STRUCTURE AND ANTIMICROBIAL ACTIVITY OF COPPER(II) COMPLEXES

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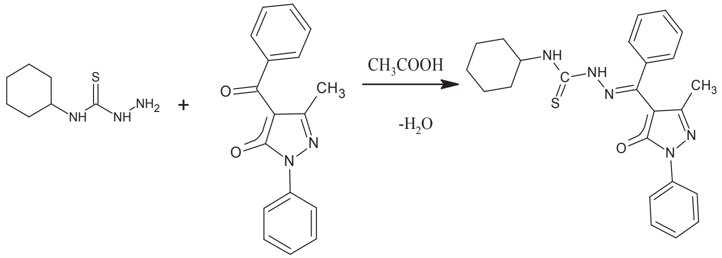
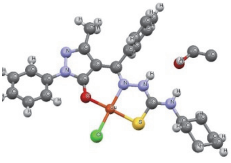
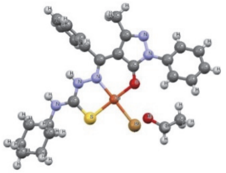
N-Cyclohexyl-2-((5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)methylene)-hydrazinecarbothioamide ($H_2L$) ligand was synthesized, according to the scheme:



Characterization of novel 4-cyclohexylthiosemicarbazone was performed by FTIR-ATR spectroscopy, $^1$H-NMR and $^{13}$C-NMR.Two coordination compounds of copper(II) with this ligand were synthesized. Structure ofcoordination compounds were confirmed by IR spectroscopy, metal analysis and by single crystal X-ray diffraction:



$[Cu(HL)Cl]\cdot C_2H_5OH$



$[Cu(HL)Br]\cdot C_2H_5OH$

The compounds were also tested for antimicrobial activity:

| Compound | *Staphylococcus aureus* | |
|---|---|---|
| | MIC mg/mL | MBC mg/mL |
| $[Cu(HL)Br]\cdot C_2H_5OH$ | 0.250 | 0.500 |
| $[Cu(HL)Cl]\cdot C_2H_5OH$ | 0.250 | 0.500 |

Coordination compounds were investigated for bacteriostatic and bactericideactivity on *Staphylococcus aureus*. The minimum inhibitory concentration for *Staphylococcus aureus* of $[Cu(HL)Br]\cdot C_2H_5OH$ and $[Cu(HL)Cl]\cdot C_2H_5OH$ is within 0.25 mg/mL, the minimum bactericide concentration is 0.5 mg/mL.

**P13**

# MODELLING THE MASS TRANSFER IN SUBLIMATION PROCESS

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The sublimation process is frequently used in the chemical industry to separate a volatile component from other non-volatile ones [1-3]. The main purpose of this paper is to develop a phenomenological model to sublimate small and large balls as well as bars and blades of naphthalene fixed in special devices that provide a flat surface in contact with the entraining agent. For this purpose, programs developed in Mathcad were used. The global mass transfer coefficient Kp was determined using a criterion equation of the type: $Sh = a + b \cdot \mathrm{Re}^{c} \cdot Sc^{d}$. The parameters in the model (a, b, c and d) were determined for each type of particle. The phenomenological model allowed to determine the naphthalene mass which was lost after a 10-second time frame from the beginning of modelling, this time being necessary in order to attenuate the oscillations that could occur upon initiating the calculation. The value of this mass was marked down as dm10 and could be considered as an average value for mass loss under such operating conditions. If it were amplified with the time frame desired, it could serve to compare and verify experimental data that could be affected by experimental errors. A quick prediction of results can thus be made if the initial experimental conditions are known. The criterion equation obtained for each type of particle also allows to calculate the individual mass transfer coefficient. The calculated standard deviations are smaller than 0.04 for the bars, large and small balls and smaller than 0.08 for the blades.

## Acknowledgments

Catalin Lisa and Silvia Curteanu is grateful for financial support from the "Program 4, Fundamental and Border Research, Exploratory Research Projects" financed by UEFISCDI, Project No. 51/2017.

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**P14**

# STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATION OF Cd(II) COORDINATION COMPLEXES WITH 4,4´-DIAMINODIPHENYLMETHANE

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In the research of supramolecular chemistry, much interest has recently been focused on the crystal engineering of coordination frameworks because of their intriguing architectures, fascinating topologies, intertwining phenomena, and potential application in functional materials [1]. The family of metallacyclic nanostructures assembled from transition metal and bridging ligands containing nitrogen donor's atoms is now a well-established group of coordination polymers, and the diversity of such coordination nanostructures makes them remarkable examples in the growing library of self-assembled entities [2].

The ligand 4,4´-diaminodiphenylmethane (dadpm) may be utilized as a building block for the construction of novel organic/inorganic hybrid materials. Herein, we report on the self-assembly reactions of dadpm ligand and cadmium(II) perchlorate or acetate, combined with the structural and IR characterizations of the monomer $[Cd(dadpm)_2(CH_3COO)_2(H_2O)_2]$ (**1**) and 1D coordination polymer $\{[Cd(dadpm)_6](ClO_4)_2\}_n$(**2**). For both compounds the IR spectra were measuredand, compared with the pure ligand, they confirm the presence of organic ligand used in the syntheses. The absorption asymmetric and symmetric $\nu(NH_2)$ bandsare observed at 3269-3392 cm$^{-1}$ and deformation vibrations $\delta(NH)$ at 1612-1627 cm$^{-1}$ regions. The bands at 2826-2886 cm$^{-1}$ regions are assigned to the $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ stretching vibrations. Compounds **1** and **2** belong to the same monoclinic crystal system, but differ in space groups, $P2_1/n$ for **1** and $C2/c$ for **2**. The X-ray analysis reveals that in **1** Cd(II) ion adopts a slightly distorted octahedral geometry with the $N_2O_4$-set of donor atoms going from two dadpm molecules in axial positions; two water molecules and two acetate anions coordinated in a monodentate mode occupy the equatorial positions (Fig. 1a). The complexes are linked in the H-bonded layer through hydrogen-bond interactions between coordinated water molecules as H-donor and the N atom of amino-ligand and carboxylic-group as acceptors. Compound **2** contains a six-coordinated Cd(II) center formed by N atoms from six different dadpm ligands, two coordinated monodentate and four - bidentate-bridging to the metal ion, forming a distorted $N_6$ octahedral coordination core of Cd (Fig. 1b). In the crystal the coordination double chains are assembled *via* hydrogen-bond interaction between $ClO_4^-$ anionand the amine ligands of adjacent Cd(II) atoms.

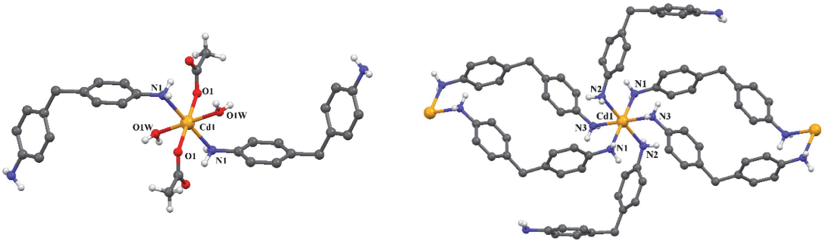

**Figure 1.** View of the Cd(II) environment in **1** (a) and **2** (b).

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**P15**

# INFLECTION POINTS ON THE ABSORBION ISOTHERMES OF STRONTIUM ION ON OXIDATE ACTIVED CARBONS

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In some publications, the adsorption isotherms of some heavy metal ions, measured at different pH values on carbonic adsorbents, have inflection points followed by the increase of the adsorption values. In these works, however, the cause of the appearance of these points is not questioned.

The purpose of the present work is to identify the causes of the appearance of the inflection points on the adsorption isotherms of the strontium ions on the activated carbons CAN-7 and CAN-8, obtained from walnut shells. The jumps on both adsorption isotherms are very clear and start on CAN-7 and oxidized CAN-8 at the same equilibrium concentrations of strontium ions. Probably, an important role in the adsorption process of strontium ions from aqueous solutions on these two active carbons has the surface chemistry of these adsorbents and the possibility of formation on the surface of the adsorbents of polymolecular layers. The appearance of the inflection points on the adsorption isotherms of the strontium ions on CAN-7 and CAN-8 oxidized active carbons are related to the interaction of the strontium ions with the non-homogeneous surface of the adsorbents (based on the phosphatic groups, weak and strong carboxylic groups), subsequent formation of the polymolecular adsorbent layer, due to the hydrogen bonds formed between the $Sr(OH)^+$ ions, but also to the collateral interactions between the strontium ions adsorbed at the interface. The interaction between hydrated strontium ions ($Sr^{2+}$) and the supermicroporous and microporous surface of adsorbents will be totally different from that of the mesopores.

**P16**

# SYNTHESIS AND INVESTIGATION OF NEW DIMERIC CHROMIUM(III) BUILDING BLOCKS

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In previous studies it has been shown that $[Cr_2(OH)_2(\mathit{nta})_2]^{2-}$ and $[Cr_2(\mu\text{-}OH)(\mu\text{-}\mathit{Ac})(\mathit{nta})_2]^{2-}$ manifested as mono- and polydentate ligands, due to their specific structural characteristics.In a continuation of the previous studies, we has focused on the diversification of the chromium(III) dimeric building blocks with the perspective to use in the design of then 1D-3D coordination polymers [1, 2].

By using homogeneous aqueous mixtures of $[Cr_2(OH)_2(\mathit{nta})_2]^{2-}$ and formic, acetic, cyano-acetic, benzoic or *iso*-nicotinic acids, the anions of Cr(III) in solution were obtained at concentration $1 \cdot 10^{-3}$ M of reactants. Determination of the end of the reactions in solutions was performed by UV-Vis spectrophotometry in time.

The Figure shows, that the characteristic peaks of Cr(III) ions, in the $\{NO_5\}$ environment, formed from $\mathit{nta}^{3-}$ and $2OH^{-}$ ligands, the characteristic peaks at 408.1 nm and 584.2 nm (Figure, blue line) shifts to higher energy values, and does not differ from the spectrum of the combination $[(\mu\text{-}H_2O)_3\{Pb(H_2O)_2\}_2\{Cr_2(\mu\text{-}OH)(\mu\text{-}\mathit{Ac})(\mathit{nta})_2\}_2]\cdot 14H_2O$ (Figure, red line) described in [2]. Thereby, we can assume, that in solution the $[Cr_2(\mu\text{-}OH)_2(\mathit{nta})_2]^{2-}$ reacts with the respective carboxylic acids with formation of new complexes, similar to the $[Cr_2(\mu\text{-}OH)(\mu\text{-}\mathit{Ac})(\mathit{nta})_2]^{2-}$ anions.

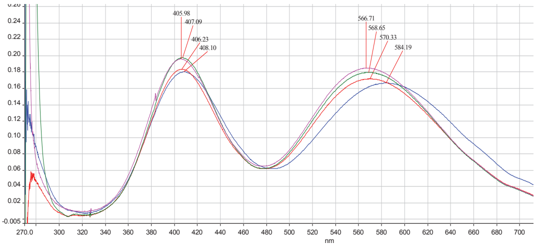

***Figure.*** *UV-Vis spectra, 1 hour after preparation. The blue line - the initial reagent, anion $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$; the red line - $[Cr_2(\mu\text{-}OH)(\mu\text{-}Ac)(nta)_2]^{2-}$; the green line – $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$ in reaction with benzoic acid (1: 1); pink line - $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$ in reaction with cyanoacetic acid.*

To confirm thishypotheses, the reaction between $[Cr_2(OH)_2(\mathit{nta})_2]^{2-}$, $Fe^{2+}$, and *α,α′-bpy* in the presence of iso-nicotinic acid was performed. Thus, a new complex with the composition $[Fe(\mathit{bpy})_3][Cr_2(\mu\text{-}OH)(\mu\text{-}\mathit{iNic})(\mathit{nta})_2]\cdot 9.5H_2O$, as a result of the interaction of the aqueous solutions, was obtained, and were characterized by IR spectroscopy, X-ray analysis and magnetochemistry.

The new anion $[Cr_2(\mu\text{-}OH)(\mu\text{-}\mathit{iNic})(\mathit{nta})_2]^{2-}$ contains the rest of the *iso*-nicotinic acid, which serves as a bridging ligand, coordinated through the O and O' atoms, between two Cr(III) atoms of dimer.

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**P17**

# MIXED-VALENT OCTANUCLEAR MANGANESE COMPLEXES WITH 1,3-BIS(3-METHOXYSALICYLIDENEAMINO)-2-PROPANOL AND ITS 5-SUBSTITUTED ANALOGUES

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There has been considerable interests indinuclear and tetranuclear manganese complexes, because such manganese units play an important role in some manganese-active enzymes[1].Dinucleating Schiff-base ligand, 1,3-bis(salicylideneamino)-2-propanol, is useful to construct mononuclear, tetranuclear, and polynuclear manganese complexes [2-4].Recently, we synthesized tetranuclear manganese complexes using the 3-methoxy-substituted Schiff-base ligands, 1,3-bis(3-methoxysalicylideneamino)-2-propanol ($H_3$msap) and its 5-bromo-substituted derivative ($H_3$bmsap)[5,6].In this study, we isolated octanuclear manganese species with an incomplete-double-cubane core. The isolated complexes were characterized by elemental analyses, IR and UV-vis spectra, and single-crystal X-ray structure analysis, elucidating the chemical formula of$[Mn_8(bmsap)_2(ClC_6H_5COO)_8(O)_4(MeOH)_2(H_2O)_2]$as shown in Figure. We report here the synthesis and crystal structures of these mixed-valent $Mn^{III}_2Mn^{II}_6$complexes.

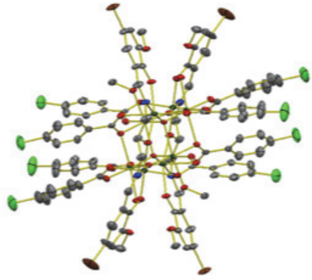

**Figure.** The crystal structure of $[Mn_8(bmsap)_2(ClC_6H_5COO)_8(O)_4(MeOH)_2(H_2O)_2]$.

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**P18**

# DOSY NMR STUDIES OF SOME Zn(II) AND Cd(II) COORDINATION POLYMERS BASED ON METHYLATED N,N'-DONOR AZINE LIGANDS

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The use of diffusion NMR measurements in the field of coordination chemistry is nowadays boosted by the extraordinary progress achieved in the study of various supramolecular architectures or smaller metallic complexes, allowing one to assess the aggregation state, character of intermolecular interactions, stability or association constants between different hosts and guests [1].

We present herein the results of our investigations on the application of the Diffusion Ordered SpectroscopY (DOSY) method on seven coordination polymers $[Zn(I)_2(4\text{-bpmhz})]_n$ (**1**), $[Cd(I)_2(4\text{-bpmhz})]_n$ (**2**), $[Zn(I)_2(3\text{-bpmhz})]_n$ (**3**), $[Cd(I)_2(3\text{-bpmhz})_2]_n$ (**4**), $[Zn(NO_3)_2(H_2O)_2(4\text{-bpmhz})]_n \cdot 0.5n(EtOH)$ (**5**), $[Cd(NO_3)_2(4\text{-bpmhz})_{3/2}(MeOH)]_n \cdot 0.5nH_2O$ (**6**) and $[Zn(NO_3)_2(3\text{-bpmhz})_2]_n$ (**7**) that were derived from methylated azine ligands of the bis-monodentate N,N'-donor type, *1,2-bis(1-(pyridin-4-yl)ethylidene)hydrazine* (4-bpmhz) and *1,2-bis(1-(pyridin-3-yl)ethylidene)hydrazine* (3-bpmhz). Compounds **1-7** were characterized in the solid state by single-crystal X-ray structural analysisand in solution by spectroscopic methods [2]. Room-temperature (298K) diffusion experiments on coordination polymers **1-7**, as well as 4-bpmhz and 3-bpmhz ligands were conducted to determine the size of molecular systems in DMSO-$d_6$ solution. The translational diffusion coefficient value (D), which is a function of the molecular size and shape, was determined for metallic complexes **1-7** and their ligands in solutions of different molarities. The D values of DMSO-$d_6$ molecules were used as reference in the cases of all studied samples. For all solutions the ratio $D_{DMSO\text{-}d6}/D_{compound}$ was calculated. After processing the experimental data that included comparison of the ratio $D_{DMSO\text{-}d6}/D_{ligand}$ to the ratio $D_{DMSO\text{-}d6}/D_{compound}$, the values varying from 84% and 96% were calculated for all samples. The obtained data are favorable to the presence in solutions of complexes **1-7** of the species with the molecular size comparable to that of free ligands. The obtained results point to the dissociation of the 1D chain structures of polymers **1-5** and **7** and 2D coordination networkof **6**in DMSO-$d_6$ solutions. For calculation of D the Stokes-Einstein equation has been used [3].

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**P19**

# THE ROLE OF MIXED VALENCE ON MAGNETIC AND ELECTRONIC PROPERTIES IN $La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$ MANGANITES

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The physical properties of $AMnO_3$ manganites, including colossal magnetoresistance (CMR), are governed by competition of different electronic and structural phases—paramagnetic insulating, charge-ordered (CO) and antiferromagnetic (AFM) insulating, and ferromagnetic metallic (FM) phases due to mixed valence of $Mn^{3+}$ and $Mn^{4+}$ ions [1,2].

This study presents the influence induced by the Mn substitution with Co and sintering conditions on the crystalline and electronic state of the $La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$ (x=0.05, 0.10, 0.15) manganites.The samples were obtained by sol-gel method, annealed in air at 1200°C and 1250°C. XRD analyses indicate the presence of rhombohedral phase (GS R-3c) for all samples. A small increase of unit cell parameters was observed with the increasing of cobalt content. In FTIR spectra, main absorption bands indicate the differences between equatorial $M-O_e$ and axial $M-O_a$ bond lengths due to the Jahn-Teller effect that confirm the polycrystalline rhombohedral (R-3c) symmetry. The molar magnetization has a maximum for samples with higher Co concentration, suggesting a contribution of Co to the magnetization process (Fig.1a). The values of Curie temperature ($T_C$) follows the same variation for both sintering temperatures, with a maximum at x = 0.1.

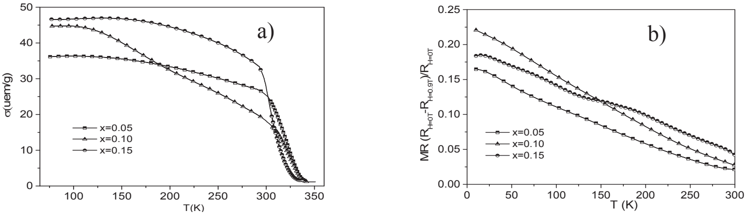

*Figure 1. Molar magnetization (a) and magnetoresistance (b) of $La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$ annealed at 1250 °C vs. temperature.*

The resistivity of all samples shows inhomogeneous dependence temperature with Co content, the metal-insulator transition can be observed near the $T_C$. The MR of the samples show almost a linear dependence by temperature (Fig. 1b), being higher at low temperatures and an enhancement of the MR effect with increasing of x value. Also, it was observed an inversion of MR order between samples with x=0.1 and 0.15 below 150 K. The variation of MR values could be attributed to the effect of grain boundaries and its decrease around $T_C$ shows a strong interaction between carrier spin and spin of Mn ions.

**Acknowledgments.**This work was supported by IUCN-Dubna project, no.39/2019, theme: 04-4-1121-2015/2020.

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**P20**

# NOVEL MESOPOROUS MATERIALS FOR ORGANIC POLLUTANTS PHOTODEGRADATION

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Due to the industrial progress during the past decades, two of the most important issues of human life are water recycling and air cleaning. The use of titanium oxide ($TiO_2$) is a promising reactive technique for the removal of pollutants from air or water as self-cleaning surfaces because of the biological and chemical stability, high photoactivity, low toxicity and low cost of $TiO_2$ [1].

On the other hand, ferrites offer two main advantages: the spinel crystal structure with available extra catalytic sites and the band gap capable of absorbing visible light. When combined with $TiO_2$, the $TiO_2$/ferrites composites are expected to show higher efficiency as photocatalysts than the individual ferrite or titania alone.

During our study, $ZnFe_2O_4$ and $ZnFe_{1.98}La_{0.02}O_4$ nanoparticles were synthesized using a sol-gel autocombustion method. Afterwards, an ultrasound (US) – assisted synthesis was employed, ferrites nanocristals being added in the reaction pot before the titanium source. Pluronic F127 was used as templating agent, which was eliminated during the microwaves assisted calcination, creating mesopores.

The properties of the synthesized samples were investigated using various techniques: X-Ray Diffraction, $N_2$-sorption measurements, SEM Imaging, UV-Vis Diffuse Reflectance Spectroscopy. The photocatalytic efficiency was investigated by UV dye degradation.

It was concluded that the $TiO_2$/ferrites composites have the ability to enhance the photocatalytic reaction, by means of efficient charge carrier transfer due to the narrow band gap of ferrites.

**Acknowledgements.** The authors thank for the financial support to Project PN-III-P1-1.1-PD-2016-1316, within PNCDI III.

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**P21**

# SULPHITATION OF WINE PRODUCTS WITH SOLUTION PREPARED OF TARTARIC ACID AND POTASSIUM SULPHITE

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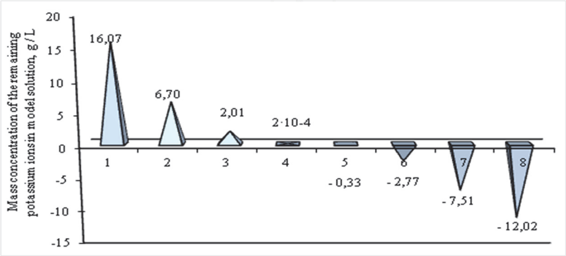
Sulphitation of wine products is a routine process widely used in the wine industry at various stages of production and regulated by normative and technological documents of wine products manufacturing. Disposing of the needs and technological possibilities of industrial enterprises, sulphitation process of wine is carried out using sulphur dioxide as sulphur source: sulphuric acid, native sulphur, liquefied sulphur dioxide and salts of sulphuric acid (meta - and sulphites) [1]. The sulphitation process of wine products using of salts of sulphites - potassium sulphite ($K_2S_2O_5$, E 224) has gained a large spread not only in craft winemaking but also in large wineries. At the same time, the basic disadvantage of this process is the exogenous enrichment of wine products with potassium ions, and the reduction of mass concentration of total titratable acids, which leads to the risk of crystalline instability resulting from the precipitation of tartaric salts thus, limiting the range of use of this process at the first stages of the manufacture of the wine products [2].

Under laboratory conditions, a process for the sulphitation of wine products has been developed by reducing the risks of crystalline instability at all stages of their production, with the use of potassium sulphite solutions. The process provides a prior preparation of a mixture of 100 $g/dm^3$ potassium sulfite solution and tartaric acid of 300 $g/dm^3$ solution at rapport 2:1 (by volume ratio) with intense stirring. According to the results, the quantitative equilibrium of precipitation is reached at a quantity of 0.3315 mol of the corresponding reactant species and at the value of 0.9995 molar ratio (Figure).



The positive value or "+" of the mass concentration denotes the excessive content of potassium ions and the negative value or "-" describes content necessary for the complete precipitation of the tartaric acid in model solution.

**Figure.** Dynamics of mass concentration of potassium ions remaining in model solution.

The prepared solution, based on potassium sulphite and tartaric acid, is used for the sulphitation into wine products, after the pre-separation of the formed precipitate, at all stages of their production. The described process was granted as national patent BOPI no. 952 of 2015. Effectiveness of the selected agent described the preservation of crystalline stability (no tartaric precipitate) and the value of saturation temperature remained constant in the samples.

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**P22**

# WATER-SOLUBLE COMPLEXES OF Cu(II) WITH SEMICARBAZONE LIGANDS: IR SPECTROSCOPY AND ANTIMICROBIAL PROPERTIES

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It is known that some of semicarbazones have the medical properties: *in vivo* anticancer [1], potential agentsanti-*Trypanosoma cruzi* [2], antituberculous activity [3] and are used as anticonvulsants [4].

In our previous work we have successful obtained the Cu(II) complex with *o*-vanillin semicarbazone ligand **L$^1$**[Cu(L$^1$-H)($H_2O$)]$_2$($SO_4$)·5.25$H_2O$ (**1**) [5] and herein we report the synthesis, IR spectroscopy of novel Cu(+2) complex with semicarbazone of 2.3-dihydroxybenzaldehyde **L$^2$** [Cu(L$^2$-H)($H_2O$)]$_2$($SO_4$)·n$H_2O$ (**2**) (Figure) and antimicrobial properties of ligands and their complexes.

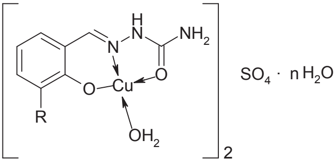

**Figure.** The chemical diagram for **1** (R = $OCH_3$, **L$^1$**) and **2**(R = OH, **L$^2$**)

Green crystals of **2**similar to crystals of **1**were obtained by the same procedure described for **1**. The complexes have been characterized by elemental analysis (Cu, C, H, N) and powder diffraction method for polycrystalline samples. The IR spectra of **1** and **2**display the characteristic band for $SO_4^{2-}$ ion at 1076-1034 and 1097-1048 cm$^{-1}$, respectively. The other main bands: $\nu_{N-H}$ 3311 and 3328 cm$^{-1}$(bs) cm$^{-1}$, $\nu_{C=O}$ 1664 and 1658 (s) cm$^{-1}$, $\nu_{C=N}$ 1548 and 1554 cm$^{-1}$ (s), $\nu_{C-O}$ 1244, 1219 and 1262, 1214 cm$^{-1}$, respectively for **1** and **2**.

Antimicrobial activity of aqueous solutions of compounds **1** and **2**, as well as organic ligands **L$^1$** and **L$^2$** in DMSO with initial concentrations of 1%, was studied by the method of serial double dilutions and was conducted on gram-positive and gram-negative test microorganisms (*Bacillus subtilis* CNMN BB-01 4,8·10$^8$ UFC/mL, *Pseudomonas fluorescens* CNMN-PFB-01 4,8·10$^8$ UFC/mL, *Pseudomonas aurantiaca CNMN PsB-08* 4,8·10$^8$ UFC/mL, *B. cereus fluorescens* CNMN-BB-07 4,8·10$^8$ UFC/mL). Thus, it has been established that MBC **L$^1$** is equal to 0.12% in a DMSO solution, and MBC **1** is equal to 0.12% in water solution; MBC **L$^2$** is 0.06% in a solution of DMSO and MBC **2** is 0.5% in an aqueous solution with respect to the test microorganisms under study (MBC of DMSO is 12% and MBC of $CuSO_4 \cdot 5H_2O$ is 0.12%).

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**P23**

# THE CRYSTAL STRUCTURE OF COPPER(II) OPEN CUBANE-LIKE COMPLEX WITH 2,3-DIHYDROXYBENZALDEHYDE SEMICARBAZONE

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Oxygen bridged tetrameric clusters with a cuban-like $\{M_4O_4\}$ core (M = $Mn^{II}$, $Fe^{II}$, $Co^{II}$, $Ni^{II}$, $Cu^{II}$, $Zn^{II}$) are well known and being used to identify the correlation between structural parameters and magnetic properties [1, 2].

Herein we report the synthesis and crystal structure of the novel tetranuclear copper(II) coordination compound $[Cu_4(H_2L)_4](NO_3)_4{\cdot}4H_2O$, where $H_3L$ is 2,3-dihydroxybenzaldehyde semicarbazone. The complex crystallizes in $P4_2/n$ space group, $a = b = 13.7080(6)$ Å, $c = 12.5284(6)$ Å, $V = 2354.2(2)$ Å$^3$, $Z = 2$. The asymmetric units consists of a $[Cu(H_2L)]^+$ moiety, one $NO_3^-$ anion and one solvent water molecule. The cationic complex reside around special position of four-fold inversion axis, thus having $S_4$ molecular symmetry. The monodeprotonated organic ligands coordinate to two metals in chelate-bridging tetradentate O, O, N, O mode forming three fused metallocycles, resulted in open cubane-like structure (Figure).

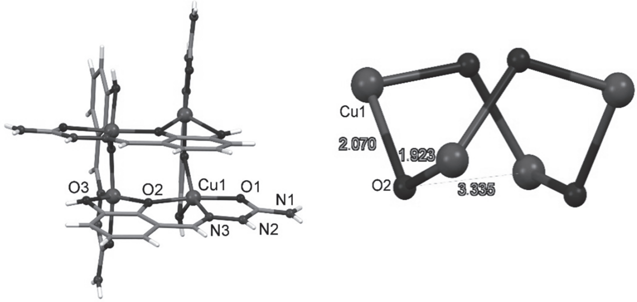

**Figure.** Molecular structure of cationic complex (*left*) and $\{Cu_4O_4\}$ core (*right*)

The Cu(II) atom is five-coordinated by four O atoms and one N atom from two ligand to form a distorted trigonal bipyrimidal $NO_4$ configuration. The equatorial plane is defined by atoms O(2)*, O(3)*, N(3) and axial position is occupied by O(1) and O(2) (Cu(1)–O(2)* 2.070(3) Å, Cu(1)–O(3)* 2.159(3) Å, Cu(1)–N(3) 1.929(4) Å, Cu(1)–O(1) 1.976(4) Å and Cu(1)–O(2) 1.924(3) Å). In the open $\{Cu_4O_4\}$ core angle O(2)–Cu(1)–O(2) = 94.8(1)° and Cu(1)–O(2)–Cu(1) = 116.1(1)°, the non-bonding distance Cu(1)···O(2) is 3.335 Å. Ions $NO_3^-$ in the external sphere are bonded to the $-NH_2$, >N–H, −OH groups of cationic complex and molecules of water through hydrogen bonds (N(1)–H···$O_{nitrate}$ 3.038 and 2.979 Å, N(2)–H···$O_{nitrate}$ 2.976 Å, O(3)–H(1)···$O_{nitrate}$ 2.617 and 2.918 Å, O–H(*w*)···$O_{nitrate}$ 3.026, 3.204 and 3.289 Å).

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**P24**

# CLARIFICATION OF THE EFFECT OF ULTRASOUND ON THE YIELD OF BIOLOGICALLY ACTIVE SUBSTANCES IN THE PROCESSING OF TOMATO SEEDS

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When extracting plant materials, soaking is recommended, however, air bubbles, clogging the capillars, do not fully give out the biologically active substances (BAS). Ultrasound (US), creating a sound-capillary effect, accelerates the displacement of these air bubbles and creates the conditions for dissolution of biologically active substances. Therefore, ultrasound allows not only intensifying the process of mass transfer but also reducing extraction time, and increase the yield of valuable components from tomato seeds.

The possibility of using ultrasound to extract biologically active substances from tomato seeds from different regions of Moldova from waste from the production of tomato juice of vegetable raw materials was studied.

Based on the studies, the following stages of two combination methods were proposed for extracting biologically active substances from tomato seeds:

1 - preliminary ultrasonic treatment of whole or crushed seeds;
2 - three-stage extraction of treated seeds, unlike four according to traditional technology.

The main parameters of the process of ultrasonic processing are determined, allowing to predict the efficiency of the output of biologically active substances compared with traditional technology.

It is shown that the combination of the traditional method of extraction with ultrasound for the extraction of valuable components from waste of plant origin is promising and competes with the traditional one by shortening the process time from 36 to 12 hours, lowering the temperature from 100 to 55ºC and yield of biologically active substances up to 1.5 times.

## *Conclusions*

1. The chemical composition of tomato seed extracts that underwent ultrasonic treatment in various modes was evaluated in comparison with extracts processed by traditional technology.
2. It is shown that significant changes in the studied parameters of biologically active substances are not observed.
3. Based on the IR and UV spectra and the results of thin-layer chromatography, one can conclude about the presence of the sum of steroid glycosides of the furostanol series in the studied samples.

**P25**

# SYNTHESIS ANDSTUDY OF THE NEW Ni(II) SEBACATE COMPOUND

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The chemistry of coordination compounds is in an abiding growing and development, thus the number of new compounds constantly increases not only due to their interesting structural characteristics but also due to remarkable particularities and properties. In the case of transition metal supramolecular compounds, magnetic behavior, electrical conductivity and catalytic activity were observed [1].

As a result of the interaction of nickel(II) salts with the sebacic acid ($C_{10}H_{18}O_4$) in presence of phenanthroline, a new $[Ni(phen)_3]_2\cdot[Ni(H_2O)_6]\cdot(C_{10}H_{16}O_4)_3\cdot30H_2O$ coordination compound was obtained (Figure). The compound crystalizes in the monoclinicspace group $P2_1/n$, with the following unit cell parameters: $a$ = 12.3042(9) Å, $b$ = 32.4582(17) Å, $c$ = 16.0286(13) Å, $\beta$ = 108.951(9)°. The structural study of the obtained pink crystals revealed that the compound has an ionic structure formed by three nickel based cations in an octahedral configuration, three sebacic dianions and 30 co-crystallized water molecules.

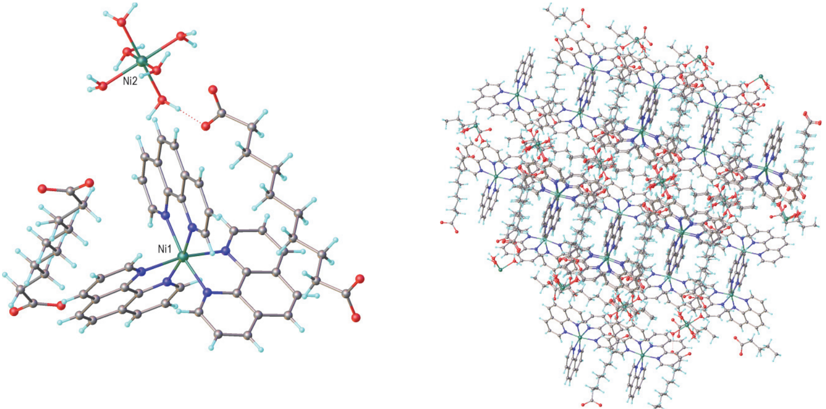

**Figure.** (**left**) View of the $\mathbf{[Ni(phen)_3]_2\cdot[Ni(H_2O)_6]\cdot(C_{10}H_{16}O_4)_3\cdot30H_2O}$ (solvate water molecules are not shown for clarity); (**right**) View of the packing diagram along axis *c*.

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**P26**

# POLYMERIC Mn(II) COORDINATION COMPOUNDS BASED ON BIS((ISO)NICOTINOYLHYDRAZONES) $N_5O_2$ DONOR LIGANDS

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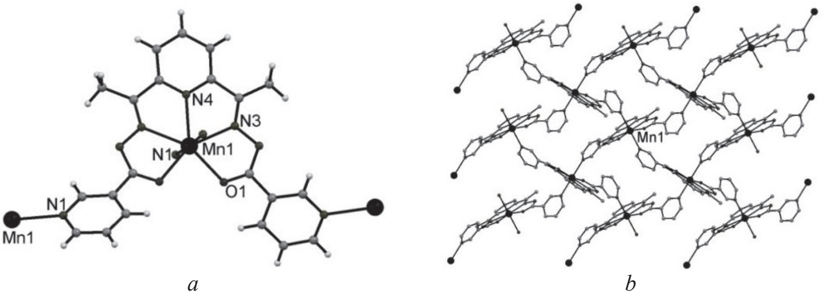
Complexes derived from 2,6-diacetylpyridine (*dap*) hydrazones and transition metal ions have yielded a surprisingly rich chemistry. The *dap* ligands, due to their multicoordination sites, are capable of efficiently stabilizing the metal center by forming unique geometries.

This study shows a new possibility for *dap* derived ligands to build up polymeric compounds. As a result of interaction $MnSO_4·5H_2O$ with 2,6-diacetylpyridine bis(isonicotinoylhydrazone) ($H_2L^1$) or 2,6-diacetylpyridine bis(nicotinoylhydrazone) ($H_2L^2$) (molar ratio of 1:1) in ethanol/dimethylformamide (*dmf*) mixture under solvothermal conditions, 2D coordination polymers $\{[Mn_3(L^1)_3(H_2O)_2]·1.5C_2H_5OH\}_n$ (**1**) and $\{[Mn(L^2)]·dmf\}_n$ (**2**) (Figure), were synthesized. The coordination spheres of the metal in**1** and in the complex $\{[Mn_3(L^1)_3(H_2O)_2]·dmso\}_n$[1] are similar, these two isostructural chemical compounds are solvatomorphs. Compound **2** crystallizes in the orthorhombic centrosymmetric space group $P2_12_12$, $a$ = 12.9449(4), $b$ = 9.5117(4), $c$ = 9.9745(4) Å. The X-ray analysis reveals the seven-coordinated ($N_5O_2$) Mn(II) ion with a pentagonal bipyramidal environment. The dianion of the 2,6-diacetylpyridine bis(nicotinoylhydrazone) moiety ($(L^2)^{2-}$) occupies the equatorial plane coordinating to metal through the pyridine nitrogen (Mn(1)–N(4) 2.321(5) Å), the two imine nitrogens (Mn(1)–N(3) 2.288(4) Å) and the two amide oxygens (Mn(1)–O(1) 2.211(2) Å). The axial Mn(1)–N(1) bond lengths are of 2.342(4) Å.



*a* *b*

**Figure.** Coordination environment of Mn(II) ion in **2** with the partial numbering scheme (*a*) and fragment of crystal structure (*b*)

The intense band, observed at 1671 cm$^{-1}$ in the IR spectrum of the compound **2**, is due to the presence of the cetone groups (distance, C=O = 1.253(6) Å). The spectrum also shows the absence of the ν(N-H) band, which in the free ligand appears at 3187 cm$^{-1}$. This is in accordance with the dianionic nature of the ligand.

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**P27**

# TETRANUCLEAR PIVALATE CLUSTER WITH A $\{Mn^{III}_2Gd^{III}_2\}$ CORE

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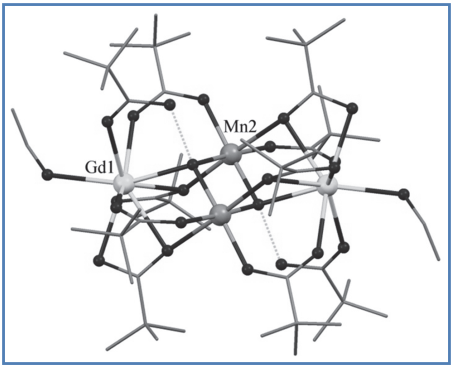
Over the past decade there has been an extraordinary interest in the synthesis, investigation and possible applications of heterometallic 3d-4f coordination clusters. A new heterometallic tetranuclear cluster $[Mn_2Gd_2O_2(piv)_8(Hpiv)_2(EtOH)_2]$ (**1**) (where Hpiv = pivalic acid) has been prepared by the reaction of $Mn(piv)_2$ with $Gd(NO_3)_3\ 6H_2O$ in the presence of triethanolamine in a mixture of ethanol and acetonitrile. The complex was characterized by IR spectroscopy and the X-ray study.

The IR spectrum of **1** contains strong and broad bands in the 1672 - 1545 and 1406 $cm^{-1}$ regions, resulting from asymmetric and symmetrical stretching vibrations of the coordinated carboxylate groups, respectively. The C–H asymmetric and symmetrical stretching vibrations for methyl and ethyl groups of carboxylates and EtOH are observed between 2962 and 2872 $cm^{-1}$, while asymmetric and symmetrical bending vibrations for these groups produce a band at 1482 $cm^{-1}$ and a doublet (1373 - 1357 $cm^{-1}$), respectively. The uncoordinated OH groups of HPiv and the coordinated OH of EtOH molecules result in a broad band of 3275 $cm^{-1}$.

Compound **1** crystallizes in the monoclinic space group *C*2/*c*, $a = 27.883(2)$, $b = 13.369(4)$, $c = 24.212(2)$ Å, $\beta = 128.04(11)°$, $V = 7107.9(11)$ Å$^3$. Single crystal X-ray analysis showed that the complex possesses a centrosymmetric tetranuclear unit $[Mn_2Gd_2O_2(piv)_8(Hpiv)_2(EtOH)_2]$ (Figure). The structure of the $\{Mn_2Gd_2\}$ core of the compound consists of two manganese(III) ions and two gadolinium(III) ions, connected by two $\mu_3$-oxo groups. The metal atoms of the Mn-Gd edges (3.475Å) in the $\{Mn_2Gd_2\}$ rhomb are additionally connected via bridge linkages formed by the entrainment of two pivalate ligands. Each of the $Mn^{III}$ ions is six-coordinated and adopts an octahedral $O_6$ configuration, and the $Gd^{III}$ ions receive the nine coordinate number. The central $Mn^{III}$ atoms are coordinated by two $\mu_3$-oxo atoms ($Mn–\mu_3$-O, 1.897(5) Å), four oxygen atoms from different pivalate ligands (Mn–O, 1.960(5) – 2.196(4) Å). The Mn…Mn separation is 2.846Å. The terminal $Gd^{III}$ atoms are surrounded by the $\mu_3$-oxygen atom ($Gd–\mu_3$-O, 2.571(6) Å), the seven oxygen atoms of the different pivalate ligands (Gd–O, 2.505(4) – 2.571(4) Å) and the oxygen atom belonging to the EtOH molecule with a Gd–O distance of 2.395(4) Å. Two coordinated pivalic acids form strong O–H…O hydrogen bonds of 2.550(6) Å with $\mu_3$-O.



**Acknowledgment.** The author is grateful to project CSSDT 15.817.02.06F.

**P28**

# SYNTHESIS, CRYSTAL STRUCTURE AND LUMINESCENT PROPERTIES OF ISORETICULAR LANTHANIDE METAL-ORGANIC FRAMEWORKS BASED ON A TETRAMETHYL-SUBSTITUTED TERPHENYLDICARBOXYLIC ACID

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Metal-organic frameworks are coordination polymers comprised of rigid organic linkers bearing coordinating functional groups connected by inorganic nodes. This class of compounds has numerous applications ranging from gas storage/separation, catalysis, luminescence, chemical sensing and even drug delivery.

Three new coordination polymers have been prepared using the rigid ligand 2′,3′,5′,6′-tetramethyl-[1,1′,4′,1″-terphenyl]-4,4″-dicarboxylate and La$^{(III)}$, Nd$^{(III)}$and Ho$^{(III)}$ under solvothermal conditions. Single-crystal X-ray diffraction has shown that these isoreticular coordination polymers are non-interpenetrated, tightly packed 3D metal-organic networks.

The complexes exhibited an excellent thermal stability, as revealed by thermogravimetric analysis. IR spectroscopy, energy dispersive X-ray analysis and powder X-ray diffraction were used to further characterize the hybrid networks. In addition, the specific surface area was determined bynitrogen adsorption measurements. The luminescent properties of these coordination polymers were also evaluated.

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**P29**

# A COMPARISON OF PHOTOCATALYTIC PROPERTIES OF NANO-$TiO_2$/DIATOMITE HYBRID COMPOSITE AND BULK TITANIA

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The nano-$TiO_2$/diatomite composite materials (DDT) were synthesized by the modified heterogeneous hydrolysis-deposition of titanium tetrachloride as a precursor, using the diatomite as the carrier. The nanosized $TiO_2$ was also prepared by the same synthesis route without diatomite. The samples further underwent to calcination at 450ºC for anatase phase development.

The as-prepared composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and microanalysis by energy dispersive spectrometry (EDS). $TiO_2$ nanoparticles in anatase form with the average grain size of around 7–14 nm were well deposited on the surface of diatomite [1].

The photo-catalytic activity of the catalysts, a decomposition/decolorization of methylene blue dye (MB) as widespread model of organic pollutant was tested under UV illumination (with the maximum emission at the wavelength of 366 nm). The UV lamp was located at a distance of 10 cm from the reaction solution, which was magnetically stirred during the experiments with a constant speed. There is a synergistic effect of grafting titanium dioxide onto the surface of diatomite: the photocatalytic activity of $TiO_2$dispersed on the diatomite surface vas found to be much higher than of the bulk titania.

The solution decolorization efficiency is inversely proportional to the initial dye concentration. A maximum photodegradation yield of MB (98.4%) on catalyst DDT (of about 20-wt% of $TiO_2$ loading) was obtained under conditions 0.2 g $L^{-1}$ photocatalyst dosage and pH=6~8 with the initialMB concentration 53mg/L in 30 minutes of UV illumination**.** The $TiO_2$ photoactivity under the same conditions was much lower: 69.4% of MB was discolored.

The photocatalytic activity of DDT composite was larger than that of the pure $TiO_2$mainly due to the high surface area and adsorption strength of the diatomite, the uniform distribution of nano-$TiO_2$ on clay mineral avoiding aggregation, on which a fairy high amount of adsorbed MB was available and was mobile under the presence of the concentration gradient around the $TiO_2$ particles.

The DDT photocatalyst possesses anatase phase $TiO_2$ with relatively smaller particles size - 10.02 nm than bulk titania - 26.20nm, which also might be responsible for higher photocatalytic activity. Moreover, the stable and much inerter porous microstructure of diatomite could be another key factor in improving its activity.

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**P30**

# LINEAR TRINUCLEAR NICKEL(II) COMPLEX WITH SALICYLALDEHYDE

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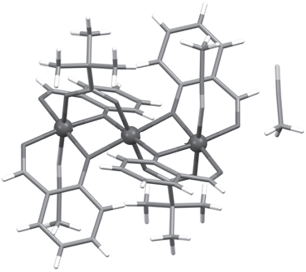
Salicylaldehyde is a commercial ligand that might be utilized as a versatile linker in constructing structures with interesting topologies. The diverse coordination ability of carboxylic group of pivalic acid is also well-known. Since nickel(II) is known to have a large single-ion zero-field splitting and often gives rise to ferromagnetic coupling, we have focused our attention especially on polynuclear Ni(II) complexes.



Herein a trinuclear complex $[Ni_3(L)_4(piv)_2(CH_3CN)_2]\cdot CH_3CN$ (**1**), which is obtained from the reaction of nickel pivalate precursor $[Ni_2(OH_2)(O_2CCMe_3)_4(HO_2CCMe_3)_4]$ and salicylaldehyde HL, is reported. Complex **1** was characterized by IR spectroscopy and single crystal X-ray crystallography. The IR spectrum of complex **1** shows strong and broad bands in the 1564−1534 and 1444−1405 $cm^{-1}$ regions, which are assigned to the asymmetric and symmetric vibrations of the coordinated carboxylic groups. A strong band at 1622 $cm^{-1}$ was assigned to the stretching frequency of the bonded aldehyde group. A medium strong band appears at 1219 $cm^{-1}$ and is assigned to the C-O stretching frequency. Medium-intensity bands in the regions 3000−2760 $cm^{-1}$ and bands at 1477−1325 $cm^{-1}$ are attributed to characteristic ν(C−H) aromatic and aliphatic C–H stretching and bending modes, respectively.

According to the crystallographic data complex **1** crystallizes in the triclinic space group *P*-1 with the asymmetric unit containing a linear arrangement of three Ni(II) centers.Three nickel(II) atoms are joined together by two carboxylate bridges with the Ni···Ni separation of 2.999 Å and four monodeprotonated salicylic ligands that coordinate in a bidentate bridging mode. The central Ni(II) atom of the trimer is located on a crystallographic inversion center and is coordinated octahedrally by two pivalate carboxylate oxygen atoms and four monodeprotonated salicylaldehyde ligands. Carboxylates form bridges to the peripheral Ni(II) atoms in the common bidentate *syn–syn* fashion, while the other four aldehyde ligands function in a bidentate mode in which two phenolic oxygen atoms of two different ligands bridge two Ni centers. In the bidentate saicylaldehyde, the second oxygen donor atoms of aldehyde group, interact with the outer nickel centers at 2.026 and 2.043 Å, respectively. These peripheral two nickel atoms have also coordinated acetonitrile molecules with the Ni–N distance of 2.177 Å. This forms also an arrangement that can be considered as a distorted NiO4N2 octahedral geometry.

The thermogravimetric analysis (TGA) of compound **1** confirms its relatively high thermal stability, as it retains its integrity up to 140°C against degradation under an air atmosphere.

**P31**

# SYNTHESIS AND STUDY OF A NEW Zn(II) MOF WITH RIGID LIGANDS

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Coordination polymers recently known as metal-organic frameworks (MOFs) have become a forefront in scientific research and public interest, due to the potential for neutral guest bonding, including gas storage studies such as hydrogen storage and gas separations.

The aim of this work was the synthesis, determination of the composition, structure, and sorption properties of Zn(II) MOFs using rigid ligands.

Here we report a method of solvothermal synthesis of Zn(II) complex using 2,3,5,6-tetramethyl-1,4-carboxyphenyl benzene (4-$CH_3$-TF) and bis-imidazolyl-bis-phenylene (BIBPh) as starting ligands. The synthesized product represents a tridimensional polymeric compound $[Zn_2(4\text{-}CH_3\text{-}TF)_2(BIBPh)(DEF)]_n$. The composition and structure of the complex was demonstrated by physical methods of analyses (X-ray, thermogravimetry, IR). Single crystal X-ray structure investigation of this coordination compound has demonstrated, that in the crystalline phase a polymeric structure was obtained, where binuclear Zn(II) groups are interconnected by two bridging tetradentate molecules of 4-$CH_3$-TF ligand and one bidentate BIBPh.

Two types of large cavities were identified in the polymer, where solvent molecules of DEF are adsorbed (Figure). Thermogravimetric study has demonstrated that heating of polymeric sample up to 250°C leads solely to elimination of solvent molecules from micropores.The degassed compound is stable up to 400°C, then an irreversible collapse of molecular framework occures.

Sorption properties have been tested through $N_2$ adsorption at 77 K and shown a maximum sorption value of ~110 $cm^3/g$.

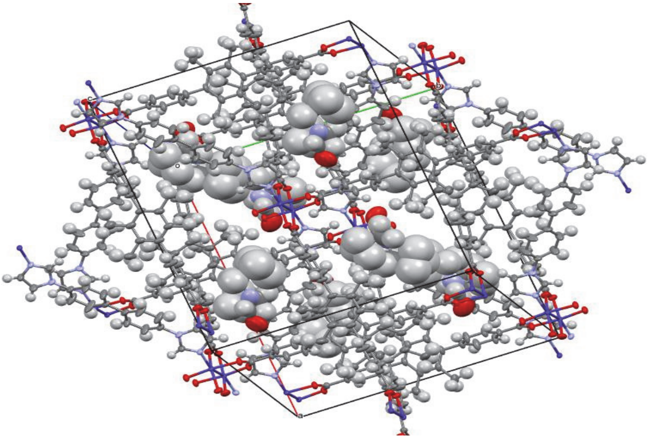

**Figure.** Molecular packing of the polymeric compound [Zn2(4-CH3-TF)2(BIBPh)(DEF)]n.

**P32**

# DEVELOPMENT OF EFFECTIVE LUMINISCENT MATERIALS BASED ON FUNCTIONALIZED MESOPOROUS ORGANOSILICA

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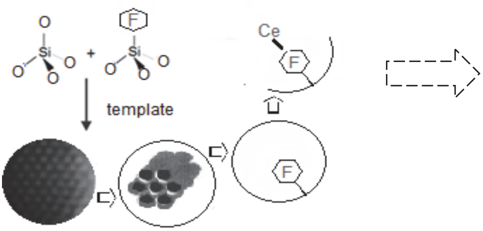
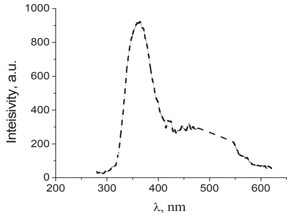
Nanoluminophores based on rare-earth elements (REEs) show important benefits over other available luminescent materials involving lighting, lasers, and detectors of many forms of radiation with high quantum yield [1]. In general, interest is not only optical but also catalytic, magnetic and adsorption applications of the REEs based materials. Hybrid organo-inorganic materials with covalent immobilized functional groups have several advantages over noncovalently bound systems: greater thermal, photochemical and chemical stability, homogeneity of structure and non-evaporation of components.

We proposed ordered phenyl/thiolpropyl functionalized mesoporous silica (SBA-15) with Ce-containing complexes as effective luminescent materials. The hybrid materials were synthesized by the template procedure with grafting functionalization.The activation of the surface layer for interaction with REEs ions was carried out by sulfonation.



*Scheme of synthesis of the samples*
*(F – functional group)*



*Emission spectrum of SBA-Ce(III) sample*
*($\lambda_{ex}$ = 254 nm)*

X-ray diffraction, infrared spectroscopy, scanning and transmission electron microscopy and nitrogen adsorption-desorption method, potentiometric and thermogravimetric analyses, were used for characterization of obtained materials. The concentration Ce(III) ions in solution was determined using ICP-OES technique. The luminescence properties of obtained materials were studied in solid stateby excitation (Ce4f □ Ce5d bands) and emission (Ce5d □ Ce4f bands) spectra. This work is also targeted towards understanding the affinity of ordered functionalized mesoporous silica to Ce(III) in relation to complexation mechanism. The high surface concentration of the functional groups affords potential sites that are essential for the formation of the REEs complexes.

**Acknowledgements.** Dr. O. Dudarko and Dr. I. Melnyk are thankful for the financial support of the joint Ukrainian-Lithuanian research project M/8-2019 from 13.05.2019.

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**P33**

# MULTIPLE COMPONENT IONIC COMPLEX $[Co^{III}(NH_3)_6][Co^{II}(H_2O)_4(3,5\text{-}Py(COO)_2)_2]Cl\cdot3H_2O$WITH PARTIAL IN SITU REDUCTION OF COBALT(III)

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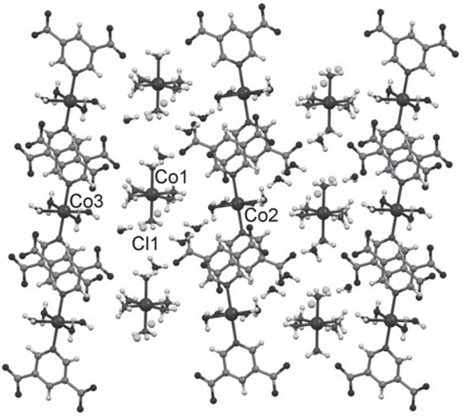
Cobalt coordination complexes that exhibit impressing redox and magnetic properties find a significant range of applications in biology and medicine [1]. Among them, hexammine cobalt(III) chloride, $[Co(NH_3)_6]Cl_3$ ("Cohex"), a textbook example of a classical Werner complex with six ammonia ligands arranged in an octahedral geometry about the Co(III) ion, stands ahead [2,3]. Known for over a century, it is widely studied nowadays due to the antimicrobial and inhibition properties and if so the family of its inclusion solids based on hydrogen bonds as second sphere interactions grows extensively [4].

The cocrystalization of hexammine cobalt(III) chloride and 3,5-pyridine-dicarboxylic acid ($3,5\text{-}Py(COOH)_2$), accompanied by the partial reduction in situ of Co(III) to Co(II), resulted in the mixed-valence Co(III,II) coordination compound $[Co^{III}(NH_3)_6][Co^{II}(H_2O)_4(3,5\text{-}Py(COO)_2)_2]Cl\cdot3H_2O$. Ionic complex crystallizes in the centrosymmetric triclinic space group *P-1*, $a$=7.4396(15), $b$=8.3675(19), $c$=24.286(3) Å, $\alpha$=87.060(15), $\beta$=83.102(15), $\gamma$=66.39(2)°, $V$=1375.2(5) Å$^3$ and comprises octahedral $[Co^{III}(NH_3)_6]^{3+}$ cations, two types of anions, chloride and $[Co^{II}(H_2O)_4(3,5\text{-}Py(COO)_2)_2]^{2-}$, and lattice water molecules. The Co(III)-N distances in the cation are in the range 1.93(1)-1.98(1) Å, while Co(II)-N distances in the anions are 2.14(2) and 2.11(1) Å, undoubtedly indicating the mixed-valence compound. In the Co(II) octahedral complex anion four coordinated water molecules occupy equatorial plane, while dicarboxylate residues coordinate in monodentate mode *via* pyridine atom in two apical positions. The crystal structure can be described as a two-dimensional array of Co(III) centers linked in the layers via hydrogen bonds with chloride anions and water molecules and alternate along the crystallographic *c* axis with the anionic layers built of the identical Co(II) complex anions interlinked *via* anion-anion OH(water)…O(COO) hydrogen bonds and stacking interactions of the pyridine rings.



**Acknowledgment**. The authors are grateful to STCU6245 project.

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**P34**

# EXCHANGE INTERACTION IN A NEW MANGANESE CALCIUM CLUSTER

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The mixed manganese carboxy-clusters have been attracting an intense interest during the last several years. There are many reasons for this, including their wide application as catalysts, as well as in study of photosynthetic processes and the perspective to improve the properties of SMM. In the present work, the synthesis and exchange interaction measurements in a new heteropolynuclear manganese cluster are described. The reaction of $[Mn_3O(C_6H_5COO)_6(py)_2(H_2O)]$ with $Ca(ClO_4)_2$ in MeCN in the presence of 2-hydoxymethylpyridine (H-HMP) forms the $[Mn_6Ca_2(HMP)_6(C_6H_5COO)_6O_3(H_2O)_{10}](ClO_4)_4$ (**1**) complexes, with a very good yield. Its molecular structure comprises a hexa-manganese ring with a dimeric calcium complex threaded into the central cavity [1]. Considering the molecular formula, each manganese is assigned to the +3 oxidation state.

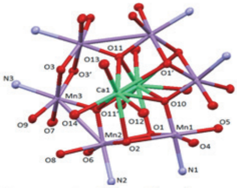

**Figure 1.** The basic coordination chemistry with labels at the manganese and calcium ions in **1**.

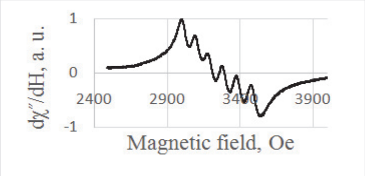

**Figure 2.** The EPR spectrum with hyperfine structure of **1**.

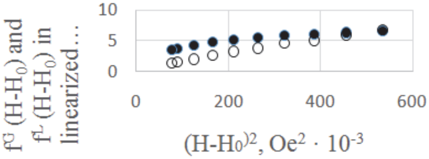

**Figure 3.** Linear anamorphoses of the EPR spectral line of **1**.

In Figure 3, the dependence of Gauss function $f^G(H\text{-}H_0)$ (black circles) and Lorentz function $f^L(H\text{-}H_0)$ (open circles) versus $(H\text{-}H_0)^2$ in linearized coordinates are presented.

The EPR spectrum of **1** consists of a large almost symmetrical line with the g-factor g = 1.993 and the width $\Delta H_{pp} = 544.1$ Oe.

This line shows a hyperfine structure with the constant $a = (90.4 \pm 3.3)$, $cm^{-1} \cdot 10^4$, due to the interaction between five 3d-electrons of the $Mn^{2+}$ ion in the ground state and the $^{55}Mn$ nucleus with the spin I = 5/2 (Figure 2). Based on the method of linear anamorphoses [2] (Figure 3), we demonstrate that the exchange field in **1** is $H_e = (530 \pm 30)$ Oe. Supplementary, it was shown that the intensity of the EPR line at temperature T = 77 K is higher than at T = 296 K: $(I_{77K})/(I_{296K}) = 3.34$, suggesting that **1** is a compound with an exchange interaction of ferromagnetic type in the ground state.

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**P35**

# SYNTHESIS, OPTICAL AND X-RAY DIFRACTOMETRY CHARACTERICRICS OF ZnO COLLOIDAL QUANTUM DOTS

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The semiconducting ZnO colloidal quantum dots are an important topic of research due to their applications in different areas such as biological systems and optoelectronic devices (LEDs, solar cells, and gas sensors) [1-4]. ZnO quantum dots are characterized by reduced degree of toxicity as compared to other II-VI, III-V, and IV-VI nanoparticles. These are therefore particularly promising in medical applications.

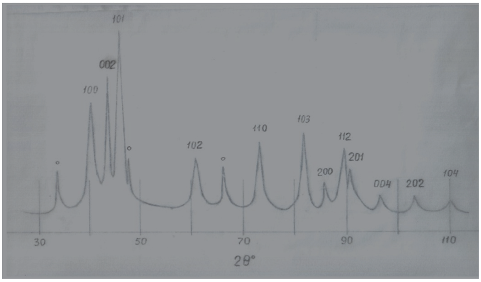

**Figure 1.**The lines of X-ray diffraction for ZnO colloidal quantum dots (DRON-UM1, diffractometer, $FeK_{\alpha}$ radiation, Mn filter).

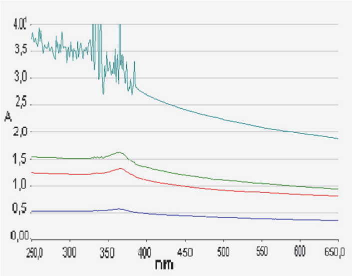

**Figure 2.**UV-Vis absorption spectra of ZnO colloidal quantum dots in methanol.

The ZnO quantum dots have been synthetized from a methanol based solution that was prepared by mixing the zinc acetate ($Zn(O_2CCH_3)_2$, ZnAc), and methanol. After this, the water was added in this mixture in such a way that a ZnAc/$H_2O$ molar ratio of 0.2 was reached, and triethanolamine ($C_6H_{15}NO_3$, TEA) was added too. The reaction mixture was stirred at 60°C during 60min. Subsequently, water was added to produce the precipitation. Afterwards, the white powder was separated by centrifugation, washed several times in methanol and dried at 100°C during 1 h.

Due to large values of the free surface energy, the ZnO quantum dots are characterized by a high degree of reactivity. In particular, using TEA as a surfactant canlead to the increase in quantum efficiency of photoluminescence.

Based on X-ray diffraction data (Figure 1), it was shown that the obtained ZnO nanocrystals of hexagonal symmetry have sizes of ~13 nm along the *c* axis and ~9 nanometers in the orthogonal direction. The UV-Vis spectra of ZnO quantum dots (Figure 2) show a 1S exciton peak at about 373 nm. When the concentration of nanoparticles in methanol is increasing (down up, mg/mL: 2.6, 3.0, 3.5, 5.4), the peak shows a multiplete structure at the concentration $c = 5.4$ mg/mL (a sludge solution).

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**P36**

# SYNTHESIS AND EPR STUDY OF MONO- AND BINUCLEAR COPPER AND OXOVANADIUM COMPLEXES WITH COMPARTMENTAL ISOTHIOSEMICARBAZONE

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On template condensation of 3-formylsalicylic acid S-methylisothiosemicarbazone with 3-formylsalicylic acid and $Cu(CH_3COO)_2{\cdot}H_2O$ (molar ratio 1:1:1) in DMF was obtained mononuclear compound $[Cu(L\text{-}(COOH)_2)]{\cdot}0.5DMF$ (**1**), where L-$(COOH)_2$ represents compartmental ligand $N_1N_4$-bis(3-carboxysalicylidenato)-S-methylisothiosemicarbazide ($\nu_a$ COOH=1723 $cm^{-1}$,v.s.). On interaction of **1** with an excess of $Cu(CH_3COO)_2{\cdot}H_2O$ in DMF in open reaction vessel the dicopper compound $[Cu_2(L\text{-}(COO)_2)]$ $3H_2O$ (**2**)was synthesized. Reaction of **1** *via* intermediate Li salt with equimolar $VO(SO_4){\cdot}5H_2O$ in DMSO was isolated heteronuclear complex $[CuVO(L\text{-}(COO)_2)]{\cdot}DMSO$ (**3**).

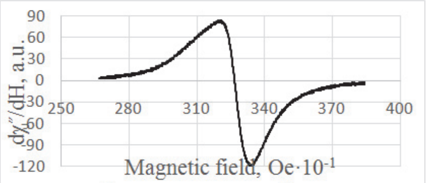

**Figure 1**. The EPR spectrum of **1**.

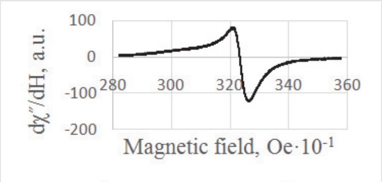

**Figure 2**. The EPR spectrum of **3**.

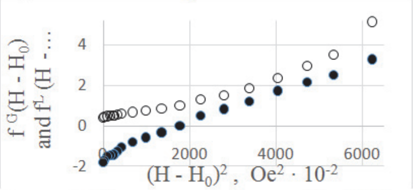

**Figure 3**. Linear anamorphoses of the EPR spectral line of **2**.

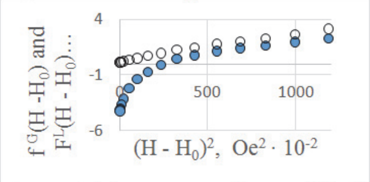

**Figure 4**. Linear anamorphoses of the EPR spectral line of **3**.

The EPR spectra at room temperature of all three complexes **1** (Figure 1), **2** and **3** (Figure 2) consist of a single resonance line without hyperfine structure with parameters: g=2.054, $\Delta H_{pp}$ = 131.5 Oe (**1**); g=2.046, $\Delta H_{pp}$=288.6 Oe (**2**); g=2.061, $\Delta H_{pp}$=53.2 Oe (**3**).

In Figure 3 and 4 the dependence of Gauss function $f^G(H\text{-}H_0)$ (black circles) and Lorentz function $f^L(H\text{-}H_0)$ (open circles) versus $(H\text{-}H_0)^2$ in linearized coordinates are presented.

Based on the method of linear anamorphoses [1] it was shown that at room temperature the narrowing of EPR lines of **2** and **3**arises due to exchange interaction between paramagnetic ions presented in **2** and, correspondingly, **3**. Using the data from Figure 3 and Figure 4, the exchange fields $H_e$=240 ±30 Oe (**2**) and $H_e$=220 ±30 Oe (**3**) were determined.

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**P37**

# CHARACTERISTICS OF NUT SHELLS ACTIVATED CARBONS

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Activated carbons, owing to their versatility, are the most frequently used adsorbents. Their exceptional performance derives from a unique combination of geometrical and chemical properties. The different size and shape of pores, as well as vacancies and steps are responsible for the geometrical heterogeneities of the activated carbon surface; additionally, the surface chemistry is another important parameter [1].

The objective of this work was to investigate the porous structure and surface chemistry characteristics of activated carbonsobtained from nut shells by the physical-chemical activation method (CAN) and modified by treatment with hydrochloric acid (CAN-Cl) [2].

In order to characterize the porous structure and surface chemistry of the studied samples, various technics including $N_2$ sorption/desorption isotherms, scanning electron microscopy (SEM), Boehm and potentiometric titration methods, Fourier Transform infrared spectroscopy (FTIR), temperature programmed desorption (TPD), thermal gravimetric analysis (TGA) were used.The redox properties of the activated carbon samples were evaluated *via* two different methods: chemiluminescence (in the system of $H_2O_2$ – luminol at pH 8) and of $ABTS^{\bullet+}$ cation radical.

Obtained results show that both types ofsamples are enough hygroscopic, humidity being around 8 %; after modification with chloride ions, the ash content decrease by about 4 times. Elemental analysis and SEM-EDX spectroscopyproved the presence of chlorine on the activated carbon sample CAN-Cl in the content up to 2 %. After treatment with chloride ions, the specific BET area increases with about 5% and the total pore volume increases with about 10 $cm^3/g$.

The characterization of activated carbons by different methods (Boehm and potentiometric titration methods and TPD) revealed the presence of lactonic, phenolic, carbonyl and quinonic groups on the surface; and the surface charge was found zero in the pH range 4.5-9. The species evolved for chlorine groups (determined by TPD method) were mainly of mass 36 ($HCl^{35}$); this means that the groups decompose mainly to HCl.

Comparative analyses of the antioxidant activity of the activated carbons (evaluated by both methods) revealed a slightly elevated activity for the initial sample (CAN) versus the modified sample (CAN-Cl).

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**P38**

# DFT STUDY OF PHOTO-TRANSFORMATION OF CYPRODINIL CAUSED BY CHANGE OF ITS TAUTOMERIC FORM UNDER SUNLIGHT ACTION

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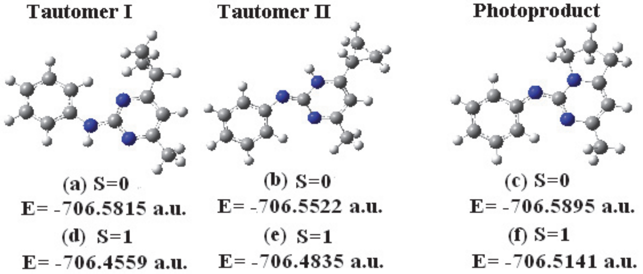
Cyprodinil, (4-cyclopropyl-6-methyl-pyrimidin-2-yl)-phenyl-amine is a fungicide of broad spectrum. Usually it is applied to control a range of various pathogens. Post harvest rests of cyprodinil on fruits and vegetables have irritant influence on human organism. Cyprodinil is resistant to action of acids and basis; however it can be rapidly degraded in water when exposed to UV light with a half live of 13.5 days [1].

In this connection the aim of our DFT study (with the use of GAUSSIAN 09 program unit [2]) consists in definition of possible mechanism of its photo-transformation. First of all, it is shown that the possible interactions between a molecule of cyprodinil and the ions H+, OH- or water itself do not lead to any transformation of cyprodinil molecular skeleton. However, calculations show that cyprodinil in its excited state is capable to further structural transformations (isomerization) forming the photoproduct (see the Figure). One can see that for the ground electronic state (S=0) its tautomeric form **I** (a) is more stable than the form **II** (b), while in the excited electronic state (S=1) the more energetically preferable form is the tautomer **II** (e). The jumping of the proton in (e) from the nitrogen atom to one of the 'banana' bonds of the cyclopropyl ring leads to its opening of three-membered ring and to the following formation of the new five-membered cycle including the above nitrogen atom (see the excited structure (f) of the **Photoproduct**). The release of the excitation energy leads to the **Photoproduct** in itsground electronic state (c) whose energy is lower than that of **Tautomers I** and **II**. The experimental results of the work [3] confirm the formation of this pfotoproduct.



Thus, unlike the case of fungicide vinclozolin whose proton-induced decay was revealed by us earlier [4], the main role in the photo-transformation of cyprodinil plays the above-mentioned change of its tautomeric form under sunlight action.

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**P39**

# INFLUENCE OF NANO-PARTICLES OF $TiO_2$ ON RELATIVE ANTIOXIDANT ACTIVITIES OF FUMARIC AND DIHYDROXYFUMARIC ACIDS: DFT INVESTIGATION OF THEIR REACTIONS WITH DPPH

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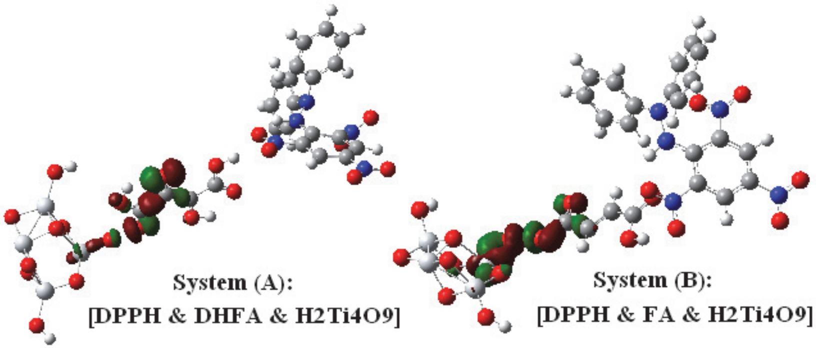
It has been shown in the work [1] that the interaction between dihydroxyfumaric acid (DHFA) and the stable radical DPPH begins with protonation of the latter and formation of the radical-cation $[DPPH\text{-}H]^{*+}$. Further, $[DPPH\text{-}H]^{*+}$ forms the charge transfer complex (CTC) with the anion of DHFA. As a result of this process the unpaired electron of DPPH will be localized on the atoms of the anionic fragment of the CTC. Our DFT computational data received by means of the program GAUSSIAN 09 (B3LYP, 6-31G) show that the same localization of the unpaired electron takes place also in the CTC between $[DPPH\text{-}H]^{*+}$ and the anion of fumaric acid (FA). Here we present the results describing the influence of the nano-cluster $H_2Ti_4O_9$ on the redistribution of the electronic density in the both above CTCs (Figure below).

One can see that in the case of DHFA (system A) the main part of electronic density of the unpaired electron is localized on the atoms of DHFA, while in the case of FA it is significantly displaced onto the $H_2Ti_4O_9$ nano-cluster. It is well known that the UV irradiation of $TiO_2$ nano-particles leads to the formation of free electrons and positively charged holes on their surface. It is clear that only for the DPPH&FA&$H_2Ti_4O_9$ system the electronic density of its unpaired electron can recombine with these photo-generated particles. Thus, we can draw the following conclusion. Nano-particles of $TiO_2$ enhance the antioxidant activity of those organic compounds for which the topology of their molecular orbitals allows the transfer of the electronic density to the $TiO_2$ nanoparticles.



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**P40**

# IONIC LIQUIDS: SIMPLE “STRUCTURE-CRITICAL TEMPERATURE” RELATIONSHIP

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In the framework of the title problem we have performed quantum-chemical calculations (DFT B3LYP method) of some ionic liquids (ILs) possessing the common anion tetrafluoroborate. The computational data have shown that for any ionic pair of all the considered ILs their HOMOs are localized mainly on their negative charged heteroatoms (F, O, N) while the atomic orbitals of their positive charged hydrogen atoms and the $sp^2$-hybridized carbon atoms enter the LUMOs. It is clear that the attractive interaction forces between two neighboring ionic pairs will appear due to all the possible atom-atomic interactions between the heteroatoms and the positive charged hydrogen and carbon atoms.

Since these attractive interactions lower the potential energy of two-particle interactions, it is logical to assume the existence of some kind of correlation between their number and the critical temperature $T_c$ of the ILs. To find this correlation dependence we use for any ionic pair the following numbers: $N_H$ – the number of its hydrogen atoms, $N_C$ – the number of $sp^2$-hybridized carbon atoms, the number $N = N_H + N_C$, and $N_{HA}$ – the number of the heteroatoms. The last value is the sum of the heteroatoms belonging to both the cation and the anion.

It is obviously, the total number of all possible attractive interactions between the two ionic pairs, will be equal to the product $P = 2N^x N_{HA}$. The following correlation analysis allows one to reveal the very simple dependence between $T_c$ and P: $T_c = g\sqrt{P}$, where $g$ is a constant which equals to 44.56 K for all the considered ILs. The calculated values of $T_c$ as well as the experimental ones [1] are given in the Table.

We suppose that the found quantitative dependence will be will also be valid for otherseries of ionic liquids.

| ILs | $N_H$ | $N_C$ | N | $N_{HA}$ | P | $T_c$ | |
|---|---|---|---|---|---|---|---|
| | | | | | | Calc. | Exp. |
| [N-epy][BF4] | 10 | 5 | 15 | 5 | 150 | 545.7 | 549.9 |
| [prmim][BF4] | 13 | 3 | 16 | 6 | 192 | 617.4 | 619.7 |
| [mommim][BF4] | 11 | 3 | 14 | 7 | 196 | 623.8 | 623.7 |
| [bdmim][BF4] | 17 | 3 | 20 | 6 | 240 | 690.3 | 671.0 |
| [C27guan][BF4] | 58 | 1 | 59 | 5* | 590 | 1082.4 | 1100.3 |

* In the case of [C27guan][BF4] the value of $N_{HA}$ was calculated by taking into account the spatial shielding of the two of its nitrogen atoms by four bulk hexyl groups.

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**P41**

# DFT EVIDENCE OF PROTON-INDUCED DECAY OF THE FUNGICIDE, IPRODIONE, ON $TIO_2$ SURFACE UNDER SOLAR IRRADIATION

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It has been shown in our previous work [1] that molecule of fungicide, vinclozolin, coordinated to the wet irradiated $TiO_2$ surface can be decomposed by means of free hydrogen atoms. Moreover, free vinclozolin molecules within water film on the given surface can be decomposed by free protons. However, the present DFT results (B3LYP, 6-31G [2]), show that free protons do not break the hydantoin ring of iprodione due to formation of stable intra-molecular hydrogen bonds. At the same time, free iprodione (IPR) molecules interact with free hydroxyl anions (which destroy their hydantoin cycles) and can be easily and irreversibly transformed (hydralized) into N-(3,5-dichloroanilinocarbonyl)-N-(isopropylaminocarbonyl) glycine (see Figure 1).

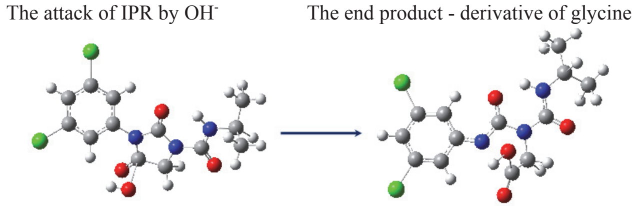
The attack of IPR by $OH^-$ The end product - derivative of glycine

**Figure 1**. Decay of the hydantoin ring of IPR by $OH^-$

The above theoretical conclusion is in a good agreement with the experimental data [3].

In their turn, the molecules of iprodione adsorbed on the surface of the nano-cluster $[Ti_{24}O_{50}H_4]$ can be decomposed by means of free protons giving the following end products: isopropylisocyanate and 3-(3,5-dichlorophenyl)-hydantoin. Figure 2 demonstrates the mechanism of this decay.

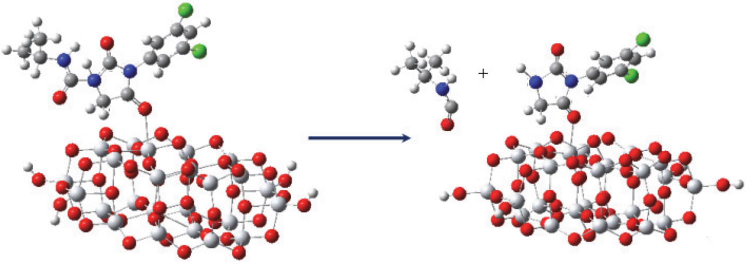

**Figure 2.** Decay of protonated IPR molecule bounded to nanocluster $[Ti_{24}O_{50}H_4]$

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**P42**

# ADSORPTION OF NITRITE IONS ON CAN-7 ACTIVE CARBON

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In the last years more and more attention has been paid to the surface chemistry of the active carbons selected for the adsorption of ions from solution [1].

The purpose of this work was to study the adsorption of nitrite ions from solutions on CAN-7 active carbon. The sample CAN-7 is a mesoporous active carbon with acidic surface due to method of obtaining (chemical activation with phosphoric acid) [2]. The presence of acidic functional groups on the active carbon surface has been evaluated by Boehm and potentiometric titration method, TPD-MS and FTIR spectroscopy [3].

For the description of the nitrite ions adsorption process on CAN-7 active carbon the influence of various experimental parameters (pH value, amount of adsorbent, initial concentration, and contacting time) was evaluated in batch experiments, at the ratio: liquid solid of 1: 500, the fraction of activated carbon was between 0.8 ÷ 2.0 mm.

Adsorption equilibrium data were fitted to Langmuir, Freundlich and Dubinin-Radushkevich isotherms and to different kinetic models (pseudo-first and pseudo-second kinetic models and intraparticle diffusion). The equilibrium adsorption data were best represented by the Langmuir isotherm. This means that the adsorption process is dominated by chemosorption on the energetic homogeneous surface.

The correlation coefficients of the pseudo-second kinetic model have values close to one, and the calculated values of adsorption are very close to the values found experimentally. This suggests that the rate-determining step in these adsorption processes may be chemosorption.

In the case of the intraparticle diffusion model, it is observed that the dependence is multilinear, indicating that the process has three stages. The slopes of the linear portions indicate the speed of the adsorption process. Thus, the diffusion speed decreases with the contact time due to the fact that the pores become smaller. The first linear region is probably due to adsorption in the activated carbon mesopores, while the second linear section represents, most likely, the transition from mesopores to micropores.

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**P43**

# X-RAY STRUCTURE AND CARACTERIZATION OF A NEW HETERONUCLEAR CuBa 1D POLYMER OF 5-METHYLSALICYLIC ACID

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The new heteronuclear1D polymer with the composition $\{[CuBa(CH_3HSal)_4(DMA)_3]\}_n$ , where DMA=N,N-dimethylacetamide has been obtained by the reaction of copper nitrate with barium5-methylsalicylate [1]. X-ray analysis data has shown that the compound has a polymeric structure along the chain formed by copper and barium atoms linked through monodeprotonated 5-methylsalicylate ligands (Figure 1) and crystallizes intriclinic space group *P-1* with the following unit cell parameters: *a*= 13.4311(12), *b*= 16.1521(8), *c*= 22.8719(17) (Å), α =87.088(5)º, *β*=89.821(7)º, γ=73.229(6)º. Copper and barium atoms are displaced alternatively along the polymeric chain, thus each copper atom is linked to two different neighbouring barium atoms through four different carboxylate bridging groups (three carboxylate groups coordinate in a bidentate bridging $\mu_2$-$\eta_1$:$\eta_1$ mode and one carboxylate group in a tridentate bridging $\mu_3$-$\eta_1$:$\eta_2$ mode).Additionally the chain is decorated by three DMA molecules coordinated to each barium atom.

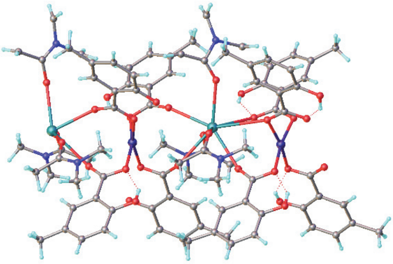

**Figure 1.** View of the X-ray structure of the heteronuclear compound.

The comparison of IR spectra of free 5-methylsalicylic acid and heteronuclear CuBa compound have confirmed the formation of a new coordinative compound. The adsorption bands corresponding to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$can be observed at about1615.5cm$^{-1}$and 1423.6 cm$^{-1}$, respectively. The difference of ~200 cm$^{-1}$ between the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands indicates the bidentate-bridging mode of the carboxylate ligands coordination [2].

For the coordination compound, in the region of 3018.7-2922.9 cm$^{-1}$ of the IR spectrum can be observed bands of medium intensity attributed to O-H vibrations; the band at ~1238.4 cm$^{-1}$ was assigned to the C-O stretching frequencies of phenolic C-OH as observed for free 5-methylsalicylic acid, thus confirming the fact that phenolic OH group is not involved in coordination.

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**P44**

# SYNTHESIS, NMR CHARACTERIZATION AND X-RAY DIFFRACTION STUDY OF A NEW ORGANIC SALT OF 2,3-DIHYDROXYBENZALDEHYDE SEMICARBAZONE

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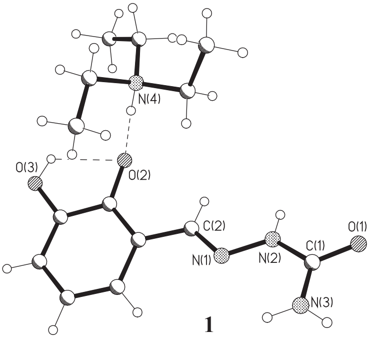
Salicylaldehyde (2-hydroxybenzaldehyde) and its derivatives are convenient carbonyl precursors for ligand systems to be noted fortheir light synthetic procedures, varied denticities, and also interesting pharmacological properties.The presence of suitable additional functional hydroxyl groups would increase the number of donor atoms of the resulting Schiff base and, as a consequence, its chelating ability and structural flexibility. Herein we report the synthesis, NMR characterization, and crystal structure of the novel organic salt with triethylamine with the formula $(Et_3NH)(H_2L)\cdot 0.5(CH_3)_2CO$ (**1**), where $H_3L$is 2,3-dihydroxybenzaldehyde semicarbazone. Single crystals of the salt **1** were obtainedfrom acetone in the presence of triethylamine. Compound **1** crystallizes in the monoclinic space group C2/c, being of the ionic type. It includes protonated triethylamine as a cation, semicarbazone with a deprotonated hydroxyl group in the 2nd position as an anion (see picture), and theacetone molecule that is disordered over two positions.



**1**

Its structure in DMSO-$d_6$ solution was confirmed by $^1H$, $^{13}C$ and $^{15}N$ NMR spectroscopy, being compared with the NMR data for $H_3L$. In the $^1H$ NMR spectrum of **1** all signals of the protons from $H_3L$ are present, except hydroxyl protons. Most likely, the very broad signal at δ 10.18 ppm, corresponding only to the amide proton in $H_3L$, includes also the cationic proton of triethylamine and the hydroxyl group in the 3rd position of **1**. The characteristic shape of this signal strongly confirms the existence of numerous hydrogen bonds in crystal packing of **1**, which were established by X-Ray study as well. Proton chemical shifts of $H_3L$ moiety in **1** present insignificant difference, with respect to $H_3L$. Signals at $\delta$ 0.93 and 2.43 ppm demonstrate the presence of triethylamine fragment, while the crystallization acetone in the molecule of **1** is proved by the peak at $\delta$ 2.08 ppm. $^{13}C$ and $^{15}N$ NMR data for the salt **1** were obtained by 1D and 2D HETCOR techniques totally validating its structure. Thus, the resonances for $^{13}C$ and $^{15}N$ nuclei in **1** practically remain unchanged, in comparison with $H_3L$, while the signals for triethylamine ($\delta$ 11.6 and 45.7 ppm) and acetone ($\delta$ 30.6 and 206.3 ppm) in its $^{13}C$ spectrum have additionally been attested. Cationic nitrogen was found by $^1H/^{15}N$ HMBC experience at $\delta$ 47 ppm, while azomethine, amide and amine nitrogen atoms resonated at $\delta$314, 156 and 77 ppm, respectively.

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**P45**

# SUPRAMOLECULAR ARCHITECTURES OF THE LUMINESCENT TRIETHANOLAMMONIUM 4-NITROBENZOATE SALT AND ITS Ni(II) COMPLEXES

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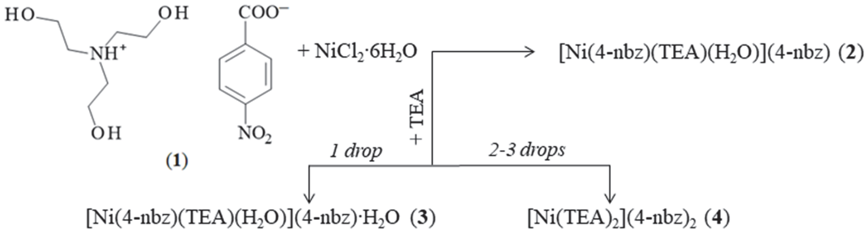
Multicomponent self-assemblies are a useful and efficient way to create molecular and supramolecular architectures with functions, which would not be realized by typical single molecules. Single crystals of new organic salt HTEA:4-nbz (**1**) and its Ni(II) complexes [Ni(4-nbz)(TEA)($H_2O$)](4-nbz) (**2**), [Ni(4-nbz)(TEA)($H_2O$)](4-nbz)·$H_2O$ (**3**) and [Ni(TEA)$_2$](4-nbz)$_2$ (**4**) (TEA=triethanolammine and 4-nbz=4-nitrobenzoate) have been successfully grown and characterized by IR spectroscopy and single crystal X-ray analysis.



Here we report the supramolecular systems constructed by combining two or three organizing forces: metal-coordination (**2-4**), hydrogen bonds (**1-4**) and $\pi$-$\pi$ stacking interactions (**1-4**). The building blocks in **1** are assembled into 1D chains along *b* axis through O–H···O and charge-assisted $N^+$–H···O and O–H···$O^-$ H-bonding. Resulted chains are further assembled in a supramolecular 2D layer *via* $\pi$-$\pi$ stacking interactions between adjacent phenyl rings. Complex cations in **2** are assembled into 1D supramolecular chains through O–H···O H-bonds. The outer-sphere 4-nbz$^-$ anion is H-bonded with two complex cations by intermolecular O–H···O H-bond interactions. The intermolecular O–H···O H-bonds unite components in well-defined 2D supramolecular layer, which are stabilized by $\pi$-$\pi$ stacking interactions between adjacent phenyl rings and further assembled in a supramolecular 3D network. In compound **3** intermolecular O–H···O H-bonds relating by the coordinating and uncoordinated water molecules, TEA ligand and outer-sphere 4-nbz$^-$ anion form a 2D H-bonding layer stabilized by $\pi$-$\pi$ stacking interactions, which are further assembled *via* weak$\pi$-$\pi$stacking interactions between adjacent phenyl rings into a supramolecular 3D network structure. The intermolecular O–H···O H-bonds unite components of **4** in well-defined 2D supramolecular layer, which are further assembled in a supramolecular 3D network *via* $\pi$-$\pi$ stacking interactions between adjacent phenyl rings of 4-nbz$^-$ anions.

The luminescence properties of compounds **1-4** were studied in the solid state at room temperature, $\lambda_{ex}$= 337 nm. The fluorescence spectrum of organic salt **1** exhibits five bands at 670, 613, 502, 370 and 360 nm. Compound **2** emits red fluorescence with characteristic emission peaks of compound **1**, while **3** emits green fluorescence with characteristic emission peak at 502 nm, as well 439 nm and ultra violet 360 nm. Compound **4** exhibits a weak green fluorescence at 502 nm and ultra violet at 360 nm.

**P46**

# SOME FACTORS THAT INFLUENCE THE RETENTION OF LANTHANIDE (III) CATIONS ON A POLYMER CONTAINING AMMONIUM QUATERNARY NITROGEN

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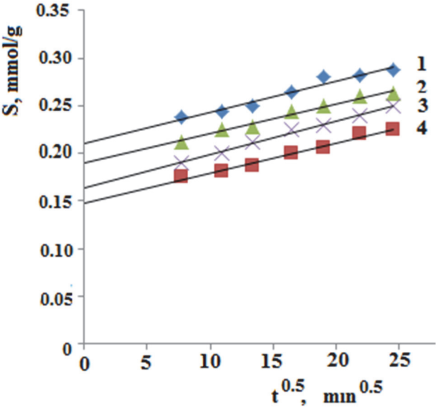
The largest amounts of Lanthanides are used in catalysis. Some of the rare earth elements are used in the glass and ceramic industries, metallurgy, electronics and even in water treatment and biomedicine. The fluorescent properties of the Lanthanide compounds are of special interest. The immobilization of cations on polymers with selective sorption properties allows the use of lanthanide compounds in processes where separation of the phases is required. Anion exchangers containing electron donating atoms (amines, hydroxyl groups) retain lanthanide cations as a result of complex formation reactions.

It is known that polymers containing quaternary ammonium nitrogen can adsorb lanthanides only in the form of anionic complexes. These polymers do not contain electron-donating atoms in their matrix and therefore, theoretically, cannot interact with metal ions. However, our previous investigation shows that such kind of polymers, in certain conditions, are able to interact with cations in $M_2(SO_4)_3$ solutions, where M is $Fe^{3+}$, $Cr^{3+}$, $Ga^{3+}$, $In^{3+}$or $Al^{3+}$.

In this communication the results of investigation on the influence of pH and temperature on Lanthanides(III) cations sorption on Purolite A-400, a polymer containing ammonium quaternary nitrogenare presented. The results of the study of the sorption kinetics of $La^{3+}$, $Nd^{3+}$, $Eu^{3+}$ and $Er^{3+}$ at 21 and 50°C are also presented.

It is shown that sorption of Lanthanide(III) cations on the Purolite A-400 polymer increases slightly with increasing temperature. Both at 21°C and 50°C with the pH increase of the solution, the sorption of the Lanthanide(III) cations increases significantly.

The kinetic curves obtained experimentally were calculated with pseudo-first order (PFO) and pseudo-second-order (PSO) kinetic models.The kinetic curves, calculated with the PSO model, are close to those obtained experimentally, which confirms that this model adequately describes the kinetics of sorption of Lanthanide(III) cations on the Purolite A-400. The non-linear dependence of -ln(1-F) = f(t) shows that the sorption rate of cations containing Lanthanides(III) on Purolite A-400 at both 21 so and at 50°C is limited by the internal diffusion. The linear dependence S = f ($t^{0.5}$) also confirms that the internal diffusion is the rate limiting step of sorption of lanthanide cations both at 21°C and at 50°C.



*Dependence $S_t = f(t^{0.5})$ for the $La^{3+}$ (1), $Eu^{3+}$ (2), $Er^{3+}$ (3) and $Nd^{3+}$ (4) sorption on Purolite A-400 at 21°C.*

**P47**

# THE EFFECT OF ULTRASONIC TREATMENT ON THE FORMATION OF NANOPARTICLES OF ZERO-VALENT IRON

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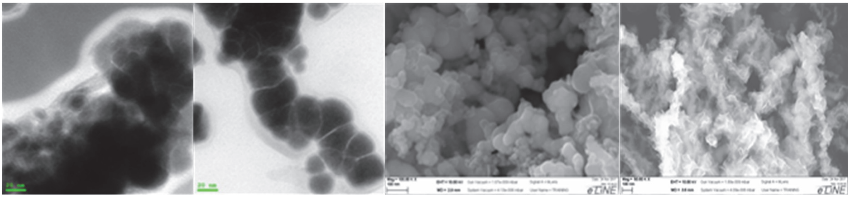
At present time, nano zero-valent iron (nZVI) compounds are increasingly used as carriers of information, magnetic fluids, delivery systems for medicines, and etc.

Nano zero-valent iron (nZVI) was prepared by chemical reduction from a ferrous salt-solution in the presence of PVP used as a stabilizer. Synthesis was performed under the ultrasound treatment and without it ($Fe^0$/PVP-USandFe$^0$/PVP). The resulting nanoparticles were characterized by X-ray powder diffraction (XRD) analysis and scanning electron microscopy (SEM), transmission microscopie (TEM) and FT-IR spectroscopie.



**(a)** **(b)** **(c)**

**Figure 1:(a)** SEM micrograph result; **(b)** ESR result; **(c)** VSM result of $Fe^0$-PVP

In Figure 1 is shown the morphological study of the obtained nanoparticles. It was proved that the synthesis carried out with ultrasonic processing allows to obtain more ordered packaging. Furthermore, the synthesized nanoparticles are protected with a polymer layer of 18-20 nm, which makes them less toxic for soil microorganisms.

**P48**

# NEW SYNTHESIZED MESOPOROUS SILICA MATERIALS FOR WATER VAPOR UPTAKE FROM THE AIR SATURATED WITH MOISTURE

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Mesoporous silica materials such as SBA-15, MCM-41, KIT-6, and MCM-48 have been synthesized by an ultrasound-modified sol-gel method. The obtained silica materials could be obtained in a short time and are of different pore sizes and shapes, and may be used in various fields due to their large internal surface area and uniformity of poresize. These features actually increase the applicationfeasibility of mesoporous silica materials for separation and removal operations. Thus, the resulted materials were characterized and their textural, structural and morphological properties were investigated.

In order to test the application feasibility of the synthesized materials in removal operations, the adsorption of water vapor was investigated by using a gravimetric system. Due to the presence of silanol groups on their surface, as well as mesopore structure, a large amount of water can be adsorbed on these ultrasound-derived mesoporous silicas, because their mesopores are suitable for capillary condensation. The obtained data were compared with the data reported in literature and further the synthesized materials were tested in water vapor uptake from the airsaturated with moisture. Additionally, the water removal property of the synthesized silica materials were compared with the same main property of commercially available silica gel, with the view to be used as desiccants.

## Acknowledgments

The authors thank for the Grant of the Ministry of Research and Innovation, RDI Program for Space Technology and Advanced Research - ROSA-STAR, project number 157/2017, for the financial support.

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**P49**

# KINETICS OF SOME FLUORQUINOLONES OXIDATION BY THE SYSTEMS UV AND UV-$H_2O_2$

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Fluorquinolones (FQ) are a class of antibiotics that manifest a broad spectrum of antibacterial activity [1]. Due to their extensive usage, fluoroquinolones may enter the aquatic environment what constitutes a danger for the ecosystem and human health by causing the increase and spread of bacteria drug resistance [2]. This is why it is very important to solve the problem of deep FQ oxidation by applying advanced oxidation processes (AOPs). It uses UV, UV/$H_2O_2$, $O_3$/UV, Fenton, photo-Fenton systems and represent a cyclic process with regeneration of $Fe^{2+}$ ions. These systems are the promising treatment options for wastewaters [2,3].

The purpose of this work was to study the kinetics of oxidation of four FQs – ofloxacin (OF), levofloxacin (LFX), ciprofloxacin (CPF) and moxifloxacin (MOX) under UV irradiation and by the UV-$H_2O_2$ system. During the work the spectrophotometric method and „DRT-1000" lamp as a irradiation source was used. Antibiotic concentrations varied from 12.5 to 30 mg/l.

It was established that under the UV irradiation the oxidation process of each drug proceeds as a zero order reaction (what is characteristic for photochemical reactions).

Antibiotics oxidation by the UV-$H_2O_2$ system proceeds with a considerably higher rate than under UV irradiation. In the UV-$H_2O_2$ system the total degradation of drugs occurs. It was determined that the reaction rate increases with the increase of oxidant and substrate concentration. Oxidant concentrations varied from $5\cdot10^{-5}$ to $5\cdot10^{-4}$. It was established that the reaction orders with respect to antibiotics have fractional values less than one, being in the range from 0.17 to 0.56. It was found that the reaction orders with respect to $H_2O_2$ also have fractional values less than one, varying from 0.49 to 0.69.

The reaction rate dependence on the pH was studied. It was determined that at the pH increase the reaction rate slightly increasing. The reaction orders with respect to $H^+$ ions have negative fractional values.

The rate equations for MOX and CPF oxidation by UV-$H_2O_2$ were established:

$$v = \kappa \frac{[MOX]^{0,27}[H_2O_2]^{0,49}}{[H^+]^{0,06}} \quad v = k \cdot \frac{[CPF]^{0,56} \cdot [H_2O_2]^{0,62}}{[H^+]^{0,15}}$$

The data obtained allowed us to conclude that the whole process of photolysis of substrates in the presence of $H_2O_2$ can be formed by the 4 main steps.

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**P50**

# SIX DECADES: REVIEW OF PATENT PORTFOLIO OF THE INSTITUTE OF CHEMISTRY

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Institute of Chemistry (I.Ch.) patent portfolio consists of three main collections of patent documents reflecting socio-political history of our state and peculiarities of different patent systems: 1) open printed author certificates of former URSS; 2) forbidden to open publishing ("Restricted" or "For administrative use only", ДСП in Russ.); 3) national patents of Republic of Moldova (MD patent). The first two collections represent SU patent documents.

As a result of analysis based on consultation of paper sources and open patent Data Bases, interviews and even using our tacit knowledge, some figures concerning portfolio were obtained:- number of SU documents (including I.Ch. as applicant) - **227**, of which **99 (44%)** represents restricted documents. We have identified also **10** documents, in which I.Ch. is not indicated as applicant or co-applicant, but these ones undoubtedly represent I.Ch. employee inventions. Additionally, it was found citation to **3** secret patent documents, which naturally are absolutely unavailable. Thus, *defacto* number of SU patent documents – at least **240**. Total filed MD patent applications – **232**. Number of granted MD patent documents – **195**, of which **6** ones are revalidated SU docs. In conclusion, the total number of patent documents has reached up at least **435**. It should be mentioned some patent milestones:

**SU165700-** the 1st I.Ch. patent document (priority 1963.04.11), inventors: Shamshurin A.A., Iampol'skaya M.A. By the way, the document with empty applicant field;

**MD112**- the 1st granted MD patent –"Composition for plastering-up", (…Lupașcu T. Ropot V.), while it represents the revalidated SU1652314;

**MD216 –** patent having the earliest claimed priority (1992.07.15, RU) –"Composition for aromatization of smoking tobacco"; inventors: Vlad P. *et al.*

**MD354** – first "genuine" national patent ("Method of obtaining (8αS)-2,5,5,8α-tetramethyl-…-oxo-trans-octahydronapthalene", inventors Vlad P. *et al.*);

Top technology fields of patent activity according to IPC subclasses (descending):
for SU docs –**C07F**, **A61K**, **C07D**, **C07C**, **A01N**, **G01N**, **C11B**, **C07J**, **C12H**, **D06P**;
for MD docs. – **C07C**, **C07D**, **A61K**, **C07F**, **C02F**, **A01N**, **C01B**, **C23F**, **C12N**, **B01J**.

Rate of patent application rejections: cca 8-10% for both SU and MD applications.

**FR1483560** is the most cited patent in foreign patents (5 forward citations), inventor Shamshurin A. *et al.* The most cited patent by MD patent examiners: **MD2386** with 23 citations; ("Process for cultivation of cyan bacterium *Spirulina platensis*"; inventors: …Turtă C, Lazarescu A.). The most cited I.C. work –"Template synthesis…" by **Gărbălău N**. and **Arion V.**, which is cited 7 times in RU patents.

Among the most economically exploited patents it should be mentioned: **SU1030446** (catalysts for vat dying of cotton fabrics); **SU1565001** (catalysts for epoxi resins hardening); **SU767083**, **MD216**, **MD217**, **MD235**, **MD524** (isolation of sclareol, synthesis of its derivatives for tobacco articles fragrances); **SU1652314**, **MD112**, **MD3252** (dry plaster mixes); **MD3602** (active carbon from agricultural wastes).

There were found **8** patent documents dealing with I.Ch. patenting abroad activity, namely **FR, CH, WO** based on SU documentsand five **RU** patents for MD inventions.

**P51**

# WATER-SOLUBLE DICOPPER COMPLEX HAVING ANTIMICROBIAL ACTIVITY

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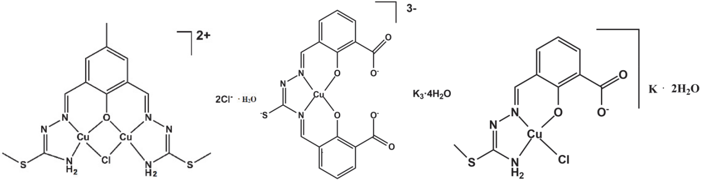
There have been synthesized some water soluble copper(II) complexes based on o-hydroxy-aromatic thiosemicarbazones having formulas (***C1*** [1], ***C2*** and ***C3*** respectively):



The complexes and starting thiosemicarbazone ligands (in DMSO) have been tested in water for antimicrobial activity against different bacteria and fungi by serial dilution method:

| Strains | ***C1*** | ***C2*** | ***C3*** |
|---|---|---|---|
| *Staphylococcus aureus* ATCC 25923 | 1/2 | 125/250 | 31/63 |
| *Bacillus cereus* ATCC 11778 | 0,5/1 | 250/500 | 31/63 |
| *Basillus subtilis* ATCC 6633 | 0,5/1 | 125/250 | 31/63 |
| *Escherichia coli* ATCC 25922 | 250/500 | l.a. | l.a. |
| *Acinetobacter baumannii* ATCC BAA-747 | 250/500 | l.a. | l.a |
| *Candida albicans* ATCC 10231 | 4/8 | l.a | 31/63 |
| *Candida parapsilosis* ATCC 22019 | 4/8 | l.a | 125/250 |
| *Cryptococcus neoformans* CECT 1043 | 2/4 | 63/125 | 31/63 |
| *Erwinia carotovora* | 70/70 | 300/600 | 1200/1200 |
| *Erwinia amylovora* | 70/70 | 300/600 | 1200/1200 |
| *Xantomonas campestris* | 70/70 | 300/600 | 1200/1200 |
| *P. fluorescens* CNMN-PFB-01 | 300/300 | 150/300 | 1200/1200 |

*(MIC/MBC – minimum inhibitory or bactericidal concentrations, µg/mL;l.a. – low activity)*

It was found that, among tested complexes, copper dimer ***C1*** manifests a pronounced antimicrobial activity, while it is selective against Gram(+) bacteria. Free thiosemicarbazones do not reveal any activity.

**Reference**

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**P52**

# SIMULATION OF ELECTRON LOCALIZATION DYNAMICS IN COATED METAL NANOCLUSTERS IN EXTERNAL ELECTRIC FIELD WITH ALLOWANCE FOR POLARIZATION

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The elaboration of models for describing of the various processes occurring in the nanostructured composite materials (NSCM) containing the nanocluster inclusions is very important both from the theoretical point of view and for the practical applications. The model presented in this paper describes the electron localization-delocalization process in the coated metal nanocluster (NC) in the low-frequency external electric field (EEF), using as an example the tetramer NC in its different conformations (linear and planar-square). So that, in addition to the tunneling of a common electron between the NC centers, the polarization induced by the EEF at the centers of the NC and its shell formed by the ligand environment of NC centers, as well as the electron-vibrational interaction are considered. It should be noted that this model allows to describe both small atomic clusters (whose centers are metal atoms) and large clusters (whose centers are quantum dots). Besides, it gives an opportunity to consider the different variants of the shell of nanocluster (NC): either single (shell covers all NC centers at once) or multiple (shell covers each NC center separately). It is shown that the interaction of a common electron with the vibrational modes of the ligand environment at each of the NC centers, together with the allowance for the polarization effects, leads to a nonlinear electron dynamics in such NCs. The nonlinearity appears explicitly in the differential equations describing the electron subsystem, owing to the exclusion of the intracluster vibrational modes of the ligand environment of the NC centers and the polarization modes describing the charge displacements at each NC center (including its ligands). The analysis of the numerical solutions of the obtained system of differential equations relative to the amplitudes of the probability of detecting an electron at the NC centers for various values of the external and internal model parameters of this system makes it possible to reveal the different regimes in the nonlinear electron localization dynamics, as well as the conditions of switching between them. As the numerical simulation shows,in the tetramer NC (without taking into account the polarization effects) there are three characteristic regimes of the electron localization dynamics. It is important to note that the controlling role of the EEF makes it possible to realize both the regimes with localization and regimes with delocalization of an electron along the direction of action of the EEF. Herewith, the variation of the frequency and amplitude of the EEF controls the duration of complete localization at the NC centers and switches the NC from the state with the localized electron into the state with a delocalized electron. Thus, at the allowance for the polarization effects along with the electron-vibrational interaction in the NC, the control of electron density distribution regimes by the EEF becomes more flexible, since, both the nonlinear response of the NC on the EEF action is taken into account and the number of tunable model parameters is increasing. As a result, of the given model provides ample opportunities to search for new regimes of electron localization in the coated NC of different kind, as well as to realize the aforementionedregimes and to identify the ways of switching between them.

**Acknowledgments.** This work was supported by the CSSDT of the Academy of Sciences of Moldova, Institutional Projects 15.817.02.03A.

**P53**

# DIRECT SYNTHESIS OF MULTIDIMENSIONAL POROUS SILICA USING A MIXTURE OF SUPRAMOLECULAR TEMPLATES

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The synthesis of multidimensional porous materials with a tailored polymodal distribution of pores combining micro- and mesopores is especially important for those chemical processes where the heterogeneous system operates at low reaction temperatures or the moderate temperatures of its regeneration are necessary [1,2]. The aim of this work is to study the spatial correspondence of structural varieties of organic template to pores and voids formed in multidimensional porous silica. The template in the work was a supramolecular mixture of non-ionic and cationic surfactants, namelyTween-80 and Stabiram.

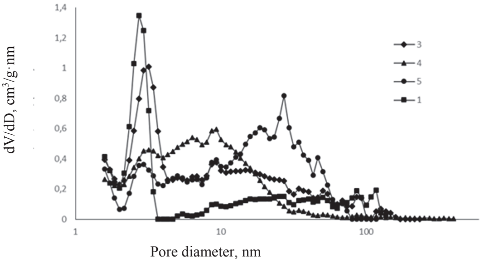

**Figure 1.** NLDFT size distribution of pores calculated from isotherms of low-temperature nitrogen adsorption-desorption on $SiO_2$ samples obtained at a molar ratio of Tween-80 / Stabiram: 1 – 0; 3 – 0.5/0.5; 4 – 0.8/0.2; 5 – ∞.

Isothermal data of superficial tension of solutions of surfactant mixture and low-temperature nitrogen sorption of multidimensional porous silica received by template synthesis prove complementarity of its properties and properties of SAA micelles. The measured isotherms of gas sorption belong to IV Type, inherent in mesoporous adsorbents. The BET specific surface area is 600-800 $m^2/g$, and the Gurvich pore volume is 0.7-1.0 $cm^3/g$. With increase in mol fraction of nonionic component these values decrease, the ordered texture of $SiO_2$, characteristic of MCM-48 mesoporous molecular sieve, collapses, $d_{211}$-spacing becomes $< 3.31$ nm, and NLDFT distribution is transformed from monomodal to polymodal one (Figure 1).

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**P54**

# PROPERTIES OF TIN FILMS ELECTRODEPOSITED FROM DIFFERENT COMPLEXES AS ANODES FOR LITHIUM-ION BATTERIES

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As the anode material lithium-ion batteries (LIB) graphite is widely used, which provides more than a thousand charge-discharge cycles. However, anodes based on carbon materials are characterized by low specific capacity (372 $mA\cdot h\cdot g^{-1}$), low discharge rate, and relatively narrow temperature interval of operation. Therefore, the development of new anodic materials for LIB with high values of specific capacity and discharge current density is very important. As a possible alternative to carbon materials, it is proposed to use thin electrolytic films of tin or its alloys, in particular with nickel, cobalt, copper, zinc, and antimony in LIB.

In modern electroplating, the use of metal complexes is one of the most simple and controlled methods for producing functional coatings with metals and alloys. The combination of properly selected ligands for complex, including polyligands, electrolytes allows to control the slowdown of the electrode process, the structure and properties of the obtained coatings.

The morphology and structure of the obtained coatings depend not only on the parameters of electrolysis, but also on the composition of the electrochemically active complex (EAC), which is directly discharged on the electrode.

The comparative electrochemical properties of tin films obtained from complex (pyrophosphate ($Na_4P_2O_7$), tartrate ($Na_2tart$), citrate ($Na_3citr$) and citrate-trilonate ($Na_3citr$ / $Na_3H_2edta$) electrolytes as anode materials in lithium-ion batteries have been investigated using the methods of potential dynamic galvanostatic sweeps in 1 M ethylene carbonate – dimethyl carbonate solution.

The magnitudes of the peak currents of lithium intercalation-deintercalation, depending on the nature of the ligand, decrease in the series: $tart^{2-} < citr^{3-} < edta^{4-} < P_2O_7^{2-}$ ions. It is shown that the nature of the ligand affects the current yield of tin, the composition of EAC and the mechanism of the process. This suggests that the composition of the discharging complex predetermines the morphology and properties of tin films and, consequently, their stability, specific capacity and efficiency of cycling in LIB. The specific capacity of thin tin films obtained from complex electrolytes and the efficiency of cycling in aprotic solvents with a lithium anode is determined not only by the nature of the ligand, but also by the anion of the tin(II) salt.

The specific discharge capacity of tin films obtained from pyrophosphate electrolyte (1000 $mA\cdot h\cdot g^{-1}$), as anodes of lithium-ion batteries, is significantly higher compared to the capacity of tin films obtained from citrate-trilonate (750 $mA\cdot h\cdot g^{-1}$) citrate (500 $mA\cdot h\cdot g^{-1}$) and tartrate (400 $mA\cdot h\cdot g^{-1}$) electrolytes. Apparently, this is due to the optimal porosity of electrolytic tin films obtained from the pyrophosphate electrolyte.

The most stable characteristics (the value of the specific capacity and the ability to reversible cycling in lithium systems) are characteristic of tin films obtained from citrate electrolyte based on tin (II) chloride.

**P55**

# CRYSTAL STRUCTURE OF 2-HYDROXY-3-CARBOXY-1-NAPHTHALDEHYDE SEMICARBAZONE COPPER(II)COMPLEX

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Semi- and thiosemicarbazones, their derivatives and metal complexes attract attention for a long time due to significant bioactivities and wide pharmacological versatility [1-3]. In continuation of our study on semi- and thiosemicarbazone compounds of 3d metals, a new copper(II) complex with new Schiff base ($H_3L$) obtained by interaction of 2-hydroxy-3-carboxy-1-naphthaldehyde and N(4)-phenyl-semicarbazide moiety has been synthesized and characterized by single crystal X-ray method.

The crystals of complex with composition $[Cu(H_2L)Br]\cdot 0.5H_2O\cdot 0.5dmso$ crystallize in the non-centrosymmetric monoclinic space group $P2_1$ with unit cell parameters: $a$ = 8.1743(5), $b$ = 28.735(2), $c$ = 8.7870(4) Å, $\beta$ = 102.643(5)°, $V$ = 2013.9(2) Å$^3$. The asymmetric unit comprises two similar square-planar Cu(II) complexes with ONOBr coordination surrounding provided by threedentate organic ligand (Cu-O distances are in the range 1.865(8)-1.935(8) Å and Cu-N 1.930(8)-1.962(8) Å), and $Br^-$ anion (Cu-Br distances are 2.334(2) and 2.339(2) Å), (Figure). The orientation of carboxylic group is stabilized by an intramolecular O–H···O hydrogen bond 2.49(1) Å. The ligands in symmetry independent complexes differ by mutual arrangement of five-membered metalocycle and phenyl moiety of semicarbazone fragment. The corresponding dihedral angles are equal to 41.4 and 9.3°. In the crystal complexes are linked in chains by N–H···Ohydrogen bonds with N2···O7 and N5···O4 distances 2.74(1) and 2.75(1) Å, respectively (Figure).

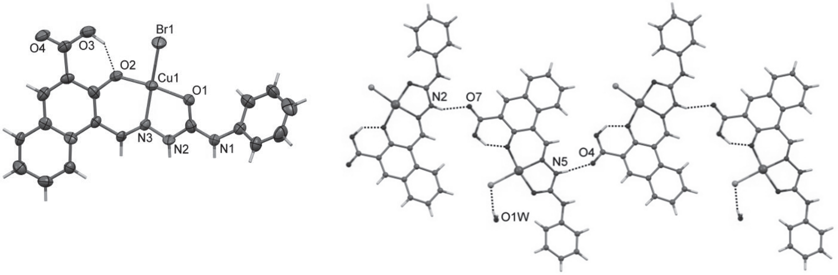

**Figure.** Molecular structure and fragment of the hydrogen bonded chain.

The crystal structure reveals infinite columns of complexes due to stacking interactions between their planar metallocycles and naphthalene moieties with average interplanar distance 3.4Å.

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**P56**

# TWO- AND THREE-DIMENSIONAL Cd(II) COORDINATION POLYMERS ASSEMBLED FROM BRIDGING SULFATE ANIONS AND ISOMERIC N,N'-DONOR SCHIFF BASE LIGANDS

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Coordination polymers, especially those porous, are a promising class of materials. Sulfate anions with rigid tetrahedral geometry are widely employed to prepare extended network structures similar to silicates, phosphates, arsenates etc. Due to the direct cation-anion coordination linkage the pathway to obtain neutral metallo-organic carcases is straighforward. Sulphates have been used in the synthesis of coordination polymers in particular open-framework compounds and also heterometallic coordination polymers. The variety and diversity exhibited by this class of compounds has been reviewed by Rao et al. [1].

To increase and adjust the metal-metal distances, we used the bridging Schiff base ligands of the N,N-donor bis-monodentate type of the class of aromatic azines,*1,2-bis(pyridin-4-ylethylidene)hydrazine)*(4-bpmhz) and *1,2-bis(pyridin-3-ylethylidene)hydra- zine)* (3-bpmhz). Following the reaction between the $CdSO_4{\cdot}8/3H_2O$ salt and the mentioned lingands, two coordination polymers were obtained by the diffusion method, 2D coordination network$[\{Cd(4\text{-}bpmhz)(SO_4)(H_2O)\}]_n$ (**1**) and the 3D coordination grid, $[Cd(3\text{-}bpmhz)(SO_4)(H_2O)]_n$(**2**) whose crystal structures were confirmed by single-crystal X-ray diffraction analysis.

Compounds **1** and **2** crystallize in the same monoclinic crystal system. For **1**: $a$=29.8591(8), $b$=10.0210(3), $c$=6.8629(5) Å, $\beta$=96.429(4)°, $V$=2040.59 Å$^3$sp. gr. $C2$. For **2**: $a$=5.6884(2), $b$=10.5861(4), $c$=13.7576(5) Å, $\beta$=93.440(4)°, $V$=826.96 Å$^3$, sp. gr. $P2_1$.

In **1** the sulfate anion is bidentate bridgingcoordinated to two cadmium cations; the metal's $N_2O_4$ octahedral geometry is formed by two sulfate anions, two azine ligands, and two water molecules. In compound **2** the sulfate anion is tridentate-bridging coordinated to three cadmium cations; each Cd(II) center adopts again $N_2O_4$ octahedral coordination geometry with two nitrogen donors from two 3-bpmhz ligands, and four oxygen donors from three sulphate anions, and one water molecule, respectively.

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**P57**

# TWO ISOMORPHOUS 1D COORDINATION POLYMERS DERIVED FROM Zn(II) AND Cd(II) IODIDE AND BRIDGED N,N'-DONOR AZOMETHINE LIGAND

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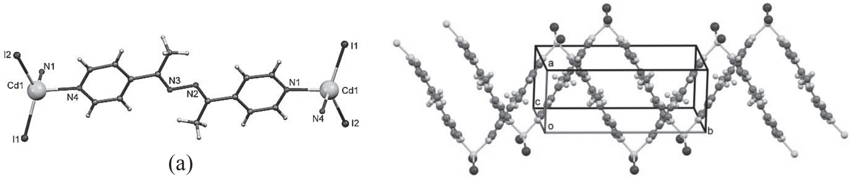
Along with the 3D coordination frameworks, the low-dimensional (1D and 2D) coordination polymers as objects of the study by materials science and crystal engineering [1, 2], some of them are exhibiting molecular ferromagnets, are synthetic conductors, non-linear optical materials, and segnetoelectrics, whose crystal structures and useful properties can be varied by fitting their components.

We report two isomorphous 1D coordination polymers constructed from the Schiff-base N,N'-type ligand,*1,2-bis(pyridin-4-ylethylidene)hydrazine)*(4-bpmhz), namely $[CdI_2(4\text{-bpmhz})]_n$(**1**) and $[ZnI_2(4\text{-bpmhz})]_n$(**2**). The structures of compounds were determined using X-ray diffraction method (Figure).



(a)

(b)

**Figure.** a) the fragment of polymer chain in **1**; b) packing of the chains

The isomorphous crystals of compounds **1** and **2** differ by the metal cation only. Compounds crystallize in the monoclinic$P2_1/n$sp. gr.: for **1**$a$=7.35379(3), $b$=17.5832(6), $c$=14.6230(4) Å, $\beta$=102.270(3)°, $V$=1847.59 Å$^3$; for **2**$a$=6.9997(8), $b$=18.3085(12), $c$=14.3436(9)Å, $\beta$=101.921(9)°, $V$=1798.5(3) Å$^3$. All components occupy general positions. The $N_2I_2$tetrahedral configuration of the metal atom is formed by two iodide anions and two 4-bpmhz ligands, Cd–I 2.6675(5) and 2.6911(5) Å, Cd–N 2.301(4) and 2.305(4) Å(Zn–I 2.528(17) and 2.550(19)Å, Zn–N 2.063(12) and 2.082(12) Å). The corresponding distances in **1** are insignificantly elongated because of the larger radius of the Cd atom compared to Zn. The zigzag coordination chains run along the crystallographic *b* axis in both crystals.

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**P58**

# SINGLE AND DOUBLE CHAIN Zn(II) COORDINATION POLYMERS BASED ON ISOMERIC BIDENTATE SCHIFF BASE LIGANDS

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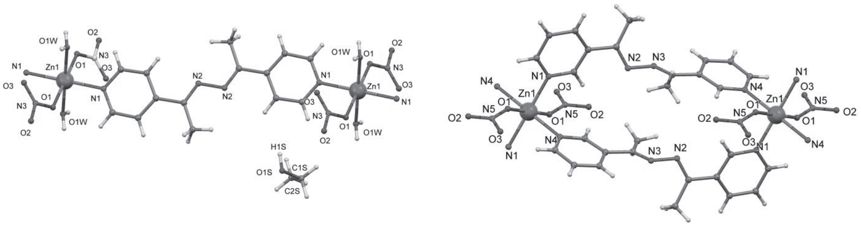
The study of inorganic-organic hybrid polymer materials has attracted considerable interest not only for their great potential applications but also for their versatile structures topologies [1]. A large number of coordination polymers have been already generated with 4,4'-bipyridyl bridging ligand [2]. Herein we report two 1D Zn(II) coordination polymers, $[Zn(NO_3)_2(H_2O)_2(4\text{-bpmhz})]_n\cdot 0.5n(EtOH)$ (**1**) and $[Zn(NO_3)_2(3\text{-bpmhz})_2]_n$ (**2**) derived from the semi-rigid Schiff-base N,N'-type ligands, *1,2-bis(pyridin-4-ylethylidene)hydrazine* (4-bpmhz) and *1,2-bis(pyridin-3-ylethylidene)hydrazine*(3-bpmhz) whose crystal structures were confirmed by single-crystal X-ray diffraction analysis.



(a) (b)

**Figure.** The fragments of coordination chains in **1** and **2**

Compound **1** crystallizes in the monoclinic *I2/c* space group: *a*=7.4726(2), *b*=11.5998(3), *c*=28.1718(9) Å, *β*=94.630(3)°, *V*=2433.98Å$^3$. Each Zn(II) ions adopts $N_2O_4$ octahedral coordination geometry with two nitrogen donors from two symmetry related 4-bpmhzligands, and four oxygen donors from two nitrate anions, and two water molecules, respectively. The traces of ethanol solvent werefound in the crystal lattice. The relatively simple linear chain is formed due to the bidentate bridging 4-bpmhz ligands, while terminal nitrate anions and water molecules prevent the further structure extension. The replacement of 4-bpmhz ligand with its positional isomer, 3-bpmhz containing the N,N'-donor atoms in the 3,3'-positions, resultsin 1D coordination polymer with the linear double-chain structure. Compound crystallizes in the monoclinic *P*2₁/*n* space group: *a*=8.5712(3), *b*=17.3275(6), *c*=10.1744(4) Å, *β*=97.142(3)°, *V*=1499.34 Å$^3$. The Zn(II) $N_4O_2$ octahedral coordination core is composed from four 3-bpmhz ligands being in significantly distorted twisted conformation, and two monodentate nitrate anions.

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**P59**

# PHOTODEGRADATION OF CONGO RED DYE AND 2,4-DICHLOROPHENOXYACETIC ACID HERBICIDE USING MESOPOROUS TITANIA PHOTOCATALYST

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The environmental pollution has become an important problem of our days. The huge development of textile industry and specially agrochemicals have led to increase the number of different dyes, pesticides and herbicides in ground water and surface waters. They have negative effects on human health and aquatic ecosystems [1]. Thus, a way to overcome these effects is to find a process through which the used chemicals are destroyed.

Our work reports a new synthesized mesoporous titania $TiO_2$ nanoparticles, involving ultrasound-assisted sol-gel method.In the typical synthesis procedure titanium isopropoxide was used as titania precursor and surfactant F127 was used as structure directing agent. When the sol was maturated, the precipitate have been separated by centrifugation, washed several times with distilled water and dried at room temperature. Afterward, the solid obtained was subjected to the thermal treatment for 4 hours, at 723,15 K, performing that way the pore emptying. By varying the surfactant/titanium-source weight ratio, as well as the ultrasonation time, nine titania samples have been obtained.The influence of the surfactant/titanium source weight ratio and different ultrasonication time on the textural, structural and morphological properties has been investigated by various physicochemical techniques (X-ray diffraction, UV Diffuse Reflectance, Nitrogen Sorption Measurements, Fourier Transform Infra Red spectroscopy, Scanning Electron Microscopy).

Afterward, the synthesized titania samples have been tested in the photodegradation process of Congo Red (dye) and 2,4-dichlorophenoxyacetic acid (herbicide). Both molecules have been choosed as model molecules to be degraded by the synthesized photocatalyst under UV-light. The obtained data have been compared and the most efficient catalyst could be used in photodegradation of such molecules.

**Acknowledgements**
This work was supported by a grant of Minister of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE-2016-0805, within PNCDI III.

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**P60**

# SYNTHESIS, CHARACTERIZATION AND *IN VITRO* ANTITUMOR EVALUATION OF NEW BINUCLEAR OXOVANADIUM(V) COMPOUNDS

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Vanadium salts and well-known vanadium coordination compounds have shown antibacterial, antifungal, antitumor, and antidiabetic activities when investigated by various biological methods [1,2].

Our goal was, firstly, to synthesize and characterize two enantiomers of a vanadium complex with Schiff-base ligandderived from salicylaldehyde and valine and, secondly, to evaluate their antitumor properties. Condensation of 2-hydroxybenzaldehyde (salicylaldehyde, sal) with L-valineor D-valine (L/D-val), respectively, yielded the tetradentate Schiff bases: $H_2$(sal-L-val) and $H_2$(sal-D-val).

Dinuclearoxovanadium(V) complexes with the molecular formulas: $[(VO)_2(\mu_2\text{-}O)(\text{sal-L-val})_2(H_2O)]$ (L-CP) [3] and $[(VO)_2(\mu_2\text{-}O)(\text{sal-D-val})_2(H_2O)]$ (D-CP) have been synthesized and characterized. Bothcomplexes have been characterized by elemental analysis, single-crystal X-ray diffraction, X-ray powder diffraction, and spectroscopic (IR, UV-Vis and circular dichroism) measurements.The protein binding capacity of the compounds was tested *in vitro* by a fluorometric method based on quenching the fluorescence of bovine serum albumin (BSA). Cytotoxic effects of compounds were examined on hepatocyte carcinoma (HepG2) cell line using XTT assay.

The spectral and structural data revealed that the coordination of tridentate/tetradentate L/D-Schiff base ligands to vanadium atoms lead to binuclear complexes in which V (V) atoms have distorted octahedral coordination geometry and the compounds exhibit optical activity. The compounds bind and quench the intrinsic fluorescence of BSA in a dose-dependent manner. They do not show cytotoxic effects on HepG2 cells at concentrations below 100 µM, but induce approximately 70% for L-CP and 60% for D-CP cell death at a concentration of 300 µM.

We have synthesized and physicochemical characterized two binuclear vanadium complexes derived from salicylaldehyde and L-valine and D-valine, respectively. Moreover, owing totheir capacity to bind to BSA and to induce cell death against HepG2 cells, the synthesized compoundsmay be the ideal candidates for cancer therapy.

**Acknowledgments.** This work was supported by a grant of Ministry of Research and Innovation, CNCS-UEFISCDI, project number PN-III-P4-ID-PCCF-2016-0050, within PNCDI III.

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**P61**

# ONE-POT FORMATION OF AN UNUSUAL MULTICOMPONENT IONIC COMPLEX $[Co^{III}(NH_3)_6]_3[Co^{II}L_6]_2$•$H_2$tea•$10H_2O$ WITH PARTIAL *IN SITU* REDUCTION OF COBALT(III)

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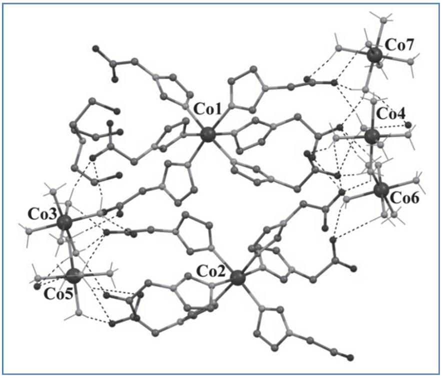
The discovery of the remarkable antiviral and a potential therapeutic properties against HIV and/or Ebola virus of hexamminecobalt(III) chloride $[Co(NH_3)_6]Cl_3$ [1, 2] stimulate the search and the development of promising multicomponent antiviral and antibacterial compounds. The multicomponent pharmaceutical solids involving hexamminecobalt(III) cations together with another bio-active molecules may be used for obtaining new promising substances and fine-tuning of physicochemical properties such as solubility, physical stability, and powder compaction. The crystallization under ambient conditions of hexamminecobalt(III) chloride and 1H-imidazole-1-acetic acid (HL) in water/methanol medium in the presence of triethanolamine ($H_3$tea) results in crystalline multicomponent ionic complex $[Co^{III}(NH_3)_6]_3[Co^{II}L_6]_2$•$H_2$tea•$10H_2O$. The compound crystalizes in monoclinic space group $P2_1/n$, $a$ = 25.050(1), $b$ = 14.450(1), $c$ = 33.873(2) Å, $\beta$ = 104.305(5)°, $V$ = 11881(1) Å$^3$ and comprises $[Co^{III}(NH_3)_6]^{3+}$ cations, $H_2tea^-$ anions, partially disordered solvent water molecules and, surprisingly, the six-coordinated anionic complexes $[Co^{II}L_6]^{4-}$ (Figure). Here, 1H-imidazole-1-acetate ligands are monodentate and coordinate to cobalt(II) atoms *via* nitrogen atom to complete their octahedral surrounding. The Co(II)–N distances in the range 2.138(11) - 2.194(11) Å undoubtedly indicate +2 oxidation state for Co and are essentially longer comparing to the Co(III)–N distances of 1.925(9) - 1.991(9) Å in the hexamminecobalt(III) cations. The conformation of twelve symmetry independent organic ligands in two symmetry independent complex anions is rather similar and dihedral angle between the planes of imidazole and carboxylic group fragments varies in the interval 64.67 - 71.68º. The survey of Cambridge structural database (CSD) revealed that the reported compound represents the first example of monocoordinated imidazole-1-acetate ligand, which usually serves as a $\mu_2$- or $\mu_3$-bridges in coordination compounds. In the crystal structure the deprotonated carboxylic groups are involved in multiple charge-assisted N–H···O hydrogen bonds between the complex cations and anions as well as with solvent water molecules.



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**P62**

# SYNTHESIS AND STRUCTURES OF COPPER(II) COORDINATION COMPOUNDS WITH ISOMERS OF CYCLIC TRIIMIDAZOLE AND THEIR DERIVATIVES

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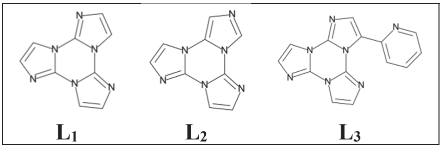
The assembling of organic and inorganic components with emissive properties into new hybrid materials can provide multifunctional smart luminescent coordination networks [1]. Cyclic triimidazole (triimidazo[1,2-*a*:1',2'-*c*:1",2"-*e*][1,3,5]triazine, $L_1$) and its derivatives with pyridinic functional groups are useful tectons for molecular design. These molecules actively contribute to intermolecular stacking, making them useful participants for syntheses of new materials with intriguing supramolecular architectures. Recently, the inherent photoluminescent properties of cyclic triimidazole ($L_1$) have been demonstrated [2], and some copper(I) halide coordination networks with this ligand have been reported [3].


$L_1$ $L_2$ $L_3$

Motivated by these results, we have prepared new coordination compounds starting from copper(II) acetate dihydrate and three triimidazole $L_1$-$L_3$ derivatives in a $CH_3CN/CH_3OH$/dmf solvent mixture. They include: one mono- $[Cu(L_2)_2(CH_3COO)_2]$, **1**, andtwo dinuclear $[Cu_2(L_1)_2(CH_3COO)_4]$, **2** and $[Cu_2(L_3)_2(CH_3COO)_4]$, **3** complexes. Compounds **1** and **3** crystallize in the triclinic space group *P*-1, and compound **2** crystallizes in the monoclinic space group *P*2₁/*c*. All compounds are centrosymmetric. The Cu(II) atom in centrosymmetric complex **1** has the $N_2O_4$ square-bipyramidal coordination core provided by two $L_2$ ligands that coordinate in a monodentate mode, and bidentate chelate $CH_3COO^-$ anions. The centrosymmetric dinuclear complexes **2** and **3** include paddle-wheel acetate dimer due to bridging function of four acetate anions, and capped by $L_1$ or $L_3$ in axial positions being mono-coordinated via imidazole nitrogen, Cu-N distances equal 2.217 and 2.238Å, respectively. The presence of stacking motifs in the reported coordination compounds responsible for the emission of free ligands [2] is a promising event for the ongoing research.

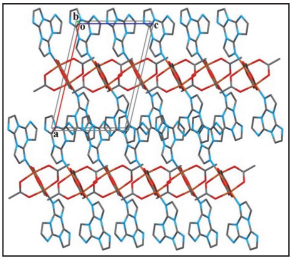


**Figure.** Fragment of crystal packing in **2**

**Acknowledgments.** Authors thank the Bilateral Moldova/Italy project 18.80013.16.03.03/It and ASM-CNR 2018-2019 project for financial support.

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**P63**

# SYNTHESIS AND STUDY OF A NEW MANGANESE(II) COORDINATION POLYMER

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Nowadays the laboratory synthesis of Metal-Organic Frameworks (MOFs) has been the objective of many synthetic chemists. Interest to these materials is actual due to their considerable porosity, inherent surface area and versatility in properties. MOFs have wide applications in areas such as storage of gases, solar energy, biomedicine, heterogeneous catalysis, etc.

We have synthesized a new coordination polymer based on 3,3',5,5'-tetrakis(4-carboxyphenyl)-2,2',4,4',6,6'-hexamethyl-1,1'-biphenyl ligand ($H_4L$) (Fig.1). The complex [Mn-L] (**1**) were synthesized under solvothermal conditions and have been characterized by IR spectroscopy, thermogravimetry and by single-crystal X-ray diffraction. It was found that the 3,3',5,5'-tetrakis(4-carboxyphenyl)-2,2',4,4',6,6'-hexamethyl-1,1'-biphenyl ligandmanifests as a tetradentate ligand and in deprotonated form $L^{4-}$ coordinates four manganese (II) atoms to form a three dimensional coordination polymer (3D) (Fig. 2) in cavities of which the DMF molecules are positioned.

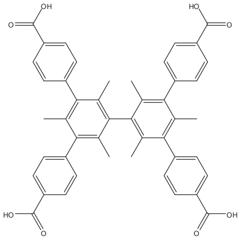

**Figure 1.** 3,3',5,5'-tetracarboxylmesitil acid

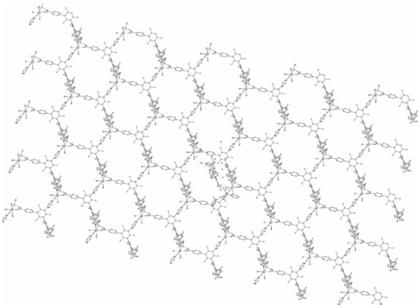

**Figure 2.** Manganese coordination polymer [Mn-L] (**1**)

In order to assess the robustness of the coordination architecture of the compound a thermogravimetric (TG) analysis was performed on the crystalline material. The thermal behavior of coordination polymers **1** demonstrates its high thermal stability.

**P64**

# CATALYTIC OZONATION OF MALACHITE GREEN DYE USING MONTMORILLONITE K10 CHEMICALLY MODIFIED WITH COPPER AND ZINC

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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 whichinvolvesthe formation of hydroxyl radicals ($OH^-$). The advantages and drawbacks of these processes are highlighted, while some of challenges, such as: the decrease of operational cost andthe adoption of strategies for processes integration are ongoing. These processes are sensitive to variations in temperature, pH, pollutant concentration, ozone concentration and the amount of catalyst used. 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 (Montmorillonite) with copper and zinc, and testing this catalyst in order to obtain a total mineralization of Malachite Green dye from solutions. Montmorillonite is a smectite clay extracted from bentonite, which is distinguished by two tetrahedron sheets arranged in the hexagonal rings. By catalytic ozonation processes can be achieved a partial or a total mineralization of 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, as presented in Fig.1. [1].

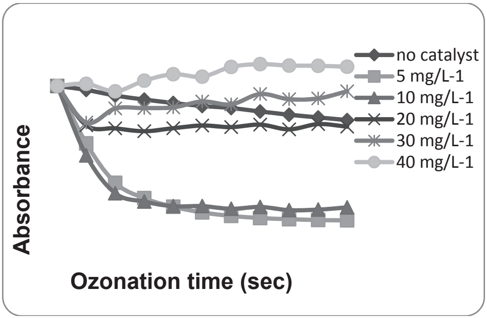

**Figure 1.** Catalytic ozonation of Malachite Green dye 5 x $10^{-5}$ M, Catalyst$_{dose}$: 0, 5, 10, 20, 30, 40 mg/$L^{-1}$, $O_{3dose}$: 0.5 g.$h^{-1}$

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**P65**

# EVALUATION OF ACTIVE CARBONS SURFACE GROUPS BY TPD-MS TECHNIQUE

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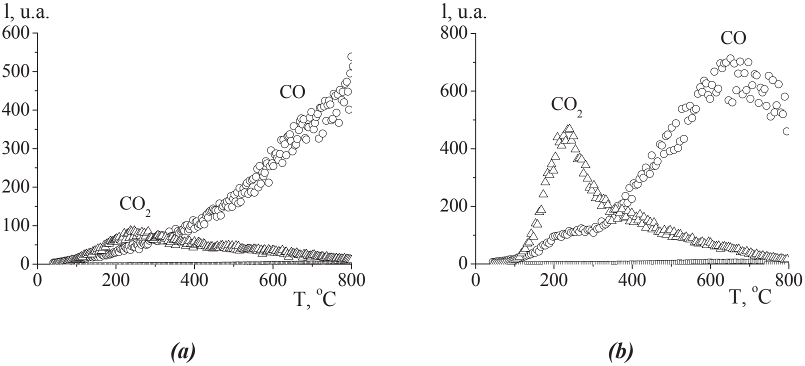
The characterization of active carbons by temperature programmed desorption (TPD-MS) involves the thermal decomposition of samples and the analysis of the gases removed using a mass spectrum. Both, the functional groups on the surface of active carbons, *e.g.* carboxylic, lactones, anhydrides, phenolic groups, carbonyl groups and quinines, and the species adsorbed on the surface can be determined by this method [1,2].

In this study two samples of active carbons were used (1) commercial available active carbon AG-5 and (2) oxidized with nitric acid AG-5ox [3]. For the TPD analysis, 10 mg of sample were placed in quartz-molybdenum tube and the tube was evacuated to $10^{-2}$ Pa, and then heated at 10ºC/min up to 800°C. The gases produced along the decomposition of surfaces groups were analyzed with a mass spectrometer.

The mass spectra of the active carbon samples are shown in Figure. At low temperatures below 400°C, the most unstable functional groups (carboxylic acids, lactones and anhydrides) are broken down and $CO_2$ and CO are removed. The broadening of the band to higher temperatures indicates different strengths of the bond between carbon and oxygen. The elimination of CO at temperatures above 600°C indicates the presence of phenolic, carbonyl and quinonic groups.



***(a)*** ***(b)***

**Figure.** Mass spectra of activated carbon samples (*a*)- AG-5 and (*b*)- AG-5ox.

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**P66**

# MIXED-VALENT TRINUCLEAR COBALT COMPLEXES WITH 1,3-BIS(SALICYLIDENEAMINO)-2-PROPANOL AND ITS SUBSTITUTED ANALOGUES

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There have been considerable interests indinuclear, oligonuclear, and polynuclear cobalt complexes, because such units may be important as some cobalt-based magnetic materials having the anisotropic magnetic properties [1]. Dinucleating Schiff-base ligand, 1,3-bis(salicylideneamino)-2-propanol ($H_3salpr$), and its substituted derivatives are good candidates for constructing such multinuclear cobalt species due to their dinuclear coordination sites [2-7]. In this study, we prepared mixed-valent cobalt species with a linear trinuclear $Co^{II}Co^{III}_2$ core by the reaction of $H_3salpr$ and its substituted analogues with cobalt salt. The isolated complexes were characterized by elemental analyses, IR and UV-Vis spectra, and single-crystal X-ray structure analysis, elucidating the chemical formula of $[Co_3(Hsalpr)_2(CH_3COO)_4]$ as shown in Figure 1. We also isolated hexanuclear species with similar reactions. We report here the synthesis and crystal structures of these mixed-valent complexes.

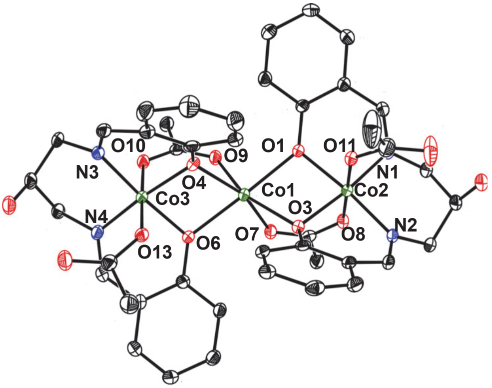

**Figure 1.** The crystal structure of $[Co_3(Hsalpr)_2(CH_3COO)_4]$.

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**P67**

# Cu(II) COORDINATION POLYMERS CONSTRUCTED FROM FLEXIBLE 2,2'-DITHIODIBENZOIC ACID AND 1,2-BIS(4-PYRIDYL)ETHANE

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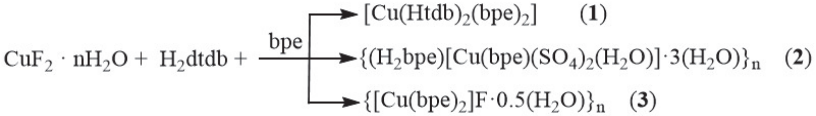
The synthesis and characterization of crystalline coordination polymers has attracted substantial interest because of the potentially useful adsorbent, magnetic or optical properties of these materials. The choice of appropriate ligands plays crucial for constructing of multinuclear compounds. Thereby, we have selected the 2,2'-dithiodibenzoic acid ($H_2$dtdb) for this study based on its multifunctionality: (1) the carboxylate groups can show different coordination modes, (2) the S–S bond makes the ligand flexible and (3) cleavage of the C–S and S–S bonds allow the fabrication of exciting coordination polymer topologies. Sometimes, after cleaving of C-S and S-S bonds, together with the newly obtained ligands, the extruded S atom is oxidized to the sulphate ion [1]. Being in line with these investigations we report herein the products of interaction of tetrafluoroborate Cu(II) with $H_2$dtdb in the presence of 1,2-bis(4-pyridyl)ethane (bpe) ligand, under the same solvothermal conditions (Scheme). The structures of obtained crystals have been characterized by single-crystal X-ray diffraction (Table) and show that compound **1** represents a mononuclear compound, while **2** and **3** are 1D and 2D coordination polymers, respectively.



The Cu(II) atom in **1** has a distorted octahedral $N_2O_4$ geometry going from two bidentate-chelate $Htdb^-$ anions and two neutral monodentate bpe ligands in the axial positions. Mononuclear compounds are combined into 1D supramolecular chains *via* intramolecular O–H···N hydrogen bonds involving the uncoordinated O atoms of $Htdb^-$ carboxylate groups as donors and the pyridine N atoms as acceptors. Compound **2** is ionic and consists of anionic 1D coordination polymer, organic cations $(H_2bpe)^{2+}$, and water molecules. The metal ion has a tetragonal pyramidal $N_2O_3$ coordination polyhedron involving N atoms of two bpe ligands, two O atoms of two coordinated $SO_4^{2-}$ monodentate anions and one O atom of water molecule. Compound **3** is ionic to and its crystal structure consists of 2D coordination polymer cation, $F^-$ anions and solvated water molecules. The copper atom is coordinated by four nitrogen atoms of four neutral bridging bpe ligands to form a tetrahedral surrounding, typical for diamondoid topology.

**Table 1.** Crystal data for **1-3**

| | **1** | **2** | **3** |
|---|---|---|---|
| CS | Triclinic | Triclinic | Tetragonal |
| SG | *P*-1 | *P*-1 | $I4_1/a$ |
| *a*(Å) | 7.4568(6) | 9.3612(7) | 19.063(2) |
| *b*(Å) | 11.5572(6) | 11.3072(7) | 19.063(2) |
| *c*(Å) | 14.0914(9) | 13.9491(10) | 7.3544(14) |
| α(º) | 90.757(5) | 85.274(5) | 90 |
| β(º) | 100.558(6) | 82.857(6) | 90 |
| γ(º) | 105.784(6) | 89.386(6) | 90 |
| $V$(Å$^3$) | 1146.26 | 1460.06 | 2672.57 |

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**P68**

# SYNTHESIS AND ANTIFUNGAL PROPERTIES OF NEW COPPER (II) COMPLEXES WITH N-CYCLOHEXYL-2-[(PYRIDIN-2-YL) METHYLIDENE]HYDRAZINE-1-CARBOTHIOAMIDE

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Thiosemicarbazone derivatives have attracted considerable attention in the past few decades, because of their potential physical, chemical, and biological properties. The heterocyclic NNS ligands play an important role in the development of coordination chemistry as they readily form complexes with most of metal ions.

The first studies of coordination compounds of N-cyclohexylthiosemicarbazones with biometals were carried out by American researcher Douglas X. West who reportedabout this synthesis.Attention has been focused on pyridin-2-yl thiosemicarbazones, particularly on their coordination compounds with biometalsregarding biological properties such as antibacterial, antiparasitic and antitumoral [1].

N-cyclohexyl-2-[(pyridin-2-yl)methylidene]hydrazine-1-carbothioamide (HL) was synthesized according to the literature method [2] with some adjustments, resulting in a good yield. The condensation was performed by stirring (and warming) a solution of cyclohexylthiosemicarbazide (prepared by gently refluxing an excess of hydrazine monohydrate with cyclohexylisothiocyanate in ethanol) with 2-formylpyridine. The reaction was catalyzed by 3 drops of glacial acetic acid.All organic compounds were confirmed by thin layer chromatography, melting point, FTIR spectra and nuclear magnetic resonance $^1$H and $^{13}$C spectra.All complexes were synthesized by refluxing HL with the corresponding copper salt in ethanol in a molar ratio of 1:1. The obtained compounds were analyzed by FTIR spectroscopy and based on the results the substituted thiosemicarbazone coordinates through azomethine-N, pyridine-N, and thiolato-S.

**Table.** Antifungal activity of Cu (II) coordination compounds

| Compound | *Candida albicans* | | *C.parapsilosis* | | *C.krusei* | | *Cryptococcus neoformans* | |
|---|---|---|---|---|---|---|---|---|
| | MIC μg/mL | MBC μg/mL | MIC μg/mL | MBC μg/mL | MIC μg/mL | MBC μg/mL | MIC μg/mL | MBC μg/mL |
| Cu(L)Cl | 1.95 | 31.25 | 1.95 | 7.81 | 0.97 | 1.95 | 0.03 | 0.03 |
| Cu(L)$CH_3COO$ | 15.62 | 31.25 | 15.62 | 31.25 | 15.62 | 31.25 | 0.06 | 0.06 |
| Cu(L)$NO_3$ | 0.48 | 15.62 | 0.97 | 1.95 | 0.97 | 3.90 | 1.95 | 1.95 |
| Cu(L)$ClO_4$ | 1.95 | 31.25 | 3.90 | 7.81 | 0.97 | 7.81 | 3.90 | 3.90 |
| Nystatin | 32.00 | 64.00 | 32.00 | 64.00 | 32.00 | 64.00 | 32.00 | 64.00 |

*Conclusion:* Four new copper (II) complexes with N-cyclohexyl-2-[(pyridin-2-yl)methylidene] hydrazine-1-carbothioamide (HL) have been synthesized. The complexes were found to be active against fungi, all compounds exhibitinhibit in the range of 0.03-15.62 μg/mL which is 2-1067 times more active than Nystatin.

**Acknowledgments.** This work was fulfilled with the financial support of the Institutional Project 15.817.02.24F.

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**P69**

# HYDROGEN-BONDED COMPLEXES CONSTRUCTED FROM HEXAMMINOCOBALT(III) CATIONS AND 4-SULFOBENZOIC DIANIONS

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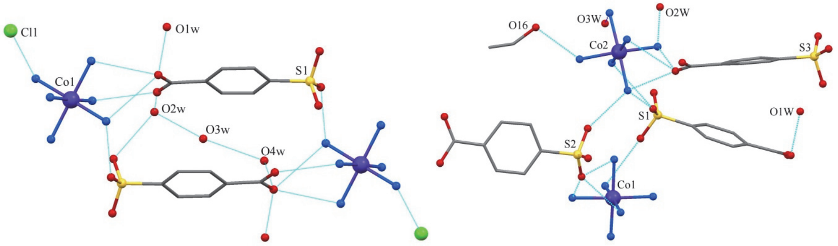
Cobalt(III) coordination compounds showed remarkable biological activities and found applications as antiviral and antibacterial agents [1]. Two new Co(III)-containing compounds $[Co^{III}(NH_3)_6]Cl(L)\cdot4H_2O$ (**1**) and $[Co^{III}(NH_3)_6]_2(L)_3\cdot EtOH\cdot3H_2O$ (**2**) have been obtained from the reaction of $[Co^{III}(NH_3)_6]Cl_3$with 4-sulfobenzoic acid potassium salt ($H_2L$) in the presence of triethanolamine in mixture of EtOH and $H_2O$ (1:1) under solvothermal (**1**) and ultrasonic (**2**) treatment. The compounds have been characterized by a single-crystal X-ray diffraction studies and IR spectroscopy.

The IR spectra of the synthesized compounds showstrong and broad bands at 1591 $cm^{-1}$ and 1544 $cm^{-1}$ corresponding to the asymmetric and symmetric stretching vibrations of the deprotonated carboxylic group of the 4-sulfobenzoic acid. The asymmetric and symmetric C–H stretching vibrations were localized in the regions of 2989 –2854 $cm^{-1}$. The hydroxyl groups of solvent EtOH and $H_2O$ molecules as well as vibrations of $NH_3$ groups result in broad bands 3500 –3251$cm^{-1}$. The stretching vibrations (asymmetric/symmetric) of sulfonic groups in both compounds are founded in the region of 1394 – 1331 $cm^{-1}$ and 1174 – 1143 $cm^{-1}$, respectively.

Compound **1** crystallizes in triclinic $P\bar{1}$ space group, $a$ = 7.652(1), $b$ = 10.243(1), $c$ = 13.028(1) Å, $\alpha$ = 76.309(5), $\beta$ = 85.404(6), $\gamma$= 87.888(5)º, $V$ = 988.8(1) $Å^3$; where as compound **2** crystallizes in monoclinic $P2_1/n$ space group, $a$ = 13.538(2), $b$ = 25.260(3), $c$ = 13.727(2)Å, $\beta$=112.56(2)º, $V$=4435(1)$Å^3$. The asymmetric unit in the structure of **1** contains $[Co^{III}(NH_3)_6]^{3+}$ cation, $Cl^-$ anion,4-sulfobenzoicdianions ($L^{2-}$) and four water molecules, while the compound **2** involves two $[Co^{III}(NH_3)_6]^{3+}$ cations, three $L^{2-}$ anions, solvate ethanol, and three water molecules. In the crystal structures the deprotonated carboxylic and sulfonic groups are involved in 3D hydrogen bonding network between the complex cations and anions as well as with solvent EtOH and water molecules, Figure 1.



a b

**Figure 1.** Fragments of the structure of **1** (a) and **2** (b).

**Acknowledgments.** This work is supported by the Science and Technology Center in Ukraine and the National Agency for Research and Development of the Republic of Moldova (17.80013.8007.10/6245STCU).

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**P70**

# SYNTHESIS OF POLYMER COMPOSITES CONTAINING ZnO DOPED Ag PARTICLES FOR PHOTOCATALYTIC DEGRADATION OF ORGANIC DYES

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In recent years many efforts have been made to use sunlight for energy production, water purification and environmental protection, in which photocatalysis plays a crucial role. Photocatalysis is a potential new method capable of eliminating relatively stable organic compounds. This method is based on the production of electron hole pairs by irradiation with light sources, of a semiconductor material such as transitional metal structures dispersed in an aqueous solution. In the last century, many scientists felt that irradiation was a faster way for catalyzing a reaction, compared to a chemical reaction. Nowadays, the increased pollution of water bodies by chemicals and wastewater treatment has become the most important crisis, because large quantities of synthetic pollutants are continually discharged into our environment [1–3]. For this reason, it is necessary to remove these chemicals from wastewaters before their discharges to water sources. Among different strategies applied photocatalysis is an efficient route for the reduction of these organic pollutants [4,5]. Among various semiconductors, ZnO is the second most popular photocatalyst with cheap price, high stability, and also nontoxic. However, this type of semiconductor suffers some limitations such as poor visible-light response and fast recombination rate of the produced electron hole pairs [6]. To overcome these issues, the fabrication of heterojunction between this semiconductor and other semiconductors possessing high photosensitivity to visible light has been proposed to improve the photocatalytic performance of ZnO [7]. In this study, ZnO doped Ag has been successfully synthesized and characterized (SEM, TEM, XRD) then incorporated in a photopolymerized matrix to be tested by the determination of photocatalytic degradation of an organic dye solution.

**Acknowledgements.** This work was supported by a grant of Ministery of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P1-1.1-PD-2016-1718 (36/2018), within PNCDI III.

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**P71**

# HEPTANUCLEAR IRON(III) PIVALATE BASED ON TOLUYLDIETHANOLAMINE

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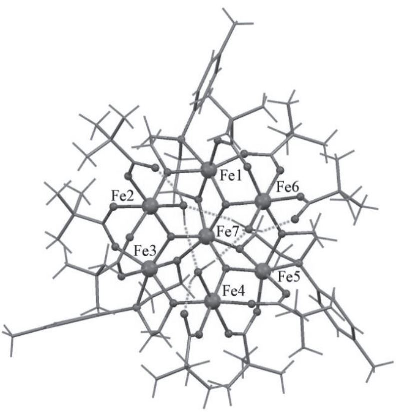
Magnetic clusters with odd number of metal ions attract attention as promising molecular magnetic material for current and future applications. Phenomenon of spin frustration may lead to uncompensated magnetic moment in such systems.

Herein we report synthesis and structural characterization of new heptanuclear iron compound based on pivalic acid (*Hpiv*) and toluyldiethanolamine (*tdeaH$_2$*) ligands, namely [$Fe_7O_3$(piv)$_9$(tdea)$_3$($H_2O$)$_3$] (**1**). The compound **1** was obtained by ultasonication of acetonitrile solution of μ-oxo trinuclear iron pivalate cluster and *tdeaH$_2$* ligand.



Structure of **1**

Single crystal X-ray diffraction analysis revealed that this compound crystalizes in triclinic $P\bar{1}$ space group with $a$ = 12.2843(2); $b$= 15.6151(7); $c$= 28.582(2) Å; $\alpha$ = 97.321(4)°; $\beta$ = 97.194(3)°; $\gamma$ = 100.278(3)°; $V$ = 5288.7(3) Å$^3$. The inorganic core of **1** consists of seven Fe(III) atoms linked by three $\mu_3$-$O^{2-}$ atoms. Six bridging pivalate moieties, three bridging double deprotonated *tdea$^{2-}$* ligands, three pivalate ligands with a monodentate coordination and three terminal water molecules completed the coordination spheres of Fe atoms. Six peripheral metal atoms reside in the vertexes of trigonal antiprism with one base (Fe1, Fe3, and Fe5) capped by Fe7 atom, which is displaced on 0.308 Å from this base.

Compound **1** possesses $C_3$ molecular symmetry. All metals centers are hexacoordinated, revealing a distorted octahedral $O_6$ or $NO_5$ coordination polyhedrons. Atom Fe(7) is coordinated by three $\mu_3$-$O^{2-}$ions and three oxygen atoms from three *tdea$^{2-}$* ligands, each of atoms Fe(1), Fe(3) and Fe(5) reveals $NO_5$ coordination surrounding made up by one $\mu_3$-$O^{2-}$anion, two O atoms and one N atom from a *tdea$^{2-}$* ligand, and two O atoms from two bridging pivalates ligands. The atoms Fe(2), Fe(4) and Fe(6) of the second base of antiprism reveal $O_6$ donor set derived from one $\mu_3$-$O^{2-}$anion, one O atom from the monodentate pivalate ligand, one O atom from the branch of *tdea$^{2-}$* ligand, two O atoms from two bridging pivalates, and one O atom from a water molecule. The shortest Fe…Fe distances 2.982(1)-2.986(1) Å were found between Fe(7) and iron atoms from the base it capped, the distances between Fe(7) and iron atoms from the another base or between irons atom of different bases are in the range 3.244(1) – 3.580(1) Å. The Fe…Fe distances in the bases of antiprism are essentially longer and fit in the interval 5.008(1)-5.162(1) Å. The coordinated water molecules form strong intramolecular hydrogen bonds (O-H…O 2.546-2.568 Å) with non-coordinated oxygen atoms of monodentate pivalate ligands and weaker H-bonds (O-H…O 2.991-3.139 Å) between themselves.

**P72**

# SYNTHESIS AND CRYSTAL STRUCTURE OF Cu(II) COORDINATION COMPOUND WITH BIS-THIOSEMICARBAZONE OF 2,6-DIFORMYL-4-METHYLPHENOL

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Transition metal complexes with ONS donor Schiff bases are of particular interest due to their unusual configurations, structural lability, interesting magnetic properties and use as functional materials. Many d-metal complexes of aromatic Schiff bases are described as catalysts due to their sensitivity to molecular environments [1].

Here we report the synthesis of a new tetranuclear coordination compound of copper(II), using bis-thiosemicarbazone of2,6–diformyl-4-methylphenol ($H_3L$) as a chelating ligand. The Schiff base ligand ($H_3L$) was synthesized by the method described in literature [2].

The Cu(II) coordination compound with the composition $[Cu_4(L)_2(DMSO)_2(H_2O)_2]SO_4$have been investigated by IR, TGA, and X-ray crystallography.

According to single–crystal X-ray diffraction studies, the core of this coordination compound is formed by a slightly distorted cubic tetranuclear cluster. The triply deprotonated ligand molecules adopt a planar conformation, using for coordination a S-O-S donor set of atoms (Figure).

The DMSO molecules were neither coordinated to metal ions nor hydrogen bonded to the ligand.

The complex $[Cu_4(L)_2(DMSO)_2(H_2O)_2]SO_4$ crystallizes in P-1 space group, with the following unit cell parameters: $a$=12.2571, $b$=14.4261, $c$=15.6373 Å and α = 92.679(15), β=107.796(16) and γ=115.140(15) °.

Thermogravimetric and magnetic investigations of this compound will be also discussed.

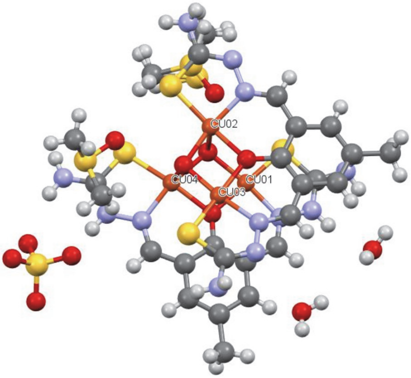

**Figure.** The structure of $[Cu_4(L)_2(DMSO)_2(H_2O)_2]SO_4$

**Acknowledgments**
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**P73**

# Ln(III)-Bi(III) COORDINATION COMPOUNDS AS MOLECULAR PRECURSORS FOR $LnBiO_3$ MIXED OXIDES

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The synthesis of inorganic materials upon thermal treatment of coordination compoundsis a convenient pathway for getting desired nano-products in pure form and of controlled morphology [1]. Considering the features in the chemistry of lanthanides (Ln) that differentiate themfrom the *d*-block metals, the design and development of suitable complexes that can be used as precursors is challenging from a synthetic point of view [2]. The problem is getting even more complicated when heterometallic Ln(III)-Bi(III) coordination compounds have to be obtained due to high hydrolysis tendency of Bi(III). Aminopolycarboxylates (APC) proved to be suitable chelating agents for assembling these two metals of a desired ratio within one molecule [3, 4].

Considering all these, the work wasfocussedon the synthesis and investigation of Ln(III)-Bi(III)-APC coordination compounds as molecular precursors for the preparation of $LnBiO_3$ mixed oxides (APC = aminopolycarboxylate; Ln(III) = La, Pr, Nd, Gd, Dy, Ho, Er).

For this purpose, seven complexes of rare-earth metals with Bismuth(III), having the metals ratio 1:1, were synthesized using triethylenetetraaminehexaacetate ($ttha^{6-}$) as polydentate ligand. The compositions of the complexes were determined based on the results of the element analysis, IR spectroscopy and thermogravimetry.

The results of IR spectroscopy revealed the presence of two series of isostructural complexes, namely $LnBi(ttha)\cdot 7H_2O$ (Ln(III) = La, Pr, Nd, Gd, Dy) and $LnBi(ttha)\cdot 10H_2O$ (Ln(III) = Ho, Er). The IR spectra of the compounds from each row are practically identical but different between the two series.

Thermogravimetric analysis performed at $10^{o}C\cdot min^{-1}$ heating rate, both in nitrogen and oxygen atmospheres, revealed the presence of three consecutive decomposition steps of the precursors: dehydration, organic ligand thermolysis and formation of inorganic residues as a result of decarboxylation.The residual mass, at already $600^{o}C$, for the decomposition under oxygen is in good agreement with the formation of the expected $LnBiO_3$ mixed-oxide, while the process is not complete even at $850^{o}C$ under nitrogen flow.

Two different heating rates, $10^{o}C\cdot min^{-1}$ and $0.5^{o}C\cdot min^{-1}$, have been applied during decomposition aiming at establishing the optimal thermal regime for getting pure $LnBiO_3$ heterometallic oxides. Though, the gravimetric analysis at $10^{o}C\cdot min^{-1}$ demonstrated that the masses of the residues are slightly higher than for the expected $LnBiO_3$, powder X-ray diffraction results confirmed the formation of pure mixed-oxides for both heating rates.

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**P74**

# SYNTHESIS AND ANTIMICROBIAL PROPERTIES OF NEW COPPER (II) COMPLEXES WITH BENZOATE OF ETHYL 4-({2-[(PYRIDIN-2-YL)METHYLIDENE]HYDRAZINECARBOTHIOYL}AMINO)

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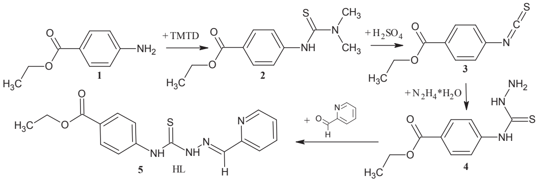
Throughout history, it has been a major worldwide problem to treat microbial diseases caused by bacteria due to the impetuous development of resistance to antibacterial drugs. Thiosemicarbazones have been investigated for medicinal studies for a long while due to their wide range of biological activities including antineoplastic, antimycobacterial, antibacterial, antifungal, antiviral, and antimalarial effects.

We have synthesized the new thiosemicarbazone(**5**). Ethyl 4-[(hydrazinecarbothioyl)-amino]benzoate (**4**) was obtained according to the following steps. First step: Ethyl 4-aminobenzoate (**1**) reacted with tetramethylthiuram disulfide (TMTD) in a molar ratio 1:1 upon heating in dimethylformamide to form ethyl 4-[(dimethylcarbamothioyl)amino]-benzoate (**2**). In the second step, compound (**2**) was decomposedin 1,4-dioxaneabsolute with sulphuric acid to form ethyl 4-isothiocyanatobenzoate (**3**). Compound (**4**) was obtained by dropping isothiocyanate(**3**) to a solution of hydrazine hydrate in ethanol.Benzoate of ethyl 4-({(2-[(pyridin-2-yl)methylidene]hydrazinecarbothioyl}amino)(**5**) (HL) was obtained from the reaction between compound **4** and formylpyridine in ethanol. The reaction mixture was refluxed for 6 h. Its purity was confirmed by thin layer chromatography, spectroscopy ($^1$H, $^{13}$C-NMR and FTIR). Scheme of synthesis ofHL.



Complexes were synthesisedas is derived here: to a hot solution of HL in ethanol were added corresponding copper salts in proportion 1:1. The mixture was heated at reflux for 1 h. Complexes precipitated as dark green crystalline solid, and collected by filtration, washed thoroughly with ethanol and then dried in air. The obtained complexes were analyzed by using FTIR spectroscopy and metal analysis. Five copper complexes (II) have been tested on antimicrobial activity. The best results were recorded ongram-positive bacteria *Staphylococcus aureus* by CuLCl.

| Sample | *Staphylococcus aureus* | | *Acinetobacterbamannii* | | *E.coli* | |
|---|---|---|---|---|---|---|
| | MIC µg/mL | MBC µg/mL | MIC µg/mL | MBC µg/mL | MIC µg/mL | MBC µg/mL |
| CuLCl | 0.12 | 0.24 | 62.5 | 125.0 | 250.0 | 500.0 |
| CuLBr | 0.48 | 0.97 | 62.5 | 125.0 | 31.25 | 62.50 |
| $CuLNO_3$ | 0.24 | 0.48 | 125.0 | 250.0 | 125.0 | 250.0 |
| $CuLCH_3COO$ | 0.24 | 0.48 | 125.0 | 250.0 | 250.0 | 500.0 |
| $CuLClO_4{\cdot}H_2O$ | 0.48 | 0.97 | 125.0 | 250.0 | 250.0 | 500.0 |
| Furacillinum | 4.67 | 9.35 | - | - | 4.67 | 4.67 |

**P75**

# POROUS COMPOSITES MADE OF POLYMER/INORGANIC FRAMEWORKS APPLIED AS DESICCANTS FOR AIR DEHUMIDIFICATION

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The dehumidification of air stream moisture in closed environments can be realized by the use of super adsorbent materials with high capacity for water uptake [1]. The transport in a selective fashion of water molecules across porous materials enables to reduce the humidity of an air stream. The application of such materials has the advantage over many commercially available desiccants. Because such materials are nontoxic and can absorb water molecules, allowing the independent control of the humidity. Therefore, it is essential to develop new super adsorbent materials for air dehumidification. For example, a technical solution proposed in this study deals with the producing of a specific super adsorbent matrix based on polymer-molecular sieves composites. In this respect, polymers were deposited onto the rigid structure of different molecular sieves yielding the composite structured networks with synergistic properties. According to the theoretical screening, such composites may be used (for water uptake) as efficient desiccants alternative to other available adsorbents. Moreover, the efficiency of these materials was proved by water adsorption experiments. In summary, the polymer-inorganic composites are important for controlling air dehumidification process.

## Acknowledgments

The authors thank the Grant of the Ministry of Research and Innovation, RDI Program for Space Technology and Advanced Research - ROSA-STAR, project number 157/2017, for the financial support.

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**P76**

# THE STUDY OF THE CHEMICAL INTERACTION OF CONTAINER TRANSPARENT COLORLESS GLASS WITH HYDROGEN FLUORIDE

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Thermochemical treatment of industrial glassware fordifferent purposes with fluorine– and chlorine–containing gaseous reagents increases their water resistance tenfold, while its mechanical strength is increased by 20-30 %, thermal resistanceand microhardness - by 10-15 % [1-2].

The aim of the undertaken experiments was to investigatethe nature of chemical interaction of container transparent colorless glass with hydrogen fluoride. Objects of investigation were bottles, jars and flasks made from transparent colorless glass. Different concentrations of hydrogen fluoride solutions were used for thermochemical treatment of glass samples. Thermochemical treatment of glass samples with hydrogen fluoride was held in laboratory and industrial conditions.

The main regimes of thermochemical treatment of glass samples in laboratory experiments are the following: temperature – between 300 to $600^0$C; quantity of hydrogen fluoride introduced into the reacting vessel - between 0.01 and 0.10 mol; duration – between 1 s and 15 min. The regimes of treatment of glass containers on processing lines: temperature - between 500 and $600^0$C, volume of hydrogen fluoride per one unit of glassware - between 0.05 and 5.00 mL, duration - between 1 and 5s.

The thermochemical treatment ofsample surface and glassware with hydrogen fluoride resulted in the formation of reaction products of different intensity. A comprehensive analysis showed that the thermochemical treatment of container transparent colorless glass with hydrogen fluoride formed reaction products containing sodium, potassium and calcium fluorides.

In laboratory experiments dealkalization of container transparent colorless glass with hydrogen fluoride increases its water and acid resistance several times, microhardness being increased by 10-15 %.

In industrial conditions, the chemical resistance of glassware isimproved by dealkalizing its surface layers with hydrogen fluorideand modifying the glass structure without extraction of sodium, potassium and calcium cations. In the second case, it seems, there is a substitution on the glass surface of the $OH^-$ groups and part of the most active bridged oxygen anions by the $F^-$ anions, thus preventing the formation of the weakest ≡Si–OH bonds.

The experiment helped to develop optimal regimes of thermochemical treatment of glass containers (bottles, jars and flasks) subjected to hydrogen fluoride in laboratory and industrial conditions.

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**P77**

# FEATURES OF USING HF-SECTIONING METHOD TO ANALYZE THE COMPOSITION AND STRUCTURE OF SURFACE LAYERS OF INDUSTRIAL GLASSES

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The aim of the undertaken experiments was to study the features revealed by the use of HF-sectioning method to analyze the composition and structure of surface layers of industrial glass for various purposes.

The essence of the HF-sectioning method consists in successive dissolution of surface layers of glass with a weak concentration of HF solution and subsequent analysis of the obtained extracts. Objects of investigation were various types of industrial glassware: containers (jars, bottles and flasks) of transparent colorless glass, bottles and flasks of green glass, illuminating and assorted glassware made from transparent colorless and milk glasses, ampoules made from medical glass and samples of sheet glass. The chemical composition of glasses, the conditions for glass melting and glassware molding for various purposes differ from each other.

We have developed a technique for HF-sectioning of samples of industrial glass of various compositions and forms. Not less than three samples were subject to etching at a time. The samples were rotated in HF solution, or kept in a stationary position. After the etching, the samples were washed with distilled water, dried, cooled and weighed with a microanalytical balance. The samples were weighed before and after etching, the mass loss of the glass dissolved in HF solution was determined, and then the thickness of the dissolved layer and glass dissolution rate in HF solution were measured. The concentration of $Na^+$, $K^+$, $Ca^{2+}$and $Mg^{2+}$ was measured in extracts after etching with the help of flame photometry.

To analyze the data obtained, we made graphs displaying the dependence of dissolution rate on the thickness of the etched layer of glass. In our experiments, the thickness of the glass layer dissolved in one etching ranged from 0.05 to 10.0 μm and the duration of one etching varied from 2.5 to 60 minutes.

We have found that the dissolution rate depends on many factors: on the composition and structure of glass; on homogeneity of samples; concentration, volume and temperature of the HF solution, hydrodynamic conditions, *etc.*

The following features of HF-sectioning of industrial glass have been revealed:

1. The graphs of the dissolution rates of all types of industrial glasses are unstable, due to their heterogeneous structure.
2. The opportunity to analyze the surface layers of glass with a thickness of 0.05 to 100 μm or more is bigger.
3. Poor reproducibility of the dissolution rate of industrial glasses for samples that are part of the same series.
4. While calculating theglass dissolution rate and the thickness of the etched layer, an error is to be introduced due to the assumption that the density of glass in the entire volume of the sample is the same. In fact, the density of the near-surface layer of glass differs from the density of the bulk of the sample.
5. The composition and structure of the outer and inner parts of the near-surface layers of the sample of hollow glassware (jars, bottles, flasks, *etc.*) are not the same.

**P78**

# CRITERIA FOR REVEALING STRUCTURAL CHANGES IN INDUSTRIAL GLASSWARE TREATED BY ELECTROMAGNETIC FIELDS

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The effect of electromagnetic fields on molten glass and newly-formed hot industrial glassware has been studied to a lesser extent. To increase the mechanical strength of glass containers in industrial conditions, Bulgarian scientists resorted totreatment with electromagnetic fields [1-2]. Depending on the regime of thermomagnetic treatment, the minimum mechanical strength of bottles increased by 1.5-2 times.

The aim of the undertaken experiments was to develop the criteria necessary to reveal the structural changes in industrial glassware for different purposes subjected to treatment with electromagnetic fields.

Objects of experiment were containers (jars, bottles and flasks) of transparent colorless glass, bottles and flasks of green glass, illuminating and assorted glassware made from transparent colorless and milk glasses,ampoules made from medical glassand samples of sheet glass.The samples of glass and glassware were exposed to constant, alternating and pulsed magnetic fields. Thermomagnetic treatment of glass samples was conducted in laboratory and industrial conditions.

Parameters of thermomagnetic treatment of glass samples in laboratory conditions are: value of vector's magnitude of the magnetic induction - up to 0.15 T, temperature – between 300 and 600°C, duration – between 1 and 300 s. The main regimes of magnetic treatment of the newly-formed glass containers in industrial conditions are: temperature – between 500 and 550°C, the value of vector's magnitude of magnetic induction – up to 0.22 T, duration – between 1 and 4 s. Jars, bottles and flasks were subjected to the influence of magnetic fields just after molding being transported into lehrs. Glass containers subjected to treatment did not require any special caution measures.

On the basis of the experiments performed, the following criteria to reveal structural changes in industrial glassware for different purposes, treated with electromagnetic fields have been identified:

1) reducing the etching rate with a HF solution of glass samples subjected to thermomagnetic treatment;

2) increasing the microhardness and mechanical strength of glass after thermomagnetic treatment.

With the increase of temperature, the value of vector's magnitude of the magnetic induction, the duration of thermomagnetic treatment, the resistance of industrial glasses to the effects of HF solution, as well as their microhardness and mechanical strength increase.

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**P79**

# MONONUCLEAR DYSPROSIUM(III) COMPLEX EXHIBITING MAGNETIC RELAXATION

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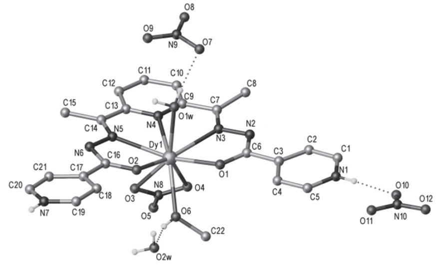
Lanthanides, thanks to their large ground-state spin and intrinsic magnetic anisotropy, are promising candidates for applications in the design of magnetic material. It is known that 2,6-diacetylpyridine is an excellent precursor for the synthesis of planar pentadentate ligands, thus promoting the formation of complex compounds with a rigid pentagonal-equatorial plane and with kinetically labile coordinating ligands at the apical sites.

Herein a mononuclear complex $[Dy(H_2L)(MeOH)(H_2O)(NO_3)](NO_3)_2 \cdot H_2O$ (**1**), which is obtained from the reaction of Dy(III) nitrate and 2,6-diacetylpyridine *bis*(isonicotinoylhydrazone) is reported. Complex **1** was characterized by IR spectroscopy and single crystal X-ray crystallography. A strong band at 1663 $cm^{-1}$ in the IR spectrum of the ligand $H_2L$ was shifted to 1635 $cm^{-1}$ and decreased in intensity, which may be the result of the C = O bond elongation and the coordination of the oxygen atom. The behaviour of the absorption band ν(NH), which is observed in the ligand spectrum at 3184 $cm^{-1}$, could not be observed due to the very high intensity bands assigned to the ν(OH) absorption of the $CH_3OH$ and $H_2O$ coordinated molecules. The band at 1591 $cm^{-1}$ attributed to the ν (C = N) vibration of the ligand is also shifted to lower energy in the complex (1549 $cm^{-1}$), indicating coordination of the nitrogen atom of the azometine bond.

Single-crystal X-ray analysis revealed that the asymmetric unit of $[Dy(H_2L)(MeOH)(H_2O)(NO_3)](NO_3)_2 \cdot H_2O$ (Figure) consists of the DyN3O2 entity in which the neutral pentadentate ligand $H_2L$ coordinates through the pyridine nitrogen atom, the hydrazonic nitrogen atoms and both oxygen atoms of the amide groups. The analysis of bond lengths in the −NH−C(=O)− fragment shows that the electrons from the deprotonation of the amido group are delocalized and form a conjugated system, and the two protons are attached to the nitrogen atoms of the pyridine ring. The Dy(III) ion is nine-coordinate due to bonded water and methanol molecules, and bidentate nitrate ion. Two nitrate ions in the outer sphere compensate the double charge of complex cation.



Magnetic AC measurements have shown that Dy(III) complex **1** exhibits two maxima of "out-of-phase" susceptibility. This observation is the sign of a slow relaxation of magnetism, and is often called field-induced SMM behaviour.

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**P80**

# Co(II, III) IZOBUTYRATES BASED ON TRIETHANOLAMINE AS BIOSTIMULATORS OF THE MICROORGANISM ENZYMESYNTHESIS

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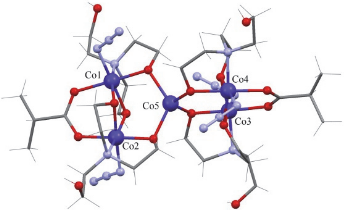
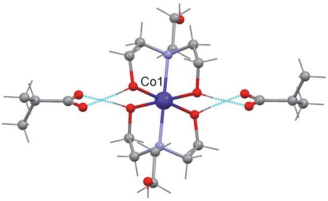
Coordination compounds of 3d metals revealexcellent catalytic activities and the past years investigations show that the complexes play an important role in the directed synthesis of biologically active substances, including enzymes of microorganism.

Two new coordination compounds, namely pentanuclear $[Co^{II}Co^{III}_4(is)_2(H_3tea)_4(N_3)_4]\cdot 1.5(H_2O)$ (**I**) and mononuclear $[Co^{II}(H_3tea)_2](is)_2$ (**II**), have been prepared by the reaction of cobalt(II) isobutyrate is with triethanolamine ($H_3tea$) in the presence of sodium azide in MeCN, and characterized by IR spectroscopy and X-ray analysis (Figure). The biological properties of these complexes have been tested for their ability to increase the biosynthesis of enzymes. The addition of **I** and **II** to the nutrient medium of *Rhizopusarrhizus* CNMN FD 03 micromycete in concentration of 5 and 10 mg/L increases biosynthesis of lipases on 43.5…78.3% (**I**) and 15.5…43.5% (**II**), depending on the applied concentration and duration of cultivation of the microorganism (Table). Our present results show that the carboxylate-triethanolamine containing compounds **I** and **II** can been used as biostimulators of the microorganism enzyme synthesis in various biotechnological processes.



**I**



**II**

**Table.** The influence of **I** and **II** on lipolytic activity (U/mL) of *Rhizopus arrhizus CNMN 03* micromycete

| Compound | Concentration, mg/L | 1day | | 2 days | | 3 days | |
|---|---|---|---|---|---|---|---|
| | | U/mL | %, to control | U/mL | %, to control | U/mL | %, to control |
| **I** | *5* | 48563 | 160.9/ 123.9 | 43160 | 110.0 | 39375 | 203.9 |
| | *10* | **53812** | **178.3**/ 143.5 | **62720** | **160.0** | **42187** | **218.4**/ 113.5 |
| | *15* | 38062 | 126.1 | 41250 | 105.0 | 39375 | 203.9 |
| **II** | *5* | 35437 | 117.4 | 56250 | 150.0 | 22500 | 116.5 |
| | *10* | **43312** | **143.5**/ 115.5 | **62720** | **160.0** | 39375 | **203.9**/ 105.0 |
| | *15* | 31500 | 104.3 | 52200 | 133.9 | 22500 | 116.5 |
| Control | - | 30188 | 100.0 | 39200 | 100.0 | 19096 | 100.0 |

**P81**

# DINUCLEAR *CIS*-DIOXIDOVANADIUM(V) COMPLEX CONTAINING HEXAAQUASODIUM CATION AS COUNTERION

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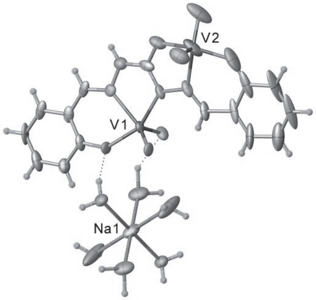
The coordination chemistryof vanadium, in particular compounds containing $VO_2^+$ ions, are of considerable interest because of their association with vanadium-dependent enzymes (eg, nitrogenase, haloperoxidase, phosphomutase, etc.). It was necessary to synthesize functional compounds for the detailed study of the structure and the chemical, and medical properties of these enzymes. (Thio)carbohydrazone ligands have a versatile coordinationability due to the presence of several donor centers, and tend to stabilize vanadium in its maximum oxidation states. Carbohydrazone based vanadium(V) complexes were previously applied as alternative selective homogeneous catalysts for the industrially significant oxidation of cyclohexane tocyclohexanol and cyclohexanone [1].

Herein a binuclear complex $[Na(H_2O)_6][(VO_2)_2(HL)]$ (**1**), obtained from the reaction of $VO(acac)_2$ and 1,5-bis(2-hydroxybenzaldehyde)carbohydrazone($H_4L$) in the presence of $Na_2CO_3$, is reported. Complex **1** was characterized by IR spectroscopy and single crystal X-ray crystallography. Spectral IR analysis of compound **1** showed the following: the very intense band in the 3700-3000 cm$^{-1}$ region with a maximum of 3330 cm$^{-1}$ is assigned to $H_2O$, its broadened character being associated with multiple hydrogen interactions; other characteristic vibrations ν(C=O) and ν(C=N) appear as intense bands with maximums at approx. 1600 and 1558 cm$^{-1}$, respectively. As expected, these bands in compound **1** are shifted compared to those of the $H_4L$ ligand; the intense and wide band ν(V=O) at 885 cm$^{-1}$ supports the presence of *cis*-$VO_2$ groups.



According to the crystallographic data the asymmetric unit of complex **1** consists of the complex dinuclear anion $[(VO_2)_2(HL)]^-$ and the $[Na(H_2O)_6]^+$ cation. The triple-deprotonated hexadentate ligand $HL^{3-}$accommodates two V(V) atoms in the form of $VO_2^+$ entities by means of the two sets of donor atoms ONO and NNO. V1 and V2 atoms are five-coordinate and use *cis*-oxo ligands to complete their coordination sphere. The bond lengths in the carbohydrazide moiety indicate that the ligand adopts the enol tautomeric form. The hexaaquasodium cation in this complex, besides charge balancing, plays a more important role. Thus, in the solid state, the obtained compound has an extensive oligomeric structure, involving an alternative arrangement of *cis*-dioxidovanadium(V) anionic units $[(VO_2)_2(HL)]^-$ and $[Na(H_2O)_6]^+$, held together by strong electrostatic interactions and hydrogen bonds, as determined by X-ray crystallographic analysis.

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**P82**

# DETERMINATION OF SURFACE GROUPS ON ACTIVATED CARBONS BY BOEHM AND POTENTIOMETRIC TITRATIONS

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The surface chemistry of activated carbons determines their moisture content, catalytic properties, acid–base character, and adsorption of polar species [1]. It is related to the presence of heteroatoms (oxygen, nitrogen, phosphorus, chlorine, sulfur *et al.*) other than carbon within the carbonaceous matrix.

In this study, activated carbons of local origin (Republic of Moldova) from the apple wood (CA-M) and nut shells (CA-N) were oxidized with nitric acid (sample CA-Mox) and mixture of nitric acid/urea (samples CA-Mox-u and CA-Nox-u) in order to improve their ion-exchange properties. The surface chemistry was characterized by using Boehm and potentiometric titration methods [2, 3]. Additionally, the ash and metals content in studied samples were determined as well as.

Obtained results showed that oxidation introduces a variety of functional groups to the surface, making it more heterogeneous (Table and Figure). There are some discrepancies in the obtained results, which may be attributed to the limitations of the Boehm titration method.

***Table.*** *The quantity and character of functional groups (mmol/g) on the surface of active carbons, determined by the Boehm method*

| Sample | Carboxylic | | Phenolic | Basic |
|---|---|---|---|---|
| | Strong acidic | Strong acidic | | |
| *CA-N* | 0.02 | 0.05 | 0.22 | 0 |
| *CA-M* | 0 | 0.35 | 0.74 | 2.25 |
| $CA\text{-}N_{ox\text{-}u}$ | 0.32 | 0.22 | 0.32 | 0 |
| $CA\text{-}M_{ox\text{-}u}$ | 0.44 | 0.33 | 0.32 | 0 |
| $CA\text{-}M_{ox}$ | 0.95 | 0.83 | 0.12 | 0.75 |

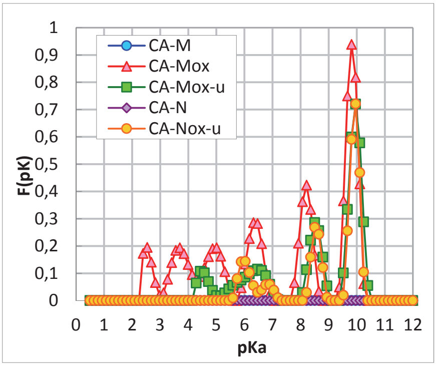

***Figure.*** *Distribution of surface groups F(pK) with respect to the protonation constants pK*

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**P83**

# SYNTHESIS, ANTIMICROBIAL AND ANTIFUNGAL PROPERTIES OF COPPER(II) COORDINATION COMPOUNDS WITH 2,4-DIHYDROXYBENZALDEHYDE 4-ALLYLTHIOSEMICARBAZONE CONTAINING AMINES

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It is known from the literature that copper(II) complexes with salicylaldehyde 4-allylthiosemicarbazone exhibit high antimicrobial activity and the introduction of substituents into the salicylidene fragment leads to a change in antimicrobial activity. The aim of this work is the synthesis of copper coordination compounds of 2,4-dihydroxybenzaldehyde 4-allylthiosemicarbazone ($H_2L$) with 1,10-phenanthroline (1,10-Phen) and 2,2′-bipyridyl (2,2'-Bpy), determination of their composition, structure, physicochemical and biological properties.

The experiments showed that, ethanolic solution of copper(II) acetate reacts with 4-allylthiosemicarbazone $H_2L$ and 1,10-phenanthroline or 2,2′-bipyridyl forming fine-crystalline colored coordination compounds. The composition of these compounds was determined using elemental analysis for C, H, N, Cu: [Cu(1,10-Phen)(L)], [Cu(2,2'-Bpy)(L)].

Single-crystals of these two coordination compounds were obtained as a result of recrystallization from dimethylformamide.

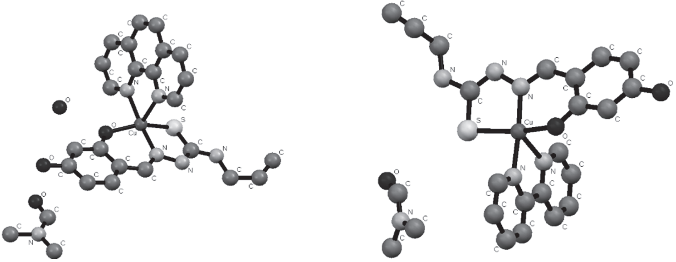

**Figure.** Structure of complexes [Cu(1,10-Phen)(L)]·DMF·$H_2O$ and [Cu(2,2'-Bpy)(L)]·DMF.

The thiosemicarbazone $H_2L$ behaves as double deprotonated tridentate ligand with O,N,S-set of donor atoms and coordinates to the central atom of copper(II) forming five- and six-membered metallocycles. The fourth and fifth coordination position are occupied by nitrogen atoms of 2,2'-Bpy or 1,10-Phen. These compounds have a monomeric structure (Figure).

Synthesized coordination compounds exhibit antimicrobial activity against gram-positive microorganisms *Staphylococcus aureus* in the range 0.49-1.95 µg/mL and antifungal activity in the range 31.25-500 µg/mL.

**Acknowledgements.**This work was fulfilled with the financial support of the Institutional Project **15.817.02.24F**.

**P84**

# A NOVEL COPPER(II) 2D COORDINATION POLYMER CONSTRUCTED OF IMINODIACETIC ACID

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The iminodiacetic acid $NH(CH_2COOH)_2$ ($H_3IDA$)may serve as a polydentate ligand and coordinates to the metal through the oxygen atoms of two carboxyl groups and nitrogen atom. In the known mononuclear and polynuclear complexes of $H_3IDA$ the molar ratio metal: ligand is 1: 1 or 1: 2 [1, 2].

The interaction $Cu(CH_3COO)_2\cdot H_2O$ salt with dianilineglyoxime and $H_3IDA$ resulted in coordination compound with composition $\{[NH_2(CH_3)_2]_2[Cu_3(HIDA)_4]\cdot H_2O\}_n$ which doesn't contain dioxyme. The obtained complex has been studied by X-ray single crystal method.Compound crystallizes in monoclinic $C2/c$ space group, $a$=40.128(3) Å, $b$=9.9510(6) Å, $c$=15.9211(9) Å, $\beta$=105.245(6)°, $V$=6133.8(7) Å$^3$. The structure of compound reveals parallel 2D anionic $[Cu_3(HIDA)_4]_n^{2n-}$layers with 4,4-grid topology, separated by $[NH_2(CH_3)_2]^+$cations and solvate water molecules. The latter are involved in N–H···O and O(w)–H···O hydrogen bonds which linked the layers. The asymmetric part of unit cell comprises three Cu(II) atoms, four bideprotonated organic ligands $(HIDA)^{2-}$, two dimethylammonium cations, and water molecule. The coordination environments are $N_2O_4$for one and $NO_5$ for two other metal atoms. The surrounding of Cu2 is provided by two organic ligands each coordinated by $NO_2$ donor atoms in *fac*-manner and resulted in square-bipyramidal coordination polyhedron. The coordination sphere of two other metal atoms (Cu1 and Cu3) is provided by $NO_2$ donor atoms of one ligand coordinated in *mer*-fashion and bridging or chelate-bridging function of the carboxylic groups of two others ligands involved in coordination to neighboring Cu2 atom (Figure) and resulted in distorted square-bipyramidal coordination environment. Thus, two of symmetry independent ligands are hexa-dentate and coordinate simultaneously to three metal atoms, while two others are tridentate and coordinate only one metal atom.

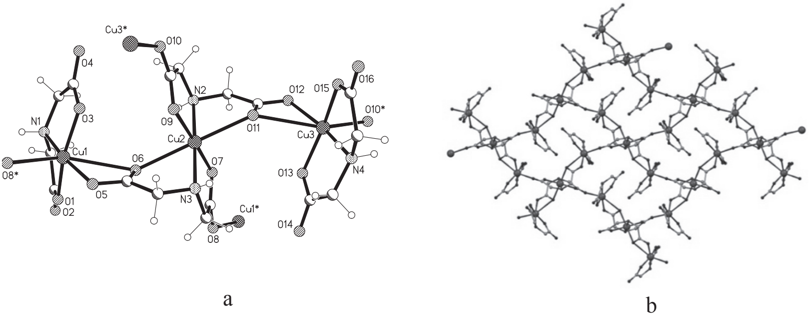

**Figure.** The structure of trinuclear fragment (a) and the anionic 2D polymeric grid (b)

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**P85**

# COORDINATION COMPOUNDS OF SOME 3*d* METALS WITH SALICYLIDENE-4-ALLYL-*S*-BENZYLISOTHIOSEMICARBAZIDE

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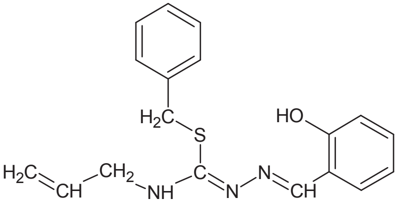
*S*-Alkylisothiosemicarbazones belong to an important class of thiosemicarbazone derivatives. Much attention has been paid to the synthesis, structure and biological properties of coordination compounds with these ligands.

The aim of this work is the synthesis of copper(II), cobalt(III) and iron(III) coordination compounds with salicylaldehyde 4-allyl-S-benzylisothiosemicarbazone (HL), determination of their composition, structure, and physicochemical properties.



HL - salicylaldehyde 4-allyl-S-benzylisothiosemicarbazone

Isothiosemicarbazone HL was synthesized by reaction between 4-allylthiosemicarbazide and benzyl chloride upon heating for 8 hours. After that, salicylaldehyde was added to the reaction mixture. In the final step, the obtained hydrochloride of salicylaldehyde 4-allyl-S-benzylisothiosemicarbazone was neutralized using potassium hydroxide. m.p. (HL) = 63-65 $^0$C.

The structure and purity of the synthesized isothiosemicarbazone HL was confirmed using $^1$H, $^{13}$C NMR spectroscopy and also X-ray analysis. All peaks in the spectra of isothiosemicarbazone HL are double. It indicates the presence of tautomeric forms of isothiosemicarbazone in solution.

The experiments showed that ethanolic solutions of copper(II) chloride, bromide, nitrate and acetate react with salicylidene-4-allyl-S-benzylisothiosemicarbazide (HL) in the molar ratio of the 1:1, forming colored microcrystalline substances. In the case of iron chloride and bromide and cobalt chloride, the reaction takes place in a molar ratio of 1:2.

The molar conductivity values in methanolic solutions show that all synthesized coordination compounds represent 1:1 electrolytes.

The analysis of IR spectra has shown that isothiosemicarbazone HL coordinates to the central atoms by deprotonated phenolic oxygen atom and azomethine and thiocarbamide nitrogen atoms. The structure of the complex $[Fe(L)_2]Br$ was confirmed using X-ray analysis. This compound has a distorted octahedral structure. The isothosemicarbazone behaves as an O, N, N tridentate monodeprotonated ligand and forms five- and six-membered metallocycles. A bromide ion is in outer sphere. The sulfur atom does not participate in the formation of bonds with the central atom.

**Acknowledgements.** This work was fulfilled with the financial support of the Institutional Project **15.817.02.24F**.

**P86**

# SYNTHESIS AND CRYSTAL STRUCTURES OF AMMONIUM SALTS OF COBALT(III) AND COBALT(II) BASED ON DIPICOLINIC ACID

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The interaction of 2,6-pyridinedicarbonyl dichloride (2,6-Py($COCl)_2$) with cobalt(II) nitrate in a solvent mixture of dioxane-dimethylacetamide in the presence of diphenylglyoxime, a new compound was obtained. The structure of this compound was investigated by XRD and shown the conversion of 2,6-Py($COCl)_2$ to a dianion of dipicolinic acid, $(2,6\text{-Py}(COO)_2)^{2-}$, during the reaction *in situ*. The interaction of dipicolinic acid with cobalt(II) nitrate in the same medium in the absence of diphenylglyoxime, but in the presence of ammonium hydroxide resulted in similar compound of Co(III) with formula $NH_4[Co(2,6\text{-Py}(COO)_2)_2]$ (**1**), that crystallizes in tetragonal $I4_1/a$ space group with $a$=7.1181(8) Å, $c$=27.976(1) Å, $V$=1417.5(2) Å$^3$. These crystals comprise the $NH_4^+$ cationsand $[Co^{III}(2,6\text{-Py}(COO)_2)_2]^-$ complex anions (Fig. 1). The bideprotonated dipicolinic ligand $(2,6\text{-Py}(COO)_2)^{2-}$is three-dentate and coordinate to cobalt(III) by ONO donor atoms forming two fused metallocycles.Thus, the coordination polyhedron of metal in **1** is provided by $NO_2$ donor atoms belong two organic ligand that form octahedral surrounding with $S_4$ molecular symmetry. The interatomic distances Co(1)–N(1) and Co(1)–O(1) in coordination polyhedron are 1.844(3) and 1.926(2)Å, respectively.

The interaction of cobalt(II) nitrate and dipicolinic acid in methanol in the presence of dioxane and dimethylacetamide and changing the order of mixing of the components led to the formation the of Co(II) compound with composition $(NH_4)_2[Co(2,6\text{-Py}(COO)_2)_2]\cdot 2H_2O$ (**2**). This compound has been studied by X-ray single crystal method and has been established that it crystallizes in triclinic $P$-1 space group with $a$=10.779(1) Å, $b$=13.480(1) Å, $c$=14.506(2) Å, $\alpha$=64.649(10)°, $\beta$=78.882(11)°, $\gamma$=88.992(8)°, $V$=1864.0(4) Å$^3$. The structure of **2** reveals $[NH_4]^+$ cations, $[Co^{II}(2,6\text{-Py}(COO)_2)_2]^{2-}$ anionic complex, and solvate water molecules (Fig. 2). In **2** the organic ligand is also tridentate, double deprotonated and coordinates to cobalt(II) through the ONO donor atoms as in **1.** The octahedral coordination polyhedron of metal in **2** is similar by **1**. The interatomic distances Co–N and Co–O in two symmetry independent coordination anions are in ranges 2.025(3) – 2.032(3) and 2.140(3) – 2.222(3) Å, respectively.

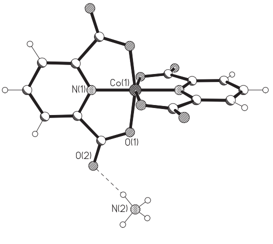

**Fig. 1.** The structure of 1.

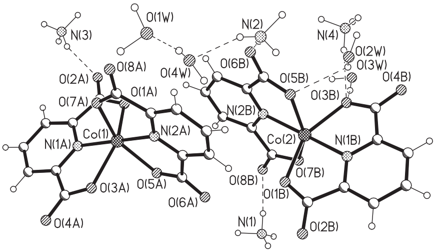

**Fig. 2.** The structure of symmetry independent compound 2.

The cations and anions in **1** are involved in N–H···O hydrogen bonds, and in **2** the components interact by hydrogen bonds N–H···O, N–H···O(w), O(w)–H···O and O(w)–H···O(w).

**P87**

# SYNTHESIS, STRUCTURE AND ANTIOXIDANT PROPERTIES OF BIS-LIGAND COMPLEX OF NICKEL WITH 2-HYDROCHI-3-METHOXIBENZALDEHYDE 4-(2,4-DIMETHYLPHENYL)THIOSEMICRBAZONE

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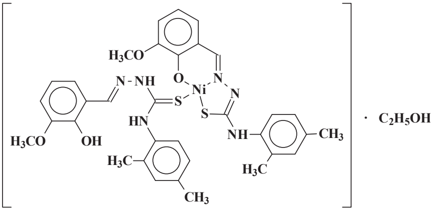
The aim of this work is the synthesis, determination of composition, structure and antioxidant properties of nickel bis-ligand complex with 2-hydroxy-3-methoxybenzaldehyde 4-(2,4-dimethylphenyl)thiosemicarbazone ($H_2L$).

The experiment showed that ethanolic solution of $Ni(OAc)_2 \cdot 4H_2O$ reacts with $H_2L$ taken in a 2:1 molar ratio forming a red-brown substance with composition $Ni(H_2L)(L) \cdot C_2H_5OH$. Single-crystals were obtained as a result of its recrystallization from dimethyl sulfoxide. Its structure was established on the basis of X-ray analysis. It was found (the space group C 2/c, unit cell parameters [Å] : a = 38.146(4); b = 9.6601(8), c = 19.7446(12); $\alpha = 90^o$, $\beta = 91,613(7)^o$, $\gamma = 90^o$; volume – 7272.87 Å$^3$) that the coordination polyhedron of the investigated coordination compound has a distorted square planar structure. There are two thiosemicarbazone molecules that perform various functions in the internal sphere.



Structure of $Ni(H_2L)(L) \cdot C_2H_5OH$

The first molecule of the thiosemicarbazone behaves like a tridentate ligand and coordinates to the nickel central atom by deprotonated phenolic oxygen atom (d(C-O) = 1.304 Å), azomethine nitrogen atom, and sulfur atom forming two five- and six-membered metallacycles. This thiosemicarbazone is in the thiolate deprotonated form. This fact is proved by the distance d(C-S) = 1.738Å which corresponds to single bonds and the distance $d(C\text{-}N)_{carbamide}$ = 1.291Å, which corresponds to double delocalized bonds. In composition of monodentate thiosemicarbazone the distance d(C-S) equals 1.710 Å which corresponds to double bonds, and the distance $d(C\text{-}N_{carbamide})$ corresponds to single bonds. Besides this in monodentate ligand the distance $d(C\text{-}O)_{phenol}$ is 1.358Å that corresponds to a phenol fragment with a protonated oxygen atom. Other interatomic distances and valent angles are standard for compounds of this class.

The studied compound exhibits the antioxidant properties in the range of concentrations $10^{-5}$ - $10^{-7}$ mol/L with the half maximal inhibitory concentration $IC_{50}$ = 0.5 μmol/L. The obtained data indicates that its antioxidant activity is 67 times higher than the characteristics of Trolox that is used in medicine as an antioxidant.

The found properties of the studied complex are of interest to medicine from the point of view of expanding the arsenal of synthetic antioxidants.

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**P88**

# BROMOCRESOL GREEN ADSORPTION OPTIMIZATION USING BIO-INSPIRED METAHEURISTIC OPTIMIZERS

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Determining the optimal conditions that lead to desired outcomes (in terms of maximizing the useful products and minimizing the losses) is of outmost importance from both economical and engineering points of view, as it leads to the reduction of consumed resources (time, materials) and of specialized personnel. In this work, two bio-inspired metaheuristic algorithms (Differential Evolution -DE- and Differential Search -DS-) are used to determine the optimal process parameters that lead to a maximum adsorption rate of bromocresol green onto activated carbon. DE is inspired by the Darwinian principle of evolution and DS is based on the Brownian motion of animals. In order to reach the optimization objective, first, a series of experiments were performed by varying the adsorbent quantity, contact time and initial bromocresol green concentration using an experimental plan developed based on Design of Experiments (DOE) approach. After that, the Response Surface Model (RSM) was applied to the gathered data in order to generate a regression equation that describes the relation between the process parameters and efficiency. This relation was then used by the two algorithms to determine the combinations of conditions reactions that generate the highest efficiency. In addition, the Minitab software that generated the responses for DOE and RSM approaches was also used for the process optimization. A comparison between the responses generated by Minitab, DE and DS are provided in Table 1.

**Table 1.** Optimization solutions

| *Solver* | *Adsorbent quantity(g)* | *time(min)* | *Bromocresol initial concentration (g/L)* | *Efficiency(%)* |
|---|---|---|---|---|
| Minitab | 1 | 80.9091 | 0.001 | 97.7689 |
| | 1 | 99.5143 | 0.001 | 95.6702 |
| | 1 | 21.4342 | 0.001 | 76.2031 |
| | 0.5037 | 83.8698 | 0.001 | 60.5167 |
| DE | 1.4195 | 85.1726 | 0.0024 | 99.8360 |
| | 1.9423 | 141.1450 | 0.0025 | 99.0436 |
| | 1.5047 | 104.7191 | 0.0027 | 98.4180 |
| | 1.7939 | 138.2743 | 0.0024 | 98.0430 |
| DS | **1.6858** | **93.3456** | **0.0030** | **99.9999** |
| | 1.8547 | 72.6265 | 0.0028 | 99.9475 |
| | 1.3523 | 122.9895 | 0.0016 | 99.9414 |
| | 1.5143 | 140.7934 | 0.0015 | 99.8614 |

**Acknowledgment.** This work was supported by "Program 1. Development of the national system for research and development. Postdoctoral research projects", UEFISCDI, project PNIII-RU-PD no. 23/2018.

**P89**

# CONVERSION OF SPRUCE BARK WASTES BY HYDROTHERMAL CARBONIZATION METHOD

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Several methods such as pyrolysis, torrefaction, hydrothermal carbonization (HTC) can be applied for thermochemical conversion of biomass, in order to obtain bioproducts with high added value. The hydrothermal carbonization process has the advantages of being non-toxic, environmentally friendly and mere scale-up since it is carried out in a simple closed system under mild temperature (150-280 °C) with self-generated pressure. Noteworthy that drying of feedstocks is not compulsory, thus avoids additional costs. [1]

This paper focused on optimize the HTC process considering two factors with three level central composite design highlighting the effects of temperature, time and water to biomass ratio on the maximum conversion yield of *Piceaabies* bark wastes.

To the best of our knowledge, no systematic studies have ever been done focusing on spruce bark like feedstock for hydrothermal carbonization process.

Before applying the thermochemical treatment, the feedstock was subjected to proximate analysis (table 1).

**Table 1.** Proximate analysis for spruce bark

| Value % | Moisture | Ash content | Extractives (alcohol-toluene 1:2) | Hemicellulose | Cellulose | Lignin |
|---|---|---|---|---|---|---|
| | 8.35 | 2.17 | 7.06 | 15.42 | 31.27 | 40.48 |

The conversion was conducted in a stainless-steel autoclave. The reactor was charged with 5 g of spruce bark and distilled water to achieve the water to biomass ratioof 1:5 or 1:10. The autoclave was heated up at different temperatures: 200, 240 and 250 °C, and at different reaction time: 1, 2.5 and 5 h.

The central composite design was successfully employed to optimize and study the individual and interactive effect process parameters on the spruce bark wastes HTC carbonization. The results showed the process parameters have significant effects on conversion yield.

The HTC final products, solid charcoal and liquid phase, were collected for characterization and further innovative applications will be proposed for each.

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**P90**

# OIL/WATER EMULSIONS FOR ADDED-VALUE TEXTILE MATERIALS AND THEIR 'IN-TIME' STABILITY

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The aim of this work is to briefly present a few data about the preparation methodology and characterization of different series of vegetal essential oil (i.e. mint, lavender, rosemary and thyme)/water (O/W) emulsions based on beeswax matrix, glycerin, emulsifying agent (Tween 80), prepared by varying the essential oil and beeswax concentrations. These O/W emulsions were preliminarily characterized by a few physical-chemical quality indicators (i.e. pH, normalized density, acidity index, peroxide index, content of conjugated dienes and trienes, total content of polyphenols and flavonoids, total fatty acids) as well as the creaming indexand sensory analysis, and also their in-time stability for a time period higher than 8 monthsat room temperature.The most stable O/W emulsions were recommended for use to a Romanian textile materials manufacturer to add value to its textile products, especially due to the potential antibacterial action of impregnatedtextile materials and also well-being effects and skin care benefits.

This work underlines also that the most recommendable emulsion must have a relative good in-time stability till the separation of organic and aqueous phases, as well as a satisfactory content of polyphenols and flavonoids, which are mainly responsible of antibacterial activity of impregnated textiles (cotton fabrics) which can be utilized for patches and bandages manufacturing for wellness and human health effects.

**Keywords:** added-value textile products, beeswax, O/W emulsion characterization, essential oil, in-time stability.

**P91**

# KINETICS OF IRON(III)-NITRITE-THIOCYANATE REACTION CATALYZED BY IODIDE IN THE PRESENCE OF DIFFERENT AMOUNT OF ANIONS OF SOME MINERAL ACIDS

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Iodine is an essential nutrient in human diet, and it can be found in several foodstuffs. Several methods of iodine determination have been proposed, including ion-selective electrodes, X-ray fluorescence, inductively coupled plasma mass spectrometry, atomic absorption spectrometry and others. Iodine can also be determined by catalytic methods. There are two main employed methods. One is based on the redox reaction between cerium(IV) and arsenic(III). The second one consists in the catalytic action of iodide on the iron(III)-nitrite-thiocyanate reaction. The iron(III)-nitrite-thiocyanate reaction involves the catalytic action of iodide on the development of the iron(III)-nitrite and thiocyanate-nitrite reactions, the indicator being the excessive amount of iron(III):

$$2Fe(III) + NO_2^- + H_2O \rightarrow 2Fe(II) + NO_3^- + 2H^+; \quad (1)$$

$$2SCN^- + 3NO_3^- + 3NO_2^- + 2H^+ \rightarrow 2CN^- + 2SO_4^{2-} + 6NO + H_2O; \quad (2)$$

$$Fe(III) + SCN^- \rightarrow Fe(SCN)^{2+}. \quad (3)$$

The catalytic effect of the iodide increases directly with its concentration under the constant conditions of the reaction at temperature ≤313 K.

This indicator system is normally used in analytical practice for the determination of iodine in the form of iodide by the kinetic spectrophotometric method at 313 K. When carrying out a large number of analyzes, observance of the indicated temperature conditions is inconvenient and energy consuming.

The purpose of this work is to study the effect of anions, such as $SO_4^{2-}$, $Cl^-$, $NO_3^-$ on the rate of the development of the iron(III)-nitrite-thiocyanate reaction and establish the optimum conditions for this reaction at room temperature.

Certain parts of the solutions of the iodide, thiocyanate, iron(III) and, certain salts of mineral acids were pipetted into a series of polyethylene tubes and then water was added to a total volume of 8.0 $cm^3$. Next to the start of the development of the catalytic reaction, 2.0 $cm^3$ of solution of sodium nitrite was added and then mixed immediately. From this moment, by the stopwatch counted time, the solution was transferred into a cuvette of the spectrophotometer and immediately the absorbance was recorded every minute during 20 min. As the acceleration response grew up, the concentration of iron(III) (equation 1) and $SCN^-$ (equation 2) dropped, and as a result, the optical density of $Fe(SCN)^{2+}$ solutions (equation 3) decreased as well.

On the basis of the experimental data obtained and the information taken from literature, it can be assumed that the addition of salts of some mineral acids may cause changes in the coordination sphere of thiocyanate iron(III) complexes and, therefore, changes the redox potential of the system. This can also lead to either the deceleration or acceleration of the studied redox reaction.

The rate of the catalytic iron(III)-nitrite-thiocyanate reaction correlates well with the complexing ability of the anions of strong mineral acids in relation to iron(III). The experimental conditions of the flow of the iron(III)-nitrite-thiocyanate reaction were optimized, which made it possible to determine iodine in the form of iodide at room temperature.

**P92**

# THE SYNTHESIS OF SILVER NANOPARTICLES BY METHANE-OXIDIZING BACTERIA *METHYLOCOCCUS CAPSULATUS* (M)

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Silver nanoparticles are widely used to obtain various materials with antiseptic properties. According to the principle of impact, methods for producing nanoparticles can be divided into two large groups: dispersion methods for obtaining nanoparticles by grinding a conventional macro sample (chemical, photochemical and radiation reduction, laser evaporation, etc.) and condensation methods for producing nanoparticles from individual atoms (gas condensation, plasma-chemical methods, etc.). By now different microorganisms such as bacterial strains, have been used to develop non-toxic methods to synthesize nanoparticles. Methods of microbial synthesis of nanoparticles are relatively cheap, environmentally safe and extremely diverse. The posibility of synthesis of silver nanoparticles by using methane-oxidizing bacteria *Methylococcus capsulatus* (M), which iscapable of utilizing methane as their only carbon and energy source was studied in this work. *Methylococcus capsulatus* (M) cells were cultivated under continuous perfusion conditions in the *Ankum 2M* fermenter in a standard mineral medium at 42ºC, pH = 5.6. The biomass of microorganisms was separated from the nutrient medium by centrifugation for 10 minutes at 7000 rpm and transferred to solutions of silver nitrate ($AgNO_3$) of various concentrations containing 5 ÷ 1000 mg/L $Ag^+$. In parallel experiments, silver salt solutions were introduced directly into the culture liquid with biomass. Incubation took place at room temperature for up to five days. Extracellular bacterial formation of silver nanoparticles was observed, which was recorded spectrophotometrically. Microparticles with a diameter of one to several microns and larger, rapidly settling particles are also formed with nano-silver. Thus, methane-oxidizing bacteria *Methylococcus capsulatus* (M) issuitable to use for synthesis of silver nanoparticles.

**P93**

# NEW CARBON PRECURSORS FOR SYNTHESIS OF GRAPHENE AND ITS OXIDES

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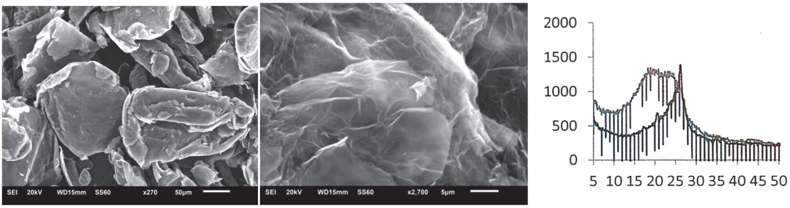
Compounds with carbon 2D and 3D structures are of great importance and perspective [1,2]. The graphite oxide, graphene oxide (GO) and reduced graphene oxide (rGO) are graphite single layer (graphene) oxidation products. Natural, synthetic, microcrystalline, expendable, expanded and graphite intercalated compoundscan be used as precursors to prepare these compounds. It is established that the reduction of the GO obtained from the samples of the different types of graphite are formed graphenes, in which the number of layers has been very different (1–10 layers or more). The purpose of the present work is studying the usability of graphite foil wastes as the precursors for GO, rGO and graphene syntheses. For this purpose, graphite foil samples have been used and at a temperature of 1000-2100°C to obtain various types of ceramic materials using the hot pressing method.The used graphite foil powders (GFP) were obtained by dry and wet grinding of wastes. The SEM image shows that each powder particle is composed of layers rolled on each other, having different forms. The thickness of the sheets was found to be ~0.5 µm. The GO was obtained using different oxidation systems ($KMnO_4$–$NaNO_3$–$H_2SO_4$, $KMnO_4$–$H_2SO_4$-$H_3PO_4$ and $KMnO_4$–$H_2SO_4$). In case of low-temperature mode oxidation of powders the C:O ratio (at.%) was found to be 1.6. During its reduction the C:O ratio was increased to be 4.3. XRD analysis confirmed, that the peak of rGO at $2\Theta$ = 18.47°-23.11° completely disappeared during the thermal reduction process and appeared a broad diffraction maximum at $2\Theta$=26.26° of graphene with defective structure (DSG).



I II III

**Figure.** SEM images of GFP (I), RGO (II) and XRD patterns of RGO and DSG (III).

The obtained products were studied by optical, scanning electron microscopes (SEM-EDX), X-ray diffraction method, IR and UV spectrometric methods. Particle sizes were determined by Winner802 DLS Photon correlation nano particle size analyzer.

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**P94**

# PHOTOCHEMICAL TRANSFORMATIONS OF CYSTEINE IN THE PRESENCE OF HUMIC ACIDS

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Thiolic substances (R-SH) are the class of biogenic organic compounds with multiple essential functions in biogeochemical systems. One of a biogenic nature thiols is cysteine (Cys), which, together with glutathione (GSH), is found in the large amounts in living organisms [1]. It is demonstrated that in the upper layers of aquatic objects R-SH suffer predominantly photochemical transformations, but the influence of humic acid (HA) in photochemical processes remains unclear [2].

According to recent research [3], humic acids are not only sensitizers in photochemical transformations. It was been demonstrated that HA can generate free radicals by the absorption of solar radiation by chromophore groups (-C=C-, -C=O, phenolic rings) of their structure, which gives them mixed properties, both photosensitizing and photoinitiating. An increase in the concentration of free radicals ($^1O_2, \dot{O}H$), generated by HA at high values of natural water mineralization and in the presence of transition metals [1-3] has been observed. However, under some conditions, HA may also act as antioxidants, regenerating photochemically oxidized aminoacid molecules, such as tryptophan [3].

The purpose of this paper is to identify some kinetic laws of Cys photolysis in the presence of humic acids, on model systems.Under laboratory conditions 4 systems were modeled, in each of them varying consecutively the concentration of one compound, while the other remained constant:

(I) Cys-AH- hv;
(II) Cys-AH- $H_2O_2$- hv;
(III-IV) Cys-AH- $H_2O_2$- $Me^{n+}$ - hv, where $Me^{n+}$ are Cu (II) and Fe (III) ions.

The experimental results confirmed that cysteine undergoes photochemical transformations in the presence of humic acids, the order of the photolysis constants experimentally calculated ($10^{-4}$-$10^{-5}$ M/s) is in line with literature data [1]. At addition of initiator and/or catalyst molecules to the system, the concentration of the -SH groups increases with time, which confirms the hypotheses proposed in literature that HA may behave as photosensitizers, photoinitiators, radical traps and antioxidants [4]. However, the chemical behaviour of HA remains a subject of research of photochemical transformations in natural waters.

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**P95**

# NATURAL WATER AUTO PURIFICATION CAPACITY THROUGH THE REDOX PROCESS (2018)

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This paper presents the results of the evaluation of the natural water auto purification capacity through chemical oxidation processes during the year 2018. The monitoring was carried out by measuring $H_2O_2$ and the peroxidase reducers (Red) contents which were the criteria for determining of kinetic waters redox state as oxidizing, unstable or reducing. Another indicator was the inhibitory capacity ($\Sigma k_iS_i$), an indicator of water pollution with OH radical scavengers. The water objects monitored were Nistru river, in Dubasari-Vadul Voda segment dam, its tributaries, Raut and Ichel rivers, at the confluence rivers segments, as well as two accumulation lakes located in the hydrographic basin of Nistru river, Ghidighici and Danceni lakes. In the investigated waters, more frequently, low or lack of $H_2O_2$ was found, thus confirming its consumption in water auto purification and inappropriate conditions for its regeneration, such as the oxygen oxidation processes. Recorded $H_2O_2$ concentrations, often < 100 µg/l, are insufficient for effective auto purification processes and for appropriate biological habitate value. The redox oxidant character of the Nistru waters was provided by $H_2O_2$ in 10.0-21.9 µg/l concentrations. In the tributaries waters, more often, the reducers concentration exceeded the $H_2O_2$ one. Peroxidase substrates were found in higher concentrations in Ichel river (2.0-10.0 µg/l) than in Raut (0.3-2.8 µg/l). The $H_2O_2$ concentration in Ichel river was observed only in June (36.7 µg/l), when in Raut the highest contents of $H_2O_2$ (34.9 µg/l) was recorded during the monitored period. Except March, in Ghidighici waters the $H_2O_2$ concentration was in 13.2-19.3 µg/l interval, while in those of Danceni lake, except for September (16.8 µg/l), when the $H_2O_2$ was missing.

In Nistru waters, the content of substances that disrupt the auto purification chain with OH radicals was lower than for the rest of the aquatic objects. Following the inhibitory capacity dynamics ($\Sigma k_iS_i$), in all monitored objects was shown that during the spring months the waters of all aquatic objects contain large concentrations of OH radical scavengers $(3.8\text{-}20.0)\cdot 10^{-5}\ s^{-1}$. In the following periods, water pollution with these substances decreases. Thus, in Nistrusriver inhibitory capacity ranges between $0.3\cdot 10^{-5}\ s^{-1}$ and $2.7\cdot 10^{-5}\ s^{-1}$. For the tributaries waters, this parameter has the values for Raut and Ichel rivers $(3.3\text{-}6.6)\cdot 10^{-5}\ s^{-1}$ and $(1.3\text{-}5.3)\cdot 10^{-5}\ s^{-1}$ respectively. Approximately at the same level is the pollution degree with OH radical scavengers in Ghidighici $(1.2\text{-}4.0)\cdot 10^{-5}\ s^{-1}$ and Danceni water lacks $(2.2\text{-}4.3)\cdot 10^{-5}\ s^{-1}$. The monitoring revealed that the auto purification capacity through chemical oxidation processes is higher in Nistru river compared to tributaries and lakes.

**P96**

# COMPONENT FOR DIESEL FUEL AND SOLVENT FOR BITUMEN ROAD BASED ON PYROLYSIS BIO-OIL

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Bio-oil is the liquid fraction obtained from the pyrolysis process being an important source of both energy and valuable commodity chemicals. The liquid is composed of a water phase (containing diverse oxygenated hydrocarbons) and an organic tar phase containing a complex mixture of several hundreds of organic compounds such as acids, alcohols, aldehydes, esters, ketones and phenols [1].

The pyrolysis-derived bio-oils from different biomasses have various compositions but the same basic properties for bio-oil usage as fuel substitute are heating value, viscosity, density and stability. The oxygen content of biomasses bio-oil is higher than that of fossil oil and consequently, they have higher reactivity and lower stability than fossil fuels and cannot be used in their present form as transportation fuels [2]. Thus there is an urgent need to develop new approaches to utilize these oils as sources of fuel additives or extenders. In this context, creating blends of bio-oil with other transportation fuels could be a viable short-term alternative to utilize an important fraction of these oils [3].

The objectives of this research were: a) conditioning of blends from bio-oil and lipid fraction and b) evaluation of bio-oil /lipids blends in order to obtain components for fuels and/or ecological additives for road bitumen. The bio-oil used in this study was obtained from the slow pyrolysis of biogas solid digestate. The physical and chemical properties of the pyrolysis oil/lipids/diesel blends were evaluated in accordance with the corresponding specification.

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**P97**

# PHOTOCATALYTIC PERFORMANCE OF FLUORESCENT ZnS NANOCOLLOIDS USED FOR DEGRADATION OF ORGANIC COMPOUNDS

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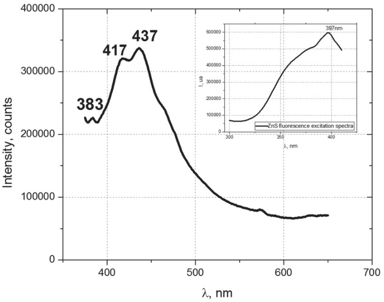
The issue of reducing organic pollutants in waste water is important and topical. We are looking for new materials that lead to the degradationof these compounds downto the level of $CO_2$ and water, under conditions that are mild and easy to achieve. Thus, the semiconductor-pollutant-ultraviolet radiation systems have proven to be effective in reducing the amount of organicsin waste water. Zinc-based materials (oxide, sulphide, mixtures, simple or doped) show good photocatalytic activities and are suited to the wastewater purification [1-4].

The paper describes synthesis, characterization and photocatalytic performance for the fluorescent ZnS. A simple hydrothermal method is used to synthesize the ZnS nanoparticles.

The physico-chemical characteristics of ZnS were analyzed using UV visible spectroscopy, photoluminescence spectroscopy (Figure), scanning electron microscopy and FTIR. Photodegradation experiments were monitored by UV-Vis spectroscopy for anionic or cationic dyes (methylene blue, methyl orangeor phenol red). The ZnS photocatalystis stable and is suitable for several cycles of use without significant reduction in efficiency.



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**P98**

# ADSORPTION OF Cu(II) BY ACTIVATED CARBONS AND EFFECTS ON THE ADSORPTIVE PERFORMANCE FROM THE pH CHANGES

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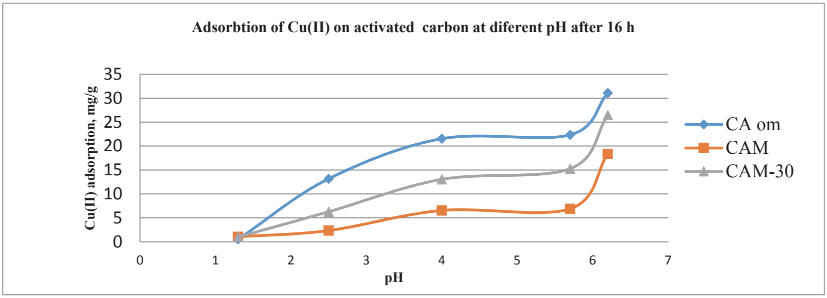
Heavy metal containing wastes are considered to be hazardous to both human life and the environment due to their acute toxicity and non-biodegradability, even when the heavy metals are present at trace concentrations. A common method for heavy metal removal from water is ion exchange. One of the efficient methods of removing heavy metals is the adsorption by activated carbons.

Adsorption is very effective process for a variety of applications, and now it is considered an economical and efficient method for metal ions removal from wastewaters. The most generally solid adsorbent is activated carbon, which is a very efficient solid adsorbent in many different applications.

The adsorption ability of activated carbon was investigated for removal of Cu (II) from single aqueous systems. Results of the initial screening allowed to select the adsorbents for kinetic and isotherm studies as well as investigating the effects on adsorptive performance from pH changes.



The adsorption processes were carried out at room temperature (20±2°C) at the initial metal concentration of 100 mg/L. The process was studied for individual metals of Cu (II) and the concentrations of solutions varied in the limits of 10-120 mg/L. The varied pH solutions were prepared adding dilute NaOH or $HNO_3$ dropwise to achieve pH values from 1.3 to 6.2. Bottles were shaken at room temperature for 16 h. Then samples were filtered. The metal equilibrium concentrations were determinated by Atomic Absorption Spectrometer.

**Acknowledgements**

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**P99**

# ETHIDIUM BROMIDE REMOVAL FROM AQUEOUS SOLUTION BY NANOHYDROXYAPATITE

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The hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] is a calcium phosphate ceramic with important applications in the medicine and chemistry fields. The hydroxyapatite has been identified as a good adsorbent material for the environmental processes due to its specific structure conferring ionic exchange property and adsorption affinity towards many polluting [1]. This biomaterial has already been applied for removing heavy metal ions and organic compounds (phenols, dyes, etc.) from water [2].

Ethidium bromide is an intercalating agent used as nucleic acid stain in molecular biology laboratories.Also, itis used in veterinary medicine to treat trypanosomiasis in cattle, a disease caused by trypanosomes.Ethidium bromide may be a mutagen, although this depends on the organism exposed and the circumstances of exposure [3].

In the present study the Ethidium bromide adsorption on the nanocrystalline hydroxyapatite was investigated. The nanohydroxyapatite was prepared by wet coprecipitation method and investigated using scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) methods. The hydroxyapatite has a high specific surface area (BET) of 81 $m^2/g$ and crystal sizes smaller than 100 nm. The pH at the point of zero charge ($pH_{pzc}$) of hydroxyapatite sample was foundto be of 7.9.

The batch adsorption experiments were performed by monitoring the pH, adsorbent dosage, Ethidium bromide solution concentration and contact time. High removal rate (R%) of Ethidium bromide of about 93.25% was obtained at pH=10 and ambient temperature. The adsorption capacity (q) was high at low adsorbent dosages and reduced at high dosages. The Ethidium bromide adsorption on hydroxyapatite may be explained to proceed via the electrostatic attraction between the negatively charged surface of the hydroxyapatite and the positively charged group of the Ethidium bromide molecule.

The results obtained indicated that the nanohydroxyapatite possessed good adsorption ability towards Ethidium bromide.

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**P100**

# ACTIVE PHOTO-CATALYST BASED ON GOETITE NANOPARTICLES

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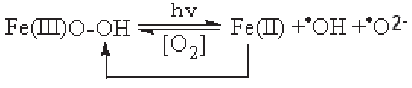
Elaboration of the new preparation methods of active photo-catalysts with highly developed surface based on the fine-disperse dironoxides, using the nano-sized $TiO_2$, is a perspective way to create a highly active photo-catalyst. The surface of the material produced can be modified in order to ensure the spatial charge separation within the particles and shift the absorption spectrum towards the lower energy area. An advantage of nano-particles, as compared to the micro-particles, is higher probability of the charges exit on the catalyst' surface.

A modified technological process has been elaborated based on the earlier proposed sol-gel process of nanostructured goetite preparation [1]. The stabilized hydrophylic goetite (feooh) particles are produced in the rotating reactor, in which the galvano-chemical dissolving of iron occurs in the field of the shortcut galvanic element iron-coke in water environment, due to the galvanic pair elements' alternating contacting with each other.

The main redox reaction running on the coke surface under aeration within the ph range pH=6÷10, is oxygen reduction reaction: $O_2 + 2H_2O + 4e = 4OH^-$ accompanied with the solution alkalinization. However, within this ph range, iron surface can be passivated so it become unavaliable for further dissolving. To prevent pasivation and provide the constant activation of iron surface, $Cl^-$ ions are introduced. Anodic dissolving of iron follows the general-type reaction: $Fe+2OH^- = Fe(OH)_2+2e$, and then, goetite formation occurs as a result of oxidation and hydrolysis processes: $4Fe(OH)_2+O_2 = 4FeOOH+2H_2O$.

The process is carried out in the solution flow in the galvano-coagulator rotating with the speed of 10-15 rot/min, filled with the package of iron shavings and coke with the ratio 1 : (2-3), forming the galvanic pair. As a result of the series of processes running within the reactor, the gelatinous sediment is formed, which is separated with flocculation treatment and subsequent sedimentation or centrifugation. As a flocculant, a mixture of polyacrylamide with NaCl has been used.

The sediments thus obtained are not ferromagnetic and have a roentgen-amorphous structure, with high dispersion. The nano-dispersed goetite is a perspective catalyst for the photo-catalytic treatment of water systems polluted with the persistent organic components. Under the UV-irradiation, a photocatalytic reaction mechanism is realized, connected with the formation of hydroxyl-radical ($^{\bullet}OH$) and superoxide-radical $^{\bullet}O^{2-}$formed as a result of the FeO(OH) photo-dissociation:



$$Fe(III)O\text{-}OH \underset{[O_2]}{\overset{h\nu}{\rightleftharpoons}} Fe(II) + {}^{\bullet}OH + {}^{\bullet}O^{2-}$$

Active radicals thus formed promote the efficient decomposition of the polluting organic molecules up to the formation of inoffensive simple salts and gas molecules.

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**P101**

# THE ROLE OF TRITERPENE COMPOUNDS IN STIMULATION OF THE SELECTIVE BIOCHEMICAL HYDROGEN PRODUCTION

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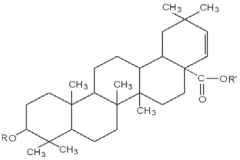
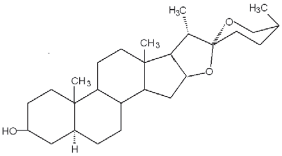
Production and using of hydrogen in the various fields of power engineering and technology is a priority area, due to its high energetic indexes and environmentally friendly applications leading in many cases to water formation. Among the numerous hydrogen production technologies biochemical processes are considered asrather efficient and cheap.

A new biohydrogen production method from biomass has been proposed, through the anaerobic digestion of municipal and agricultural wastes with high organics contents [1]. Thevinasseasawastefromwinematerialsandalcoholdistillationwas used as biomass, to which the digestion stimulating additives were added – isoprenoid bioactive substances (BAS) of vegetable origin, in the amount of $1\cdot10^{-3} \pm 5\cdot10^{-4}$ mass.%.

The digestion process is carried out under the mesophyl conditions at pH = 5.2 -7.5 and at the temperature 33±2ºC, with biomass agitation and permanent hydrogen removal from the bioreactor. Triterpene compounds were used as BAS, extracted with water-alcohol mixture, specifically: gypsogenin, gypsogenin glycosides or neotigenin saponin – steroide of $C_{27}$-spirostane series:





Their effect on the bacteria's vitalactivity may beconnected with the electrons biochemical transfer from water molecules on protons and consequent emission of the molecular hydrogen. One of the main biochemical reactions (theso-called *water-gas shift reaction*) is the conversion of carbon monoxide (CO) forming with water molecules carbondioxide and hydrogen: $CO + H_2O \rightarrow CO_2 + H_2$, used by the bacteria for the additional energy obtaining. CO and $H_2$ formation at the primary stages of biomass digestion was confirmed by chromatographic studies. To carry out this process, amodified bioreactor design has been proposed [2].

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**P102**

# ELECTROCHEMICAL NEUTRALIZATION OF THE DISTILLERY BY-PRODUCTS

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The brandy alcohol usually contains a series of admixtures, among then upto 57 mg/L aldehydes – undesirable component which regulated contents in the final product should not exceed 2-4 mg/L [1]. One of the most commonly used methods of the distillery products neutralization is the absorption on active carbons [2]. However, the active carbon, in addition to absorption, catalyses also the redox reactions, among then ethanol oxidation to acetaldehyde and then to the acetic acid, following the scheme of reaction: $C_2H_5OH + O_2 \rightarrow CH_3CHO + H_2O \rightarrow CH_3COOH$. The reaction rate at the first stage (ethanol oxidation to acetaldehyde) is higher than acetaldehyde oxidation to acid, so this process is linked with the formation of increased amounts of acetaldehyde which, unlike the acetic acid, is not absorbed by the carbon and makes part of the final product.

To remove the aldehydes and other admixtures of alcohol digestion products from the distillate, a new technology was proposed, including the undesired products reduction with the electrochemically generated active hydrogen [3]. The proposed processis carried out in the flow-through conditions with the linear flow rate of 0.1-0.3 m/s. The treated liquid is passed through the three-dimensional Ni cathode covered with catalytic layer, within the cathodic compartment of diaphragm electrolyzer, under the cathode current density of 0.15-0.5 A/dm$^2$. A new type of the voluminous porous material made of foamy metal with high active surface, modified with the coating containing small percentage of Re, MoorW, was used. A total active surface of the cathode was by 2-3 orders higher than the visible surface.

Hydrogen reduction on the cathode is connected with water molecules dissociation $H_2O \leftrightarrow H^+ + OH^-$ and hydrogen ions discharge, including a series of competing reactions with primary emission of protonated hydrogen ($^{\bullet}H_{ads}$): $H^+ + e \rightarrow {}^{\bullet}H_{ads}$, which ensures the high efficiency of aldehydes reduction. Further on, a part of atomic hydrogen, which is not involved in aldehydes reduction, will be molized, following the recombination reaction: $^{\bullet}H_{ads.} + {}^{\bullet}H_{ads.} \rightarrow H_2$, or as a result of electrochemical desorption (Geyrovsky reaction): $H_3O^+ + {}^{\bullet}H_{ads.} + e \rightarrow H_2 + H_2O$. Another significant advantage of three-dimensional cathodes application with modified catalytically active surface is low overvoltage of hydrogen emission, making 0.03-0.05 V, which is substantially lower than for Ni electrodes. Due to this fact, the overall energy consumption to electrolytic process is much lower as compared to the application of plate Ni electrodes.

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**P103**

# Cu-DOPED NANOTUBE PHOTOCATALYST FOR CARBON DIOXIDE CONVERSION IN METHANE

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Catalytic production of methane and other hydrocarbon fuels by the carbon dioxide conversion in gaseous phase with water vapour under the influence of the large range of the wavelengths of solar irradiation is a perspective process promoting the resolving of energy problem and reducing of greenhouse gases emissions in atmosphere. To make this process efficient, there is a need to substantially enlargen the adsorption spectrum of $TiO_2$. It was shown [1, 2] that doping can essentiallybroaden the adsorption spectrum of Ti oxide, modifies the redox potential of running processes, promotes the free radicals formation and rises the quantum efficiency due to the decreasing the recombination degree of electrons and holes.

A method was elaborated of $TiO_2$ nanotubes array production doped with metal (Cu) from low-concentrated solution. The experimental set-up proposed (Fig.1) implies the possibility of vacuuming. It was found that due to the application of ultrasound, following the vacuuming of working solution, it became possible to cover the external and internal surface of nanotubes with thin metal layer.

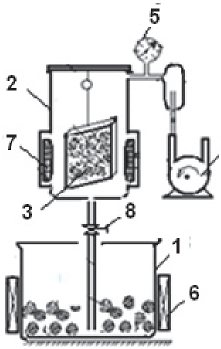

**Fig. 1.** Functional scheme of the experimental set-up for the TiO2 nanotubes doping with metals:
1 – reservoir;
2 – anodes;
3 – porous cathode;
4 – pump;
5 – manometer;
6 – solenoid;
7 – 8 – valve.

The samples of nanotubular $TiO_2$ doped with Cu ions, as compared to pure titaniumdioxide, have high erelectroconductivity (*p*-type), and their electro-neutral condition is determined by the electrons transfer from the valence zone with holes formation, ensuring the better photo-catalytic properties of the formed material.

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**P104**

# STUDY OF DPPH RADICAL INTERACTION WITH SOME ORGANIC ACIDS

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The DPPH$^\bullet$ scavenging reaction is widely diffused as an easy to use method of antioxidant capacity evaluation [1]. The proton transfer reaction from a free radical scavenger to the DPPH$^\bullet$ causes a decrease in absorbance at 517 nm, which can be followed by a common spectrophotometer set in the visible region.

Antioxidants are listed as additives in food, cosmetic and pharmaceutical products for the property to inhibit oxidation by donating an electron to the reactive species (RS) [2], this resulting in their neutralization [3]. As an organic acid, ascorbic acid (AA) is, probably, the most studied antioxidant, and the most powerful one, being a good DPPH$^\bullet$ scavenging agent. J. Pokorny et al. mentioned the chelating activity of organic acids as antioxidant capacity, since it reduces the pro-oxidant activity of iron and other heavy metal ions [4]. Even so, researches showed that the majority of the organic acids like citric, gallic, malic, cinnamic have a low or any activity against free radicals, including DPPH$^\bullet$.

Recent studies reported that mixing organic acids with already known RS scavengers, leads to a greater activity than the sum of the individual antioxidant effects applied separately, this supporting the concept of the synergism effect. Roberto Lo Scalzo, in his work, proved that acetic, malic and citric acids gave no DPPH$^\bullet$ scavenging activity in the absence of ascorbic acid, while their action was significant when used in the presence of AA [5]. When testing with the DPPH$^\bullet$ oxidant, the same organic acids in combination with $\alpha$-terpinene increased its activity it showing a synergistic effect [6]. Interactions in combined tea extracts with ascorbic acid show an enhancement of the antioxidant activity [7]. An organic acid profile composed of oxalic, cis-aconitic, citric, pyruvic, malic and fumaric acids was found in the roots of some medicinal plants, the studies revealing the contribution of these acids to the synergistic antioxidants effects [8].

Few reference data have been found on the possible synergistic action of organic acids when mixed with already known DPPH$^\bullet$ scavenger – ascorbic acid, found in large quantities innatural products [9]. In the present study, the influence of citric, tartaric, dihydroxyfumaric, gallic and benzoic acids on the antioxidant capacity of the ascorbic acid in the reaction of DPPH radical annihilation is investigated. The comparative analyses of the radical scavenging properties of the mixtures and of the single compound solutions are realised and presented.

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**P105**

# $Cd^{2+}$-SELECTIVE ELECTRODE WITH THE SCHIFF BASE AS IONOPHORE

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This article reflects the results of the study of analytical parameters for a series of $Cd^{2+}$-selective electrodes from various bibliographic sources, to highlight the nature of the ionophores and their application.

A potentiometric sensor with polymeric membrane based on the selective complexation of the Schiff base $N_1,N_5$-bis(salicylidene-S-methyl)isothiocarbohydrazone and $Cd^{2+}$ ion was assembled.

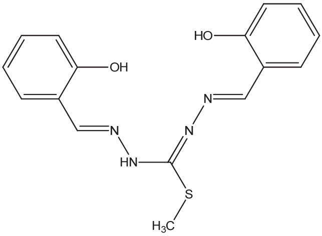

**Figure 1.** The structure of the ionophore
$N_1,N_5$-bis(salicylidene-S-methyl)isothiocarbohydrazone.

It has been demonstrated that the presence of the lipophilic additive sodium tetraphenylborate in the polymeric membrane significantly improved the slope. The electrode exhibits a Nerstian response within the range of $1.0 \cdot 10^{-1} – 1.0 \cdot 10^{-4}$ mol/L with the slopes mean 28.6 mV/decade, a response time of 20 seconds and the limit of detection of the sensor is $10^{-5}$ mol/L. The optimum pH range of the sensor is 2.0-8.5. Interference of some cations was also evaluated.The negative effect of the potentiometric measurements has $Cu^{2+}$ and $Pb^{2+}$ ions due to the possibility of their coordination with the polymer membrane ligand.

To determine the cadmium content in the sample model the direct potentiometric method and as a potentiometric potential indicator in titration with standard solution of Trilon B are applied. The results indicate that this electrode is sensitive for determination of $Cd^{2+}$.

Potentiometric detection based on ion-selective electrodes offers advantages of speed and ease of procedures, simple instrumentation, relatively fast response time, wide dynamic range, reasonable selectivity, and low cost [1].

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**P106**

# CHEMICAL COMPOSITION, PROCESSES OF POLLUTION AND AUTOPURIFICATION OF THE GHIDIGHICI LAKE WATERS (2015-2018)

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To assess chemical composition, degree of pollution and self-purification capacity of the Nistru river basin, the waters condition of the Ghidighici reservoir lake, formed on the Bac River, Dniester tributary was studied [1, 2]. During the years 2015-2018, 4-6 seasonal expeditions were organized annually with the water sampling, classical hydrochemical field studies, preservation of samples and their analysis in the laboratory.

During the research period in the storage lake alkaline water masses were formed, with an average pH of 9.2, which permanently contained carbonate ions. pH values ranged from 8.7 to 10.2, which corresponds to alkaline or strongly alkaline waters and exceeds the admissible values for surface waters. Increased alkalinity of water can contribute to the formation of toxicity and conditions of pathogenic microorganisms and development bacteria. The sum of the main ions varied between 823 mg/dm$^3$ and 3017 mg/dm$^3$, with an average of 1539 mg/dm$^3$. The waters were characterized with the unstable and variable content of the main ions by changing the cations and the dominant anions in the hydrochemical index of the waters. The waters in the lake can be attributed to the hydrogen carbonate-sulphate class, sodium and magnesium type. The waters of Lake Ghidighici have increased alkalinity, excessive mineralization, increased sodium ions contents, which can contribute to salinization and alkalinisation of soils. The use of these waters for irrigation purposes is limited.

The contents of dissolved oxygen during the research period varied in the range from 3.1 mg/dm$^3$ to 15.7 mg/dm3, with the multiannual average 9.3 mg/dm3. The waters contained substantial amounts of organic substances. The average content of organic biodegradable substances (CBO$_5$) was 5.0 mg O$_2$/dm$^3$, which by 60% exceeds the admissible values for aquatic ecosystems and attributes water to class V - highly polluted, red code. In the waters of the lake the increased amounts of organically degradable substances (CCO$_{Cr}$) were found. The content of these substances practically permanently exceeded the admissible values and presented a real danger for the lake ecosystem.

According to the nitrite and ammonium ions the waters of the lake can be attributed to class III - moderately polluted waters, yellow code. The data show the presence of phosphates in very large quantities, the average being 0.72 mg/dm$^3$. This contributes to the rapid eutrophication of the lake, which can have unintended consequences in the ecosystem of Bac and Dniester. The waters are extremely polluted with nutrients and organic substances. In most cases, the waters in these lakes are of class V of pollution (red code).

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**P107**

# THE DIETHYLENE GLYCOL INFLUENCE IN THE COAGULATION PROCESS OF ACTIVE AND DIRECT DYES

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Textile waste water resulting from finishing of textile materials has a complex and diverse composition, due to a variety of raw materials and technological processes used. General characteristics of waste water for textile dyeing are related to a high content of organic matter (dyes, auxiliary agents) being very colourful and toxic [1].

The aim of this thesis is to study experimentally on model systems, the influence of DEG diethylen glycol on the coagulation of active (Active Red-AR120) and direct (Direct Blue- DB 71) dyes. The pH value and the concentration of aluminium ions are the main parameters influencing the coagulation process. From the experimental studies it was determined that the optimal pH for the coagulation of the DEG with a concentration of 60 mg/L is 5.5 and the $Al^{3+}$ concentration is 1.62 mg/L. Under such conditions, a high efficiency of the coagulation process was obtained (90-93%). In actual fact, waste water is a complex system that contains dyes and various toxic auxiliary substances. In order to optimize the process of coagulation of the textile waste water, various systems similar to their composition have been modeled. The experimental studies in coagulation of the AR - DEG and DB - DEG model systems, with a 200 mg/L dye level, found that the optimal pH is 5.0-5.5 and pH ~ 4.5 respectively. And the optimal $Al^{3+}$ concentration is 2.7 mg/L for the AR-DEG model system and 5.40 mg/L for the DB - DEG system, taking into account the rational use of the reagents.

From the experimental researches of the coagulation process of AR and DB, it has been established that maximum efficacy is obtained at pH as compared to systems containing DEG. And the optimum concentration of $Al^{3+}$ is 1.35 mg/L for AR and 2.7 mg/L for DB [2]. So we conclude that DEG has no influence on the optimum pH in the systems containing dyes. The coagulation of DB and AR dyes has been studied according to $Al^{3+}$ concentration and it has been found that the $[Al^{3+}]/[Col.]$ ratio depends on the nature of the dyes: for AR is 0.006 and for DB is 0.013. However, in the presence of DEG this ratio increases (DB - 0.020, and for RA-0.010).The dyes in model systems with DEG behave differently because they have different coagulation nature and structure. DB dye has higher removal efficiency compared to the model system containing AR.

For purification by coagulation of the model system composed of DB - DEG, a double coagulant concentration is required compared to the model system consisting of AR and DEG. This process takes place because there are several negatively charged polar groups in the structure of the AR dye, which more easily interact with the colloidal micelles of the positively charged coagulant. Based on the electrostatic effect, large agglomerates are formed, which are eliminated by filtering the model system [3].

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**P108**

# TESTING OF ACTIVE CARBONS FOR REMOVAL OF NITRITE IONS FROM WATER

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Water influences the health of the population directly through its qualities, respectively by its composition. A number of non-communicable diseases are considered to be determined by the chemical composition of water [1, 2].

In this work, the results of active carbon (initial and oxidized samples) testing for removal of nitrite ions in oxic condition have been reported. The removal of nitrite ions from water was carried out in a semi-pilot plant equipped with air bubbles and a vessel for the capture of aerated $NO_x$ gases. Indigenous active carbons, produced from nut shells and apple wood, with a working fraction of 0.63-0.80mm were used. The kinetics of nitrite ions removal was studied at different pH values (2.5-8.5) and the solid: liquid ratio (1:200). In order to investigate the process (adsorption-oxidation-aeration) of nitrite ions removal from natural water, a sample of underground water (Tamara spring, Valea Morilor, Chisinau, R. Moldova) was used.

Obtained results reveal that in the presence of active carbons, the rate of nitrite ions removal from the solution increases from 0.5% to 70%, at the same time, the proportion of nitrite ions oxidized to nitrate ions is 20-30%. In case of nitrite ions removal from natural water the contribution of active carbons is 9.5-15.5%, while the amount of nitrite ions oxidized to nitrate ions constitutes 6-10%.

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**P109**

# EXPERIMENTAL STUDIES FOR REDUCED COSTS AND IMPROVE THE EFFICIENCY OF CLARIFICATION SYSTEMS

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Water clarification determines remove of suspended solids and particulate matter, by improving settling [1]. In this paper, we studied water clarification used in the treatment of industrial effluent from ammonia plants. Clarification is the first step of wastewater treatment and consist in coagulation, flocculation, and sedimentation [1, 2]. Coagulation is used for the removal of the colloid-sized suspended matter and consist in destabilization by charge neutralization. Flocculation is the process of getting together the destabilized with forming agglomerated particles, or "floc". Finally, flocculated particles are removal from suspension by sedimentation. In present iron and aluminium coagulants, are used, its hydrolysis products having a significant role in the coagulation process. The pH affects particle surface charge and floc precipitation, but the pH for the best clarification performance not always coincide with the optimum pH for floc formation [3]. The efficiency of clarification depends greatly on the nature of the turbidity particles, the amount of turbidity, and the mixing or reaction energies available during coagulation. The waters with NTU (Nephelometric Turbidity Units) up to 60 can be clarified with the best results by a combination of an inorganic salt and cationic polymer. At turbidity greater than 60 NTU, a polymeric primary coagulant alone is normally sufficient. In this paper was studying the removal of total suspended solids (TSS) and turbidity NTU from ammonia plant wastewater. The performance of the coagulant was tested using a JAR Tester. The turbidity was measured with a Cole Parmer Model 8391-40 turbidity meter. The experiments are carried on real industrial waters, in the period January-May 2019. For the TSS removal, 100 mL of the waste water was filled in the jar tester and stirred at 130 rpm for 10 min, in order to maintain a homogeneous TSS distribution. The coagulant sample was weighed carefully to make 0.2-0.8 ppm in the wastewater sample. On the other hand was used ppm of the 2-12 ppm 7221 coagulant, a low molecular weight cationic coagulant. Simultaneous experiments were realized with both coagulants. After the coagulant was added, the wastewater was stirred at 30 rpm for 10 min and then at 5 rpm for 10 min. The pH in the test was adjusted by adding sulphuric acid and sodium hydroxide solutions. The initial TSS was 180 g/L. The pH in the test was adjusted in the range of 7–8.5.

In the case of aluminium sulphate maximum removal degree was 88% for 0.7 ppm dosage, and for 71221 maximum degree was 86% for 10 ppm. The removal degree was improved by using 0.6 ppm aluminium sulphate and 4 ppm 71221 coagulant, when was obtained 95% removal degree. The mixture of coagulants was more effective than conventional treatment in TSS removal, and determines an improved efficiency and reduced costs in clarification processes.

**Acknowledgments.** This work was supported by a research grant of the TUIASI.

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**P110**

# REMOVAL OF ALUMINIUM IONS FROM RESIDUAL WATERS BY MESOPOROUS MATERIALS

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Due to the fact that we assist to a continuously increasing of the concentration of heavy metals in waters on impose to take concrete and efficient measures at the level of the pollution from the different industry, laboratories. The synthesis and application of adsorptive materials with low cost and high efficiency recovery of heavy metals from residual waters is necessary for environmental protection. In this work, the capacity of hydroxyapatite with different treatment as inexpensive sorbent for aluminium removal from water solutions was investigated. Experiments were performed in batch technique at different pH values, temperatures, sorbent dosage, contact time and initial aluminium concentration.Thermodynamic studies gave negative $\Delta G$ values for all the sorbents suggesting that the aluminium ions adsorption process was spontaneous and thermodynamically favorable.

The adsorption behavior of the sorbents was fitted to five isotherm models and the data fitted the Langmuir isotherm well.

The kinetics of adsorption was evaluated using three kinetic models. The rate of aluminium adsorption was successfully described by a pseudo-second-order kinetic model.The obtained results indicated that hydroxyapatite treated with Pluronic P123 surfactant has a higher sorption capacity toward aluminium ions (117.65 $mg\cdot g^{-1}$) than hydroxyapatite untreated (104.17 $mg\cdot g^{-1}$) and hydroxyapatite treated with Pluronic F127 surfactant (109.89 $mg\cdot g^{-1}$).

The uptake of Al(III) by these sorbents is a reversible process and the sorbents can be used in five desorption/sorption cycles without significant loss in their adsorption capacities.

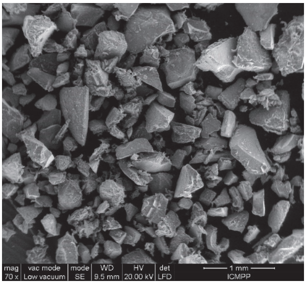

**Figure.** SEM image of sorbent after sorption of Al(III) ions.

**P111**

# COMPARATIVE ANALYSIS OF CHEMICAL COMPOSITION AND PROPERTIES OF NATURAL MINERAL WATERS OF THE REPUBLIC OF MOLDOVA BY THE METHOD OF MATHEMATICAL MODELING

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Social interest in natural mineral waters is determined by their impact on water-salt metabolism, therapeutic effect and the effectiveness of metabolic processes in the human body.

At present, the most important deposits of Eurasian natural mineral waters have been discovered and studied, the chemical composition and physicochemical properties of water have been determined, and their medical and biological assessment has been carried out. However, studies of the composition and properties of newly discovered regional mineral waters with a view to assessing their therapeutic effect on human health remain very promising. The chemical composition of waters is determined by the processes of mixing waters of different horizons, such as carbon dioxide, fresh waters and highly mineralized relict sea waters.

Natural waters are characterized by total mineralization, dissolved carbon dioxide, pH, electrical conductivity and other physicochemical parameters. On the Eurasian continent a large number of mineral water deposits are successfully exploited, the chemical composition of which is quite close to each other due to the genetic similarity of the geological conditions of their formation.

Previously, we [1], on the basis of set theory and differential equations, developed a mathematical model linking a specific type of water with ionic composition and mineralization. According to the proposed model, the therapeutic properties of mineral waters are determined by the composition of anions forming water (chloride, sulphate, bicarbonate), whose properties determine the effectiveness of their effect on the chemical composition of human physiological fluids.

The proposed mathematical model allowed, along with the classification of well-known Eurasian mineral waters, to identify newly discovered regional sources of natural waters for their conformity to approved Eurasian waters, and can also be recommended for organizing a monitoring system for developed fields for their use in balneological practice.

Mineral water deposits are being developed on the territory of the Republic of Moldova, the chemical composition of which is quite close to each other due to the genetic similarity of the hydrogeological conditions of their formation.

In the present work it is shown that the natural mineral waters of the Republic of Moldova are a collection of waters, for example, of the hydrocarbonate-chloride type (Soroka No. 1, Varnitsa unique), the hydrocarbonate-sulfate type (Chisinau, Aqualife, Gura Cainarului), the sulfate-hydrocarbonate type, (Resan, Cahul, Real, Lider) and evaluated their compliance with the mineral waters of Germany, Czech Republic, Italy, Spain and Romania.

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**P112**

# ANTIMICROBIAL PROPERTIES OF INTACT AND OXIDIZED EXTRACTS ISOLATED FROM COMMERCIAL GREEN AND BLACK TEA

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Tea (*Camellia sinensis L.*) is one of the ancestral cultures cultivated by man, currently spread in about 50 countries on all continents, tea consumption being a favorite drink throughout the world. Research has shown antibacterial and antifungal activity of tea extracts [1, 2]. The purpose of the research was to elucidate the antimicrobial activities of intact and oxidized tannins isolated from commercial green and black tea leaves.

Antimicrobial tannin activity was tested on *Bacillus, Pseudomonas, Erwinia, Xantomonas*, and *Alternaria* and *Fusarium* filamentous fungi. The bacteria *B. subtilis*, *Ps. fluorescens*, *E. amylovora, E. carotovora, X. campestris* were cultured on peptone agar, supplemented with tannins at concentrations of 1.25; 0.6; 0.3; 0.15; 0.07; 0.035; 0.0017; 0.0085; 0.004%. The bacterial concentration of 4.8 x $10^8$ UFC / ml used in research is the bacterial turbidity of 2.0 according to McFarland index. Screening of antifungal activity of tannins was performed by supplementing them at concentrations of 0.002; 0.01; 0.05; 0.25% on PDA nutritional medium (potato dextrosis agar).

Intact tannin extracts from green tea showed antibacterial activity (*B. subtilis, P. fluorescens, E. amylovora, E. carotovora, X. campestris*) in the concentration range 0.07 ... 0.25% and oxidized – 0.017 ... 1.25%, which indicates that the increase of the total content of functional groups (carboxyl and phenolic) in the process of oxidation of extracts leads to increased antibacterial activity. Thus, the oxidation of green tea tannin extracts contributed to the significant increase in the antifungal activity (*A. alternata, F. oxysporum, F. solani*), manifested by the inhibition of colony growth and the decrease of mycelial density, especially in the concentration of 0.25%.

Black tea tannin extracts showed antibacterial properties in the concentration range of 0.035% -0.07% and anticandidal at the concentration of 0.017%. The strongest suppressive effect for *D. sorokiniana* was confirmed at a concentration of 0.05%, the diameter of the colony being 13.6-20.0% lower than in the control variant. In all of the studied variants the mycelial density was 3-3.5 times lower than in the control variant. Also, under the influence of these extracts there was a significant discoloring of the mycelium, which denotes the strong capacities of pigmentogenesis inhibition, which leads to a decrease in the adaptability and pathogenic potential of the fungi.

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**P113**

# EVALUATION OF THE QUALITY OF WATER FROM DIFFERENT SOURCES OF MOLDOVA

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Water quality is one of the major challenges faced by the society in the 21st century, which can compromise human health, limit food production, impair ecosystem function and slow down economic growth. Water quality deterioration directly affects environmental, social and economic problems. Availability of water resources becomes increasingly limited due to fresh water pollution, caused by the discharge of untreated or insufficiently treated waste water to rivers, lakes and coastal areas. In September 2015, at the 70th Session of the UN General Assembly, the Sustainable Development Goals by 2030 were adopted. This document emphasizes the water quality issues as one of the major international problems. The requirements to the quality of drinking water in Moldova are regulated by the Governmental Decision № 934 of 15.08.2007 concerning Sanitary Norms of mineral waters and drinking waters. It states the maximal admissible concentrations for the parameters negatively affecting human health.

During 2018, 145 water samples from wells and artesian wells from different regions of Moldova were analyzed, and the conformity of their chemical composition to the Governmental Decision № 934 was evaluated. Only 44 samples (30%) of them complied with requirements to the drinking water quality for all the parameters. For 145 samples, 1379 analysis were carried out. In 20% of cases, the concentrations of the analyzed parameters exceeded the maximum allowable concentration.

1) In 69.7% of cases, one or more parameters of the water from the analyzed wells and artesian wells did not meet the drinking water requirements. The exceedance of the concentration can vary greatly for different parameters.
2) The characteristic features of the waters from artesian wells are increased amount of ammonia and ammonium ions, hydrogen sulfide and soluble sulfides, sodium ions, increased oxidability, and the content of the salts causing water hardness below the maximal allowable value.
3) The characteristics of the waters from wells are high values of nitrate content, water hardness and dry residue.
4) None of the analyzed samples had heavy metals (Cd, Pb, Ni, Cr) content exceeding the allowable limits.
5) All analyzed bottled waters conformed the Governmental Decision № 934 with data indicated on the product label.

The present research confirmed the need for evaluation of the quality of water from different sources with the aim of providing the population with good quality drinking water.

**P114**

# THE INDIRECT METHOD OF ATOMIC ABSORPTION DETERMINATION OF NITRATE ION IN COLORED WATER

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Nitrate ions are toxic pollutants. Their maximal allowable concentration in drinking and mineral waters is 50 mg/L. Most wells of Moldova contain high concentrations of nitrate ions. Thus, nitrate ion concentration monitoring in waters of Moldova is a very relevant issue.

For determination of nitrate ions in colored water, the methods of choice will be the methods not compromised by sample color, e.g. chromatographic, capillary electrophoresis. These methods are expensive and involve special equipment.

We suggest an indirect atomic absorption method of determination of nitrate by the excess of silver ions (after formation of the silver -1,10-phenantroline-nitrarate ternary complex).

The indirect atomic absorption method of determination of nitrate is based on the formation of insoluble complex $[Ag(Phen)_2]NO_3$ when an excess of $[Ag(Phen)_2]^+$ is added to the nitrate containing sample. After separation of insoluble precipitate of $[Ag(Phen)_2]NO_3$ complex, the excess of silver ions is determined by atomic absorption method.

Optimal conditions of atomic absorption determination of silver were found; the linear interval of calibration curves was set (correlation coefficient not less than 0.999).

Metrological characteristics of methods were evaluated. The accuracy of determination of nitrate ion, carried out according to the suggested method, was evaluated by the standardized solution of nitrate ion with the concentration of 62.0 mg/L. The recovery was 96.8%. The variable error of the suggested method was evaluated as a variation coefficient, calculated for 10 measurements. CV (n=10) – 6.57%.

The evaluation of the accuracy of determination of nitrate by the suggested method was also carried out using a real colored water sample by standard addition method. From 50mg/l introduced, 47.3 mg/l were recovered. The recovery was 94.6%.

*Conclusions:*

1. The method of determination of nitrate ion in the form of its silver phenanthroline complex in colored waters by indirect atomic absorption method by excess of silver ions is suggested.
2. The conditions for silver determination by atomic absorption spectrometry are adjusted.
3. The accuracy of this method is evaluated by the standardized solution.
4. The accuracy of this method is evaluated on real colored water sample by the standard addition method.
5. The variable error was determined as variation coefficient.

**P115**

# TREATMENT OF DIRECT RED DYE AND FREE-FORMALDEHYDE SISTEM BY ELECTROFLOTATION

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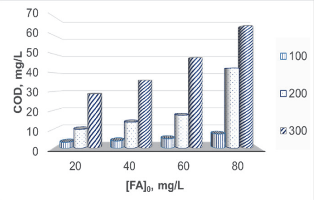
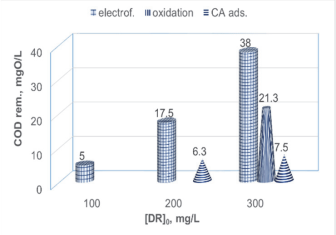
The applications of electrochemical technologies based on electroflotation for removal of such pollutants as organic compounds expressed through Chemical Oxygen Demand (COD) from wastewaters are discussed [1]. Experiments were performed into an electroflotation cell with two electrodes: carbon anode and a stainless steel cathode which were placed on the bottom of the cell in order to establish the optimal operational conditions (e.g.: electroflotation time, electric current intensity) for removal efficiencies of more than 95% COD. The objectives were to (i) determine the chemical oxygen demand (COD) of mixtures containing direct red dye and free-formaldehyde (DR-FA) and (ii) establish the sequence of effluent treatment methods. COD (mgO/L) concentration was measured by potassium dichromate standard method using UV-Vis spectrophotometer T 80+.

The laboratory research was focused on DR-FA systems with electrofloatation with different concentrations of dye and free-formaldehyde. Synthetic samples of wastewater which contain direct red dye (concentration ranges from 100 to 300 mg/L) and free-formaldehyde (concentration ranges from 20 to 800 mg/L) were introduced into the electroflotation cell. Experiments were carried out at the room temperature, at a steady rate, for 10 min. In all experiments 0.002 L NaOH (1M) was added to increase the conductibility. The pH value of synthetic wastewaters was 6.5. The solution current density was 0.5 Am$^{-2}$. It can be considered favourable for electro flotation.



It is to be noticed that the electroflotation method applied in the first step is effective only for the system which has 100 mg/L concentration of dye.At double dye concentrations, COD values increase in 3 times and when the system contains 300 mg/L of dye the COD values are 9 times higher than in the first system.According to the results (Fig. 1), the effect of removal depends largely on the concentration of the dye because the method is based on the principle of the electrochemical processes of oxygen and hydrogen evolution during electrolysis of wastewaters.The gas bubbles have raised the associated dye particles to the surface of the liquid. However, if the concentration of the dye grows, the molecular weight of the particles will also increase and will not concentrate the foam. Thus, it was necessary to combine physico-chemical methods to achieve CMA (6-8 mgO/L). The DR-FA system with a 200 mg/L concentration of dye and 20-80 mg/L of free-formaldehyde was treated by electro flotation and adsorption by active charcoal.The last system was treated by combining of 3 methods: electrofloating-oxidation with Fenton's reagent and adsorption of mineralized/ degraded compounds on active charcoal (Fig. 2).



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**P116**

# THE TROPHICAL STATE OF LAKES FROM THE DNIESTER RIVER BASIN

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The trophic status of the lake ecosystem is the result of a complex interaction of processes that occur under the influence of natural and anthropogenic factors not only in the reservoir itself, but also in the entire hydrographic basin.

Increasing nutrient and organic content is therefore a particular threat to the internal environment, especially small reservoirs whose self-purification capacity is significantly reduced, generating eutrophication by stimulating excessive algal growth.Eutrophication status of lakes was assessed using conventional classification [3] on the one hand, and Carlson trophic status index (TSI) on the other hand [1].

The ecological potential of the lakes in the study area by the trophic index was assessed by determining the transparency (Secchi disc), the content of chlorophyll ”a”, total phosphorus and oxygen saturation [2].

The concentration of chlorophyll ”a” in the lakes studied ranges from <1 μg/L in Ghidighici lake (used for irrigation, recreation and fishing) to 242.7 μg/L in Salas Lake (used as a food reproduction of the Gura Bacului farm); the $P_{tot}$ values range from 0.85 μg/L in Lake 1, Telita Noua and Ghidighici lake to 32.61 μg/L in Salas Lake; the transparency is within the range of 0.2-0.6 m. Based on these parameters, the $TSI_{tot}$ and the trophic status of lakes have oligotrophic characteristics for lakes 1 Telita Noua and Ghidighici, mesotroph for Lake Telita Noua and eutrophic for Salas Lake (table). The trophic status, after oxygen saturation of the water of the studied lakes, has oligotrophic and ultra-oligotrophic characteristics (70 - 111%).

**Table.** Interpretation of values of the trophic status index of lakes in the area of the study area

| Sample | Chl, μg/L | SD, m | $P_{tot}$ , μg/L | Saturation, % | $TSI_{Chl}$ | $TSI_{SD}$ | $TSI_{Ptot}$ | $TSI_{tot}$ and trophical state |
|---|---|---|---|---|---|---|---|---|
| Lake 1, Telita Noua | 0 | 0.4 | 0.85 | 74.07 | 30.6- | 73.2 | 1.8 | 35.2 - oligotrophic |
| Lake 2, Telita Noua | 23.68 | 0.12 | 4.24 | 109 | 33.8 | 76.5 | 25 | 45.1 - mezotrophic |
| Lake Salas | 242.7 | 0.2 | 32.61 | 97.5 | 36.1 | 83.2 | 54.4 | 58- eutrophic |
| Lake Ghidighici, at the dam | <1 | 0.5 | 0.85 | 111 | 30.6 | 70 | 1.8 | 34 oligotrophic |

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**P117**

# VEGETAL ACTIVE CARBONS FOR ADSORPTION OF TOXIC METAL IONS

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The presence of heavy metals in the environment is a major concern due to their toxicity to many life forms. With the increase in the number of nuclear power reactors, the radioactive pollution of water and soil is growing. Heavy and radioactive metals (such as Pb, Cd, As, Cs, Sr, Co, Hg etc.) are persistent pollutants with potential hazards, which are characterized with a high toxicity, difficult biodegradation, and are easily accumulated in organisms [1]. Adsorption on active carbons is one of the procedures used for binding of toxic metals [2,3].

In this study, activated carbons of local origin (Republic of Moldova) were tested for adsorption of toxic metal ions. Active carbons from the apple wood (CA-M) and nut sells (CA-N) were oxidized with nitric acid (sample CA-Mox) and mixture of nitric acid/urea (samples CA-Mox-u and CA-Nox-u) in order to improve their ion-exchange properties. Activated carbon surface functional groups were evaluated by the Boehm titration method. Obtained oxidized samples were tested for adsorption of toxic metal ions (Co, Sr, Cd, Pb, Hg, Cs) from aqueous solutions. The samples CA-Mox-u and CA-Mox showed the higher affinity for cobalt(II), strontium(II) and lead(II) ions. Obtained results (sorption isotherms, pH and conductivity values of equilibrium solutions) suggest the ion-exchange mechanism as the main one for adsorption of cobalt (II) ions on samples CA-Mox and CA-Mox-u.Comparative analysis of active carbons sorption capacity for toxic metal ions from solutions reveal the oxidized samples (CA-Mox, CA-Mox-u, CA-Nox-u) as efficient adsorbents.

## Acknowledgements

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**P118**

# EFFECT OF THE ADDITION OF AMMONIUM FERRIC CITRATE AND TITANIUM DIOXIDE ON THE SURFACE PHOTOCHEMISTRY OF SOME DICARBOXIMID GROUP FUNGICIDES

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Implementation of intensive agriculture with positive aspects gives also a problem of pollution of agriculture products, soil and as a consequence ground water with organic pollutants. The possible way to resolve this problem is the usage of additives, which can accelerate phototransformation of pollutants. Caused by high agriculture impact dicarboximide fungicides were chosen as model specifically iprodione, procimidone and vinclozolin. As additives the substances were chosen allowed for use in alimentation as food additives: titanium dioxide (E171) and ammonium ferric citrate (E 381).

The pesticides were spread on silica and cellulose surfaces and the photo-degradation was followed under UV and sunlight irradiation. The main reaction pathways involve heterolitic and homolitic cleavage and cleavage of the N─CO bond. The main products are 3.5- dichlorphenyl isocyanate and 3.5- dichloroaniline, obtained without additives and with ammonium ferric citrate and titanium dioxide addition. In case of titanium dioxide the degradation is much faster and no photo-products were detected in case of $TiO_2$ usage (0.3 % w/w), sprayed as a water suspension. In case of $TiO_2$ water suspension with concentration 0.1 % products identic to ones obtained during natural phototransformation were detected.

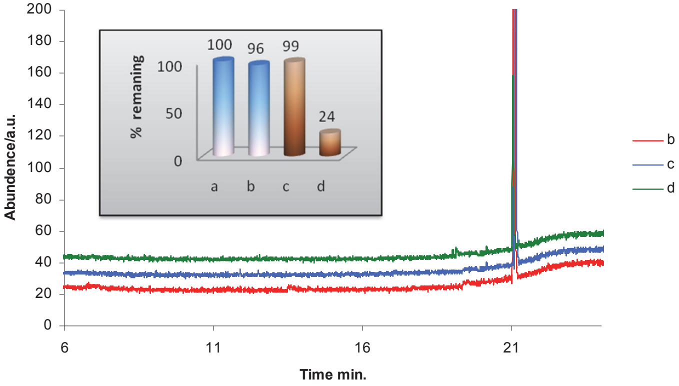

**Figure.** GS-MS traces and remaining residues of the fungicide procymidone after two hours irradiation under sunlight on silica. (a) non-irradiated without additive; (b) sunlight irradiated without additive; (c) non-irradiated with $TiO_2$ and (d) sunlight irradiated with $TiO_2$.

**P119**

# WATER-MISCIBLE PIGMENTS FROM TIRE PYROLYSIS RESIDUES: PREPARATION AND PHYSICO-CHEMICAL CHARACTERISATION

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Pyrolysis is a widespread recycling technology of polymeric waste. Used tires being pyrolysis lead to the formation of three components: fuel fraction which being subjected to purification to yield gasoline and diesel fuel, steel wire which is recycled and carbon black that is accumulated contaminating the thus environment.This is explained by the specific properties of carbon black: small, hydrophobic particles that easily disperse and pollute the environment, is a possible carcinogen for humans; short-term exposure to high concentrations can cause discomfort in the upper respiratory tract.At the same time, the carbon black obtained from tire pyrolysis, contains a significant amount of fuel and is not miscible in polar solvents such as water.This makes the field of use of carbon black is narrow –it is necessary remove adsorbed fuel from particles and render them hydrophilic properties,thus obtaining a black pigment, the fields of use of which substantially increase:pigment for the production of pavement, decorative mortar, lacquers and paints, supplement for construction and repair of road.

Investigated tire pyrolysis residue is a homogeneous, finely dispersed, water-immiscible black mixture. In order to assess the thermal stability of the residue, thermal analysis was performed in a dynamic air atmosphere. Based on the results of the thermal analysis, preventive degassing of the soot at 200-250°C is recommended for evacuate volatile substances for preventing their accumulation and explosion. To obtain a homogeneous product oxidation with air is recommended to be carried out at 350-400°C by continuous mixing.

An important parameter of pigments and additives is the specific surface of adsorption. Having a high specific surface area, the pigment better interacts with components of the mixture, contributing to greater homogeneity and stability of mixture. The nitrogen adsorption isotherms at 77K were measured for the initial and oxidized sample. The results of the measurements showed that the specific surface increases significantly from 20 $m^2/g$ to 60 $m^2/g$.

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**P120**

# EVALUATION OF TOTAL CAROTENOID CONTENT IN FUNCTIONAL FOOD PRODUCTS ENRICHED WITH ROSEHIP POWDER *(ROSA CANINA)*

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There is an increased interest for sources of natural antioxidants such as carotenoids in order to enrich food products to increase the product shelf life. The rosehip berries *(Rosa Canina)* are natural concentrate of vitamins (C, P, B1, B2, E, K), carotenoids, folic acid, volatile oil, etc. The aim of this study is to evaluate the physico-chemical characteristics of functional food products enriched with rosehip powder. For this purpose, it is intended to analyze the total carotenoid content of the studied rosehip powder by spectrophotometric methods. The results showed an amount of $\beta$-carotene 17.18±0.04 mg/L; lycopene 18.13±0.02 mg/L; zeaxanthin 18.02±0.04 mg/L. Evaluating the carotenoids content of functional products enriched with rosehip powder we can conclude that there is a high possibility to motivate the continuous use of this compounds in the production of functional food products. Also, there are possibilities to replace synthetic additives with natural ones thus offering to consumers high quality and safe for consumption food products.

**P121**

# CONCURRENT CHEMICAL EQUILIBRIA IN NATURAL AQUEOUS SYSTEMS

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Long-term prediction of the concurrent chemical processes and their practical consequences is only feasible by using simulation models. The paper presents an original thermodynamic approach to the study of complex chemical equilibria in real conditions, taking into account the complex formation reactions in natural aqueous multicomponent systems, as natural waters and soil solutions. Its quintessence consists in the thermodynamic analysis of the conditions of various processes on the basis of their derived total thermodynamic characteristics. In the case of complex formation reactions in heterogeneous multicomponent systems, the total change of Gibbs energy cannot be presented as a sum of contributions of several separate reactions [1]. The thermodynamic and computer modeling in heterogeneous multicomponent systems "mineral – natural aqueous systems" are extensively used [2,3]. Methods for solving the problems of shift from chemical-analytical, descriptive characteristics of the systems to the quantitative study of their chemical equilibria by thermodynamic and computer modeling are described. The analyzed processes include the heterogeneous interaction of minerals and aqueous solution, homogeneous reactions of hydrolysis and complex formation, as well as the acid-base, redox, buffers, and other important soil properties. Despite numerous studies of soil solutions in natural and laboratory conditions, many questions of their composition and transformation, as well as assessment of anthropogenic impacts and forecasting natural processes, remain unresolved. The development of our understanding on the relationship of processes and their quantitative assessment, based on thermodynamic equations of chemical equilibria, allow in many considered cases to replace the time-consuming determination of total content and mobile forms of chemical elements on easily measured pH values, the analytical (total) concentration of components, etc.

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**P122**

# BUFFER ACTION OF HETEROGENEOUS MULTICOMPONENT SYSTEMS "MINERAL – NATURAL WATERS"

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The determination of the buffer capacity of natural waters and soil allows calculating the pollutant amounts which delivery does not essentially break the natural character of their functioning. This question is the major one in the soil sciences, ecology and wildlife management. The complexity of the soil solution composition containing mineral phases and a large set of involved chemical compounds determine the possibility of simultaneous chemical reactions along with the capacity of solid phases of minerals to maintain relatively constant the aqueous solution composition [1]. Under real conditions, the buffer action of natural heterogeneous aqueous systems is expressed as the consumption of any element from solution, which causes the partial dissolution of solid phases and as a result the chemical composition of the solution is restored.The provision of plants is generally assessed by the potential buffering capacity of soils in relation to the elements of plant nutrition. The smaller the ion activity changes as conditions change, the higher the buffering capacity of the soil, the more stable conditions of plant nutrition [2].

The main focus in this paper is to show how to use the developed buffer theory for assessing and predicting the long-term phenomena of attenuation and natural remediation of ionic pollutants in contaminated aquatic ecosystems, as natural waters and soil solutions. This theory is used for analyzing the way by which metal ions move and transform within the environment, their distribution in ecosystems, their deposition and cycling in the terrestrial environment. The buffer theory is based on the rigorous thermodynamic analysis of complex chemical equilibria under environmental conditions in aquatic ecosystems. It has been established that both homogeneous and heterogeneous systems manifest a buffer action towards all their components. The buffer properties in relation to the solid phase components are amplified with an increase of solubility due to protolytic or complex formation equilibria in aqueous saturated solutions. It has been established, that the buffer capacities of components are mutually proportional, whereas for heterogeneous systems these relationships depend on the stoichiometric composition of solid phases.

The use of the developed buffer approach yields extended knowledge and a deeper understanding of the processes that control the concentrations of various components. The obtained results are intended to provide researchers with a tool needed to set reliable limits of ionic pollutant levels in the environment.

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**P123**

# THERMODYNAMIC APPROACH FOR STUDYING COMPLEX CHEMICAL EQUILIBRIA IN REAL CONDITIONS

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As a result of thermodynamic data accumulation, an expected topic for chemical thermodynamics arises based on the thermodynamic data known for separate reactions, to calculate the integral thermodynamic characteristics of the previously unstudied processes. The multi-component heterogeneous system is formulated herein as biphasic system "precipitate (solid phase) - solution (liquid phase)", in which a series of simultaneous reactions occur and the contribution of each depends on the chemical composition of the system, that is the ratio of the concentrations of the constituent components [1]. In this regard, an increased interest acquires the direct and indirect problems of the chemical thermodynamics in the heterogeneous multi-component systems. In this context, the direct problem consists in calculating the thermodynamic functions of the overall process based on the thermodynamic characteristics of the particular reactions. The indirect problem is to calculate the thermodynamic characteristics of separate reactions based from the overall functions. On the other hand, the practical importance of buffer systems, as well as the need for focused search and the creation of new perspective buffer systems, have made the necessity to develop quantitative principles of the theory of buffering properties of multicomponent heterogeneous systems.

The paper presents a new thermodynamic approach to the study of complex chemical equilibria in real conditions, taking into account the complex formation reactions in multicomponent heterogeneous systems. Its quintessence consists in the thermodynamic analysis of the conditions of various processes on the basis of their total thermodynamic characteristics. In the case of taking place of reactions of complex formation, hydrolysis and protonation in heterogeneous multicomponent systems, the total change of Gibbs energy cannot be presented as a sum of contributions of several separate reactions [2]. Original methods for determining such thermodynamic characteristics as the solubility and solubility product, as well as the stability constant of chemical compounds of the arbitrary composition in the heterogeneous multicomponent systems are also described. The quintessence of the elaborated formal thermodynamic approach consists in the analysis of the conditions of different processes based on the overall thermodynamic characteristics. The authors prove that in the case of the multi-component heterogeneous complexation complexation reactions, the total Gibbs energy variation cannot be presented as a sum of the contributions of separate reactions. The calculation of the global Gibbs energy variation of complex chemical processes allows determination of the thermodynamic stability domains of solid phases, the direction and optimum conditions for chemical processes under conditions close to the real ones.

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**P124**

# INDEX OF AMMONIA IONS NITRIFICATION IN BAC RIVER WATER

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Ammonia and nitrogen concentrations more than 1 mg/L in natural waters have been given as indicator of organic pollution, caused by livestock, intensive agriculture, industrial effluents and liberation of domestic sewage in courses of superficial waters, and can be toxic to aquatic species if they are higher than 2.5 mg/L [1].

Unpolluted waters contain small amounts of ammonia and ammonia compounds, usually <0.1 mg/L nitrogen. Total ammonia concentration in surface water are typically less than 0.2 mg/L N but may reach 2-3 mg/L N [2]. In the nitrogen cycle the oxidation of ammonia to nitrate by microorganisms is a key process, resulting in nitrogen loss from ecosystems, eutrophication of surface and ground waters.

One Nitrification Index (NI) was proposed for chloraminated drinking water in distribution system [3]. In order to evaluate the nitrification process in surface waters was developed a NI, which characterizes the intensity of ammonium nitrification under natural conditions (in the presence of biota and the existing pollution level) with the formula (in mg/L N): NI = $(N\text{-}NO_3 \cdot 100) : (N\text{-}NO_3^- + N\text{-}NO_2^- + N\text{-}NH_4^+)$.

In this study was determinated the ammonia, nitrite and nitrate nitrogen content in river Bâc in comparison with Dniester river water for calculation of theNI. It has been found that the NI of Dniester river water has value of 94% (effective nitrification) with the exception of water downstream of the Bâc river, where NI is only of 13%. Nitrification is practically absent in Bâc river water until the Dniester spill (2.6%) (Table).Based on the NI values, obtained in the laboratory modelling, it is concluded that in the addition of ammonium ions, which can be discharged by the waste water, in just 30 days nitrification of the ammonium ions has passed both stages.

**Table.** Dynamic of NI in the study of surface waters, based on the laboratory modelling results

| Sample | river Dniester | | The Bâc river until the Dniester spill |
|---|---|---|---|
| | Upstream of Bâc river overflow | Downstream of Bâc river overflowing | |
| Natural water | 94 | 13 | 2,6 |
| day 1 | 96 | 10 | 4 |
| day 10 | 29 | 17 | 6 |
| day 20 | 97 | 98 | 74 |
| day 30 | 100 | 100 | 97 |

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**P125**

# STUDY ON THE ACTION OF NANOPARTICLES OF $Fe_3O_4$ AND $Fe_0$ ON MICROORGANISMS

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Metal nanoparticles are currently used in various areas. It has been a significant increase in the number of phytotechnology research, NP use of Fe, also affecting the microbial population, microalgae and cyanobacteria. The results obtained previously within the IMB of Moldova have shown that iron-based nanoparticles can enhance the activity of microorganisms as well as the efficiency of soil bioremediation processes of POPs (Persistent organic pollutants) by: (a) the radical reduction of the number of manipulations necessary to remedy the polluted soil, (b) reducing the 3-fold processing time required to decompose the pollutant into the soil, and (c) increasing the degree of pollutant mineralization in soil by 4 times.

Because the strains of microorganisms selected as potential POPs have a well-outlined perspective for use in various polluted soil bioremediation processes and technologies, there is a clear need to preserve and conserve these strains.

As a subject of study were: (1) - 3 strains of microorganisms from CNMN selected as potential POPs destroyers: *Penicillium* sp.11; *Streptomyces* sp. 205 and *Bacillus* sp. 2; (2) $Fe_3O_4$ and Fe(0) nanoparticles, synthesized in Solid State Structures Laboratory of the Institute of Electronic Engineering and Nanotechnology "D. Ghiţu ", to whom we thank.

To obtain the biological material subjected to lyophilization the strains were grown in glass tubes, *Penicillium* sp. 11 and *Streptomyces* sp. 205 on Czapek agar medium with glucose for 7-14 days at t°= +30°C and +27°C, respectively, and the strain *Bacillus* sp. 2 for 48 hours to +35°C. For lyophilization strains were used in the stationary growth phase.

As a protective medium served: *Penicillium* sp. 11 strain - skimmed milk + 7% glucose; *Streptomyces* sp. 205 - 2.5% gelatin + 7.5% glucose; *Bacillus* sp. 2 - skimmed milk + 12% sucrose (control medium) and their variants, using as a supplement NPof $Fe_3O_4$ and Fe(0) in concentration (mg/L): 1; 5; 10.

The lyophilization was carried out on freeze-drier „LABCONCO” FreeZone Plus 6 Liter Cascade Console Freeze Dry System (SUA), at a condenser temperature of -88 ... -94°C in vacuum 6-7 Pa, the pre-freezing temperature for *Penicillium* sp. 11 and *Streptomyces* sp. 205 was -50°C, and for the strain *Bacillus* sp. of -20°C for 12 hours.

The titre of the suspension subjected to lyophilization and the viability of the cultures after lyophilization were determined. The culture viability was calculated according to the formula $c\% = (\log UFCml^{-1}{}_{fin} / \log UFCml^{-1}{}_{in}) \times 100\%$, where $\log UFC\ mL^{-1}{}_{in}$ is the logarithm of the number of colony forming units before lyophilization, $\log UFC\ mL^{-1}{}_{fin}$ - logarithm of the number of colony forming units after lyophilization or preservation and c - viability of the strains in percent.

The results obtained in this study have shown that the use of both nanomagnetite and nanoparticles of Fe(0) in concentrations of 1 - 10 mg/L in the protective medium for the lyophilization of the nano-bioremediating potential strains: *Penicillium* sp. 11, *Streptomyces* sp. 205 and *Bacillus* sp. 2 did not result in essential changes in strain viability, so it varies within the control up to 3-5% and can not be recommended as lyoprotectors for freeze-drying and long-term maintenance of the studied strains.

**P126**

# EQUILIBRIUM STUDY OF PENTACHLOROPHENOL SORPTION IN SOIL MATRIX

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The main objective of the study was to evaluate the sorption equilibrium of pentachlorophenol (PCP) on soil and to predict the mechanisms of the sorption process. Experimental investigations were carried out in batch system, using an urban soil (collected from Iasi, N-E of Romania) for the sorption of PCP molecules from aqueous solutions. In the studied temperature range, the resulted isotherms (Figure 1) indicated that the amount of PCP sorbed on the soil particles increases with the temperature, in the range 10 to 25°C. Further, in the temperature range 25-50°C, the amount of pesticide molecules retained decreases with temperature rising. The decrease of sorption capacity with temperature indicates that low temperatures may favor the sorption of pentachlorophenol in the selected soil.

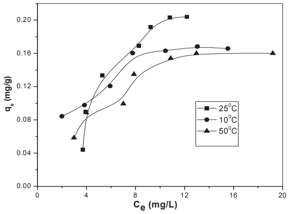

**Figure 1.** Equilibrium isotherms of PCP onto soil at different temperatures
(T = 10, 25, 50°C; t= 72 h; $m_{sol}$=1 g)

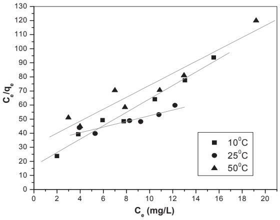

**Figure 2**. Langmuir isotherm applied for PCP sorption onto soil at different temperatures
(T = 10, 25, 50°C; t= 72 h; $m_{sol}$=1 g)

The experimental data were analyzed using different mathematical models available for pollutants sorption onto soil, such as: Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Halsey. Experimental results fitted better the Langmuir model (Figure 2), suggesting the homogeneous nature of the process, and that the sorption process takes place in monolayer. Also, the values of separation factor, $R_L$, between 0-1 indicate that the process is favorable for the retention of PCP molecules onto soil particles. According to Freundlich isotherm model, the obtained values of $1/n < 1$, suggest that the pesticide sorption in soil occurs rather through weak, physical bonds (through van der Waals forces) being most prevalent than chemical bonds. The values of adsorption intensity 1/n, less than the unit, confirms that the mobility of the compound in soil can be significantly higher at high concentrations. Considering the experimental results, we can conclude that pentachlorophenol shows high mobility in the investigated soil, and the sorption mechanism is well described by Langmuir equation.

***Acknowledgements***

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**P127**

# RESIDENCE TIME DISTRIBUTION DIAGNOSIS ON FOUR LAMPS PHOTOCHEMICAL REACTOR

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The four lamps photochemical reactor under study is the central element of a laboratory scale hybrid wastewater treatment system that combines photo, sono and chemical methods. It is equipped with four UV-C lamps protected with quartz tubes that can be used in three configurations of one, three or four at one time and it is designed to function either horizontally or vertically.

Residence time distribution method (RTD) or "tracer" method was proposed by Dankwerts in 1953 [1] and was further developed by Levenspiel [2, 3]. Nowadays it is considered a classical analysis method and a convenient diagnosis tool for understanding the vessel hydrodynamic and characterization of flow systems [4].

A sodium chloride solution of 20% mass concentration was used as a tracer, the response being registered with a WTW conductivity meter Cond 315i. The RTD methodology was used to characterize mixing and flow inside the real reactor and to compare with an ideal model.

Since the primary data, (obtained earlier) clearly indicated the occurrence of short-circuits (tracer leaving the photochemical reactor very fast) even at low volumetric flow rates, some design solutions were considered. The most appropriate from constructive point of view was the modification of the inlet nozzle geometry in such manner that the inlet flow would enter not parallel with the reactor axis, quartz tubes and walls (axial flow) as in the initial design but perpendicularly on the reactor axis (radial flow). Consequently, the quartz tubes could act like baffles or turbulence promoters improving the mixing within the reactor.

This paper presents a RTD based comparative study of axial vs radial flow in horizontal and vertical set-up of a four lamps photochemical reactor. The evidence of short-circuits and dead-zones was experimentally demonstrated using the tracer method. Constructive design solution were considered in order to achieve a convenient mean residence time.

**Acknowledgements.** This work was supported by a research grant of the TUIASI, project number GnaC2018_20/2019.

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## P128

# CHARACTERIZATION OF POTASSIUM CARBONATE SOLUTIONS PROMOTED BY ETHYLENEDIAMINE AND TRIETHYLENETETRAMINE. DENSITY OF AQUEOUS SOLUTIONS: MEASURING AND CORRELATION

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Potassium carbonate solution ($K_2CO_3$) is a widely used solvent for $CO_2$ removal due to the low toxicity, low tendency of degradation, less energy requirement, high solubility in carbonate / bicarbonate system and other concerns asthe corrosion. For absorption, an aqueous solution of 20-40% $K_2CO_3$ is used as close as possible to the saturation without the phenomenon of crystallization [1,2,3]. Since the rate of $CO_2$ absorption is relatively slow in $K_2CO_3$, the use of various promoters has been required. In this work, ethylenediamine (EDA) and triethylenetetramine (TETA) were chosen as rate promoter candidates.

Prior to the experimental determinations specific to the absorption process, all the physical properties involved must be known: the viscosity and density of the solution, the $CO_2$ diffusion coefficient in the amine solution, as well as the Henry constant for $CO_2$ in the amine solution [2,3]. The densities of the ternary aqueous solutions ($K_2CO_3$-Amine-$H_2O$) have been measured for a blending 25 wt % potassium carbonate, amine concentrations between 1 and 10 wt %, at atmospheric pressure and temperatures from 303 K to 343 K (Figure). The densities for each solution have been measured with an Anton Paar digital vibrating glass tube densimeter, DMA 4500 model [3]. The experimental data have been correlated with temperature through a semi-empirical equation with three coefficients which depend on the concentration and on the amine type with the equation $\rho = a+bT+cT^2$ and the constants a, b, c have been identified by regression.

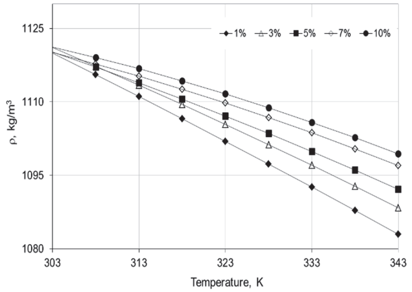

**Figure.** Density variation of $K_2CO_3$ aqueous solution with EDA as promoter

**Acknowledgements.**This work was supported by a research grant of the TUIASI, project number GnaC2018_10 /2019.

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**P129**

# USE OF AUTOCHTHONOUS ACTIVE CARBONS FOR CREATININE IMMOBILIZATION

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The considerable increase in the number of exogenous and endogenous intoxications, diseases and pathological conditions, caused by the deplorable situation of the environmental conditions, is a very important issue of contemporary society. One of the most effective methods of detoxification of the human body is enterosorption based on the immobilization and elimination of toxins from the gastrointestinal tract. The most required enterosorbents are made from activated carbon derived from plant products, because their morphological structure favors the production of coals with high mechanical strength and increased adsorption capacity [1]. The performance (structural and adsorbent) qualities give these coals large opportunities for use in the treatment of intoxications and different pathologies [2]. With the prospect of use as enterosorbents, autochthonous activated carbons obtained from apple wood (CA-M 30) and nutshells (CA-N 30) were investigated. In order to obtain these active carbon samples, the physico-chemical process of activation was carried out in the laboratory under pilot conditions at 850ºC. The porous structure of the investigated activated carbon was determined from nitrogen adsorption isotherms ($N_2$, 77 K) using the AUTOSORB-1 automated analyzer.

In order to model intoxication situations with toxic substances, organic substances often serve as markers of exogenous and endogenous metabolites. For the purpose of studying the adsorption processes of small and medium molecular toxins (uremic toxins, methanol, ethanol etc), creatinine is used quite often, which is an indicator of renal function and monitoring its concentration within 24 hours can provide information about overall renal function. For the determination of creatinine, the method proposed by Jaffe (1972) in the modification of Beckman (1986) was used. The adsorption processes were investigated under static conditions at 22°C after the equilibrium of the process was established. The contact time of the creatinine solution with the examined active carbon samples was determined from the curve of the adsorption kinetics. Thus, it was found that during the first hour of contact time of the total amount of creatinine (Co = 100 mg/L) about 50% is immobilized, after six hours - almost 75% and 24 hours were sufficient for the balance of the adsorption process. The adsorption capacity of the adsorbed carbonate towards creatinine was determined from their adsorption isotherms. It was determined that the maximum active carbon adsorption values studied were 58 mg/g for charcoal obtained from apple wood and about 67 mg/g for coal from nut shells. The obtained data allow concluding that the investigated carbonate adsorbents obtained from the vegetable raw material are able to absorb endogenous metabolic products, like creatinine and are of interest for their use as enterosorbents.

**Acknowledgement**
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**P130**

# THE CHARACTERIZATION OF THE EXTRACT OBTAINED FROM CHESTNUT SEEDS

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The study of biologically active substances of natural origin, useful for the elaboration of the therapeutic substances, has become a major priority of the contemporary scientific community. Compounds with increased biological activity are contained practically in most plants, but in larger quantities they are in the bark, wood and leaves of oak, poplar, walnut, acacia; in leaves/roots of medicinal plants; in the fruits, beans and seeds of some species of trees and shrubs such as chestnut, blueberries, sea buckthorns, currants, horns, vines etc. [1]. Based on their therapeutic characteristics (anti-inflammatory, vasodilator, phlebotonic, anticoagulants and blood fluidizing agents), chestnut seeds were selected as a plant source for the production and study of bioactive polyphenolic compounds with a potential for use in the pharmaceutical industry.

For the extraction of polyphenolic compounds from the chestnut seeds (*Aesculus hippocastanum*), the static mechanical agitation (maceration and periodic leakage) method was carried out in three consecutive 24 hour phases, using as the solvent the 70% hydroalcoholic solution and the mass/volume of 1:5. The unified and rotavaporated extracts were dried at 45°C. The degree of extraction of the polyphenolic compounds in chestnut seeds is about 6.5% and the total polyphenolic compounds (CTCF), expressed as mg of Gallic acid per gram of plant product, is 42.15 mg GA/g. The antioxidant activity of the extract obtained from chestnut seeds, determined in the 0.5% solution, with the application of ABTS (2,2-azinobis 3-ethylbenzothiazoline-6-sulfonic acid) and DPPH (2,2 diphenyl-1-picrylhydrazyl) is quite high (AA = 77.42% for DPPH test and AA = 83.91% for ABTS test).

Hydroalcoholic extracts, obtained from plant products usually have a low degree of water solubility, which substantially reduces their potential for use. As a result of hydrogen peroxide treatment (tannin-water solubilization process described in MD 3125), new organic compounds containing functional carboxylic, peroxide, alcoholic, phenolic groups, etc., are formed [2]. The Boehm method was used to determine the total acidic (carboxyl and phenolic) functional group content. It was determined that the total acidic functional group content of the sample subjected to oxidation modification is about the order of 3.02 mg-eq/g, of which around 87% are the carboxylic groups.

The antimicrobial activity of chestnut seed extract was tested on the bacteria: *Bacillus subtilis, Pseudomonas fluorescens, Erwinia amylovora, Xantomonas campestris* and fungi: *Candida utilis*. The obtained data denote a pronounced inhibitory action on non-pathogenic and phytopathogenic bacteria and fungi, the value of activity being higher in the case of the oxidized form of the extract (effective concentration - 0.3%).

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**P131**

# EVALUATION OF THE ACTION OF Fe NANOPARTICLES ON FILAMENTOUS FUNGI

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In order to increase the biosynthetic potential of microorganisms of biotechnological interest, nanotechnology is widely applied. Areas of application of nanotechnology have become: medicine, pharmacology, biotechnology, production and processing of agricultural products, agricultural engineering, technical service, etc.

The purpose of the research was to evaluate the action of Fe nanoparticles (NP) on filamentous fungi.20 strains of micromycetes from the National Collection of Non-pathogenic Microorganisms belonging to the genus: *Aspergillus* (5), *Trichoderma* (5) and *Penicillium*(10) served as the object of the study. The action of NP: $Fe_2O_3$ (2-10 nm), $Fe_2ZnO_4$ (8-15 nm), and $Fe_2CuO_4$ (20-30 nm) has been studied on growth, morpho-cultural characteristics and antifungal activity of mentioned strains. The microbicids were cultured on both Czapekagarized and submersed media and the Czapek medium supplemented with NP of $Fe_2O_3$, $Fe_2ZnO_4$ and $Fe_2CuO_4$ at a concentration of 0.001%. Cultivation on agarizedCzapek medium was carried out on Petri dishes for 10-14 days at 28-30°C, after which the morpho-cultural characteristics of the strains were examined visually and microscopically. The submerged cultivation was carried out in 250 mL Erlenmeyer flasks on a shaker, speed-rotating 180-200 r.p.m. at 28-30°C for 6 days. As an *inoculum*, a volume of 5% spore suspension of $5x10^6$ cells/mL of the studied cultures was used. As a control the sample was investigated without application of NP. Separation of the biomass from the culture fluid was performed by filtration and gravimetrically calculated. The amount of biomass obtained was calculated per liter of the liquid medium.

The antifungal activity of the strains, belonging to the genus *Penicillium* and *Trichoderma*, was determined by the agglomeration method of the agar, after the diameter of the phytopathogen growth inhibition zone. As test strains phytopathogens were studied: *Aspergillus niger*, *Alternariaalternata*, *Botrytis cinerea*, *Fusariumsolani*, *Fusariumoxysporum*. Experiences were performed in 3 repetitions. Data processing was done using MS Office Excel 2010.

The results obtained have shown that in the cultivation of micromycetes on the agar medium supplemented with NP of $Fe_2O_3$, $Fe_2ZnO_4$ and $Fe_2CuO_4$, significant changes in the studied cultures are not produced. Some changes in the order of color or colony size have been recorded in some strains.

In the submerged cultivation of *Trichoderma* strains in Czapek supplemented with NP of $Fe_2O_3$, $Fe_2ZnO_4$ and $Fe_2CuO_4$, the growth was at the control or diminished variant. NP of $Fe_2O_3$, $Fe_2ZnO_4$, and $Fe_2CuO_4$ have been more beneficial for the growth and accumulation of biomass of strains belonging to the *Penicillium* genus. The mean value of this index varied within ± 15% of the control, more significant increases was obtained in the NP $Fe_2O_3$ and $Fe_2ZnO_4$ variants.

Also, the use of NP $Fe_2ZnO_4$ in the microbicide culture medium of *Penicillium* and *Trichoderma* species significantly stimulates their antifungal activity against phytopathogens. Pathogen inhibition zones exceed the control variant by 5-30%.

In conclusion, the NP of $Fe_2O_3$, $Fe_2ZnO_4$ and $Fe_2CuO_4$ used in the cultivation of micromycetes belonging to *Aspergillus*, *Penicillium* and *Trichoderma* genera can modify their morpho-cultural and biosynthetic properties and therefore can be used in biotechnology.

**P132**

# ASSESSMENT OF WATER QUALITY OF PRUT RIVER USING HEAVY METAL POLLUTION INDEX AND METAL INDEX

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The Prut Riveris one of the most important rivers that cross the territory of Republic of Moldova and constitutes an important source of water supply for the country. The water quality of Prut River in Republic of Moldova is monitored monthly by the State Hydrometeorological Service. Moreover, different teams of researchers from Moldova, Romania and Ukraine are actively involved in the assessment of the water quality of Prut River based on various physicochemical parameters. One of the most common and toxic pollutants found in rivers water are heavy metals.

Thus, the goal of this study was to determine the concentration of heavy metals in Prut River water and to evaluate the water quality using heavy metal pollution index (HPI) and metal index (MI). The HPI values were calculated using the formula proposed by Mohan et al. in 1996 [1], and compared with the scale used by Tiwari et al. [2]. The MI values of water samples were calculated according to Tamasi and Cini [3], and for assessment of water quality was used classification applied by Yusuf et al. [4]. In calculations were used the maximum allowable concentration for surface water regulated by the Moldovan standards [5].

Water samples were collected from the Prut River between the autumn of 2016 and winter of 2018. The sampling was carried out in Criva, Sculeni, and Cislita-Prut villages. The concentration of Mn, Cd, Pb, Hg, Ni, Cu, and Zn were monitored by applying inductively coupled plasma mass spectrometry method (ICP-MS), using a Perkin Elmer Elan DRC II ICP-MS instrument. The concentrations of Mn, Cu, and Zn were found to be well below the highest permissible value for drinking water (class I of water quality) regulated by the Moldovan standards. The Pb and Hg concentrations were below the limit of detection in all samples. The concentrations of Cu corresponded to class II of water quality. The highest concentration of Cd was observed in autumn (2.2 μg/L) at sampling point in Sculeni village. In spring the concentration of this metal waselevated (class IV of water quality) throughout the entire river flow.

The MI values of water samples were 0.46 near village Criva, 0.54 in Cislita-Prut village, and 0.96 in Sculeni village. Thus the water of Prut river is pure (class II) according this index. The HPI values of the samples were below the critical pollution index (100). The highest HPI (71) was observed at the sampling point in Sculeni village (high class). The HPI values for water sampled in Criva and Cislita-Prut villages indicated the medium class of heavy metal pollution.

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**P133**

# TESTING THE ACIDITY OF THE SOAPS

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According to the literature data, the normal level of skin pH is of 4.7 [1]. However, many dermatologists would agree that the level of 5.5 is optimal, considering that the skin has a balanced level. When the skin suffers from a pH imbalance, the bacteria that protect the skin no longer work as well; thus, when the pH is alkaline, the skin is prone to eczema, and if it is too acidic, prone to acne [1]. It is advisable to choose cleaning products that have a pH similar to that of the skin (between 4.5 and 7), the pH differs slightly according to age.

The soaps-cream combine delicate cleaning agents with moisturizing cream and offer gentle exfoliation and dead cells removal. Soaps-cream do not dry out the skin as ordinary soaps do [2].

Free acidity of cosmetic products is the percentage of free fatty acids found in the analyzed product and is conventionally expressed in the most representative fatty acid. For cosmetic products based on ordinary oils from soy, sunflower, peanuts and pumpkin, the free acidity is expressed in oleic acid (OA) [3].

The purpose of this work was to evaluate the free acidity of commercial soaps by direct titration of the samples with KOH (0.1N) solution in the presence of the phenolphthalein as indicator [4]. Two skin care cosmetics, cream soaps were used in the research: (1) cream soap „Purifying and creamy” and (2) soap „Dove”, beauty cream bar, ¼ moisturizing cream.

According to the obtained results, cream soap „Purifying and creamy” has an acidity content expressed in oleic acid (OA = 5.08 ± 0.11%) of approximately 8 times compared to soap ”Dove”, beauty cream bar, ¼ moisturizer (OA = 42.1 ± 0.2%). The results are plausible as the sample of cream soap „Purifying and creamy” is proposed for babies with normal - dry skin.

In conclusion, the pH value of skin cleansing products should be acidic and not neutral or alkaline and soaps containing fatty acid cream are ideal products for normal or dry skin.

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**P134**

# PHYSICO-CHEMICAL PROPERTIES OF THE FINEST LIGHT FRACTION OF SUBAQUATIC SEDIMENTS OF A EUTROPHIC LAKE

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The natural accumulation of soil particles washed by rainwater, their transporting and storing is a natural and inevitable phenomenon of the lake colmatation. Decreasing this process through protective strips is only partially successful [1]. The elucidation of the ways of exploiting sediments with the maximum yield in the process of the lake decolmatation is one of the basic purposes of this paper. The samples of underwater sediment from the right bank, thicket of the Ghidighici Lake have been taken. By stirring the water-sediment system and the separation in time of the suspension from the sedimented part along with periodically adding new quantities of distilled water, fractions of dispersion systems of different density and hydration have been obtained. In total, seven fractions have been separated, of which five minerals: heavy sand (1), semi heavy sandy (2), sandy-clayey (3), clayey (4), ultrafine (7) and two organic fractions; organic rough (5) and organic medium (6). The name of each fraction describes the general composition of the fraction. For example, the first separate fraction called "heavy sand" contains large sand granules and fragments of scallop shells. A separate case is the seventh fraction, the lightest one, in which the intensively hydrated fine minerals predominate. This fraction separates with great difficulty, the reason being the long duration of staying suspended. In order to facilitate the separation process of this fraction, it has been combined with a cationic surface agent (Ct SA), which forms combinations with ions from the particle structure. A series of combinations of the same amount of suspension (samples containing a constant sediment mass) were modeled in the laboratory, to which were added increasing volumes of 10-4 mol/L of N-cetylpyridine, the volume of each sample being equal. Concentrations of the series of samples were within the range of 2•10-6 - 60•10-6 mol/L of Ct SA. An obvious flocculation process occurred in samples with concentrations in the range of 16•10-6 - 48•10-6 mol/L, while in the sample with the concentration of 32•10-6 mol/L of N-cetylpyridine the flocculation was delayed. The fastest flocculation (in less than one minute) occurred in samples with a concentration of 24•10-6 and 40•10-6 mol/L of Ct SA. The braking effect of formation of floccules is most likely conditioned by particle restructuring and recombination of cationic ions with new anionic groups. For the samples treated with small amounts of Ct SA, a reference one, but also that of the closest to the beginning of flocculation process, the titrations showed a masking effect of the anionic groups. Therefore, N-cetylpyridine has also the role of masking the anionic groups of fine clay particles. The restructuring effect is repeated symmetrically at concentrations of about 32•10-6 mol/L of N-cetylpyridine. This is also confirmed by the NaOH titration of sedimented floccules, as the filling of the negative charges occurs at the gradual addition of Ct SA. On the other hand, the UV spectrum highlights the fact that, starting with concentrations of 32•10-6 mol/L of N-cetylpyridine, it is present in the solution samples in which flocculation has occurred. Therefore, other types of equilibrium with another ratio of cationic substance are required to supplement the groups still uncoupled with N-cetylpyridine, the concentration of which would be required to increase in solution. This fraction exhibits a good adsorption capacity of about 2.7 mmol/g of N-cetylpyridine.

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**P135**

# PAPERMAKING FIBER PRODUCTION BY CORN STALKS MICROWAVE ASSISTED COOKING

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The pulp and paper industry is a good example of biorefinery concept, which incorporates the production of materials, chemicals and energy, through established technological processes that maximizes the value of wood chain. In pulp and paper industry, wood is traditionally the most used virgin fiber source causing forest overexploitation in many parts of the world. The industry is facing a continuous need for virgin fiber resources to overcome different market demands. Moreover, packaging is lately turning towards green alternatives by replacing plastics with fiber based materials such as paper and cardboard. In such context a shift of the industry to processing nonwood fiber sources is acknowledged. Attractiveness of nonwood fiber sources resides in their lower lignin content, availability and shorter growing cycle. The idea of the present study is focused towards exploring the possibility of using corn stalks (*Zea mays*) as raw materials for bio-based industry applications. This category of agricultural waste is cheap and highly available. Corn stalks are generated in amounts of about 1.7-4.5 t/ha depending on the cultivated variety [1]. The chemical composition of corn stalks is displayed in Table 1 [2]. Corn stalks processing can lead to cellulosic fibers suitable for packaging paper production, sugars that are to become feedstock for the fermentative processes such as bioethanol production.

**Table 1.** Chemical composition of corn stalks constituent parts.

| *Component* | *Chemical composition, %* | | | |
|---|---|---|---|---|
| | ***Cellulose*** | ***Lignin*** | ***Pentosans*** | ***Ash*** |
| Stalks | 39.4 | 20.1 | 25.2 | 0.81 |
| Pit | 31.6 | 17.0 | 27.3 | 0.79 |
| Leaves | 31.3 | 17.4 | 21.2 | 7.0 |

Microwave irradiation of materials containing polar molecules induces their heating. This phenomenon has multiple applications ranging from food heating to chemical processing and organic synthesis. Microwave effect on the biomass during alkali or acid treatments could enhance the separation of its' components. Our experimentally trials integrates a number of tree modules: first module includes preliminary microwave heating pretreatments of corn stalks aiming at the removal of hemicelluloses and sugar monomers; a secondary module deals with alkali pulping also under microwave irradiation of corn stalks to separate cellulosic fibers, which are to become raw materials for paper production and ecological packaging. Our findings provide information regarding the possibilities and opportunities to process low-cost raw materials such as corn stalks to produce high-value bio-based materials.

**Aknoledgements.** This work was supported by a research grant of the TUIASI, project number GnaC2018_15 /2019.

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**P136**

# REPRODUCIBILITY ASSESSMENT FOR NMR METABOLOMICS

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NMR spectroscopy is the most informative spectroscopic technique for structure elucidation of liquid compounds or compounds in solution. However, the NMR technique is less sensitive than other spectroscopic techniques and, in the same time, it is more affected by experimental factors. These drawbacks delayed the introduction of fully automated NMR analyzers in comparison with analyzers based on techniques like LC/GC-MS.

NMR metabolomics relies on high reproducibility of the recorded spectra and high stability of experimental conditions.

Our group has a long lasting interest in NMR metabolomics applied to plant and body fluids. We have been involved in one of the first inter-laboratory trials on blood plasma, when this technique was in the early development stage (1996), and we have been recently conducted an intra-laboratory test on quantitation of metabolites in fruit juices (2013).

Latest generation of NMR instruments provide higher stability and reproducibility of results opening new gates in plant and animal metabolism.

We present here our preliminary results on an NMR inter-laboratory, multi-operator quantitation trial for metabolites in complex natural matrices.

**Acknowledgements**

This work was supported by the Ministry of Research and Innovation, CNCS - UEFISCDI, project ERANET-INCOMERA-2018-BENDIS, within the PNCDI III and EU H2020 programs and project PN-III-P4-ID-PCCF-2016-0050 (5DnanoP)within the PNCDI III program.

**P137**

# CYTOTOXICITY EVALUATION OF POLYPHENOL-LOADED MAGNETIC NANOPARTICLES ON HUMAN ENDOTHELIAL CELLS

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The multidisciplinary nanotechnology research field encompasses the design, synthesis, characterization and handling of particles with a diameter of 1 to 100 nm. These nanoparticles have attracted a lot of interest as specific drug delivery systems to sites of interest, such as the vascular wall, which undergoes pathological changes following the installation of cardiovascular diseases (CVD) [1]. Polyphenols, plant-derived organic compounds, have well documented anti-inflammatory activity and are actively investigated currently for their therapeutic potential in the treatment of CVD [2]. The aim of the present study was the synthesis, characterization, as well as testing the cytotoxic effect of polyphenol-loaded magnetic nanoparticles (MNPs) on the human endothelial cell (EC) line EA.hy926.

Chitosan-coated MNPs and loaded with polyphenols (caffeic acid, tannic acid and gallic acid) were obtained by the co-precipitation method [3]. These MNPs were physico-chemically characterized by different methods: the structure was determined by X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy, the morphology was determined by Scanning Electron Microscopy (SEM) and the hydrodynamic diameter in aqueous solution was measured by Dynamic Light Scattering (DLS). EA.hy926 cells were incubated for 24 hours with different concentrations of MNPs and polyphenol-loaded MNPs, ranging from 10 to 500 µg/ml. The cells exposed to corresponding concentrations of free polyphenols, ranging from 1 to 50 µg/ml were used for comparison. Cell viability was assessed via XTT {2,3-bis (2-methoxy-4-nitro-5-sulfophenyl)-5-[(phenylamino) carbonyl]-2H-tetrazolium hydroxide} assay.

Following the physico-chemical characterization, it was concluded that the primary particles are nanometer-sized (about 3-4 nm) and have a spherical shape, but their morphology changes depending on the therapeutic agent loaded. The hydrodynamic diameter of the MNPs dispersed in water was around 700 nm. In general, the EC viability is not highly affected by the exposure for 24 hours to $Fe_3O_4$ MNPs. Only in the case of incubation of EC with caffeic acid-loaded MNPs, a gradual, dose-dependent decrease of viability could be observed but this was not greater than 35%, corresponding to the maximum concentration tested (500 µg/ml).

In conclusion, chitosan-coated polyphenol-loaded MNPs tested in this study do not significantly induce EC death up to a concentration of 200 µg/ml MNPs and guides to further studies to search for their potential benefits as anti-inflammatory medicines.

**Acknowledgements.** The study was supported by UEFISCDI, INTERA project, PN-III-P3-1.2-PCCDI-2017-0697, contract no. 13PCCDI/2018.

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**P138**

# ATTEMPTED SYNTHESIS OF 2,6,10-TRIBROMO AND 2,6,10-TRIMETHYLTRIBENZOTRIQUINACENE

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Tribenzotriquinacene (TBTQ) is a bowl-shaped hydrocarbon, synthesized for the first time in 1984 by employing a 2-(diphenylmethyl)-1,3-indanediol derivative as an intermediate, which is subjected to a cyclodehydration reaction to yield the desired compound [1]. If a symmetrically substituted TBTQ is required, however, this method is not the best suited, as it leads to a mixture of isomers. An alternative way to synthesize the TBTQ framework was described in 2012 [2], that makes use of a 1,3-diphenyl-1,3-propanediol derivative as an intermediate. While both methods suffer from moderate yields at best, the advantage of the latter is that symmetrically substituted TBTQs can be obtained as single products and not as mixtures of isomers.

In this work, we describe the attempted synthesis of two trisubstituted TBTQs, namely 2,6,10-tribromo (**5a**) and 2,6,10-trimethyl tribenzotriquinacene (**5b**) using the appropriately substituted 1,3-propanediols. While in the case of **5a**, only side-chain reaction products were identified, **5b** was obtained with an isolated yield of 6%. All products were characterized using NMR spectroscopy. All brominated products were also characterized through single crystal X-Ray diffraction.

## Acknowledgement

CNCS - UEFISCDI support within PNCDI III is acknowledged by the author for project numberPN-III-P1-1.1-PD-2016-1117

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**P139**

# SELECTIVE OXIDIZED POLYSACCHARIDES FOR HYDROGELS PREPARATION WITH WOUND DRESSING PROPERTIES

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Two naturally occurring polymers, i.e. cellulose and pullulan have been selectively oxidized employing the well-established TEMPO/NaClO/NaBr protocol, in order to introduce carboxylic groups. The C6-oxidized products were used for preparing hydrogels with polyvinyl alcohol (PVA), using various ratios of oxidized polysaccharides/PVA.

The resulted hydrogels were thoroughly investigated using spectral and microscopic techniques and their rheological and swelling features were analyzed. These hydrogels were further tested for the incorporation and release of L-arginine.

The loading of L-arginine takes place by physical phenomena, such as diffusion, but also by chemical phenomena, when it is possible to form imine-type bonds, especially to materials with oxidized pullulan, which have a prolonged release of the drug to physiological pH.

The main advantages when using the oxidized cellulose or pullulan for the hydrogels preparation, are:

- water is used as a sole solvent for both components oxidized polysaccharide and PVA, avoiding the use of complicated solvent mixtures required by the unoxidized cellulose,
- due to the extremely high number of COOH groups incorporated after oxidation, the oxidized polysaccharide component takes over the role of crosslinking agent, in this case the supplemental presence of a crosslinking agent, being not necessary.

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**P140**

# ATTEMPTS TO OBTAIN 5-HYDROXYMETHYLFURFURAL

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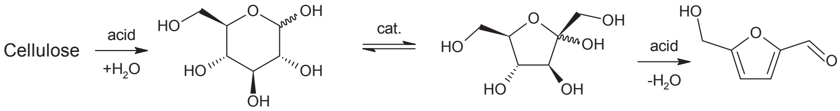
The diminishing of the fossil carbon reserves made the researchers to move to biomass derived feedstocks. Our aim is to obtain biodegradable aromatic polyester-polyols for rigid polyurethane foams starting from 5-hydroxymethylfurfural (5-HMF) and its derivatives. This compound is a very versatile building block, that can be obtained from fructose or glucose starting from cellulose, lignin and hemicellulose. The interest in this area is continuously growing, in the last decades a lot of papers being published, all of this work is already comprised in three reviews[1-3].The processes presented cannot be used for large-scale production (although the raw material is cheap, the production cost is expensive). The synthesis of 5-HMF can be achieved in monophasic systems or biphasic solvents systems. A various number of solvents are used such as water, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) or ionic liquids and mixture of this. The reaction can be conducted in homogenous or heterogenous catalysis, using inorganic salts, organic acid or ion exchanging resins.



Our previous work focused on the synthesis of 5-HMF in a monophasic system using DMSO as solvent and p-toluenesulfonic acid as catalyst, leading to high conversions and no secondary products in the case of fructose. In order to minimize the contact time between the product and the acidic medium, and to improve the final result we carried out the reactions in a various number of biphasic solvent systems, one where the dehydration takes place and one where the final product is extracted. The reactions were studied using nuclear magnetic resonance spectroscopy. The results will be discussed in terms of efficiency regarding chemical yield and energetic yield.

**Acknowledgements.** The financial support from UEFISCDI, Complex Projects CDI, no 70PCCDI/2018 – MAUS is gratefully acknowledged.

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**P141**

# STEREOSELECTIVE SYNTHESIS AND STRUCTURAL STUDY OF DERIVATIVES OF 2'-BENZOYL-1-BENZYL-1'-PHENYL -1',2', 5',6',7',7a'-HEXAHYDROSPIRO [INDOLIN-3,3'-PYRROLIZINE]-2-ONE

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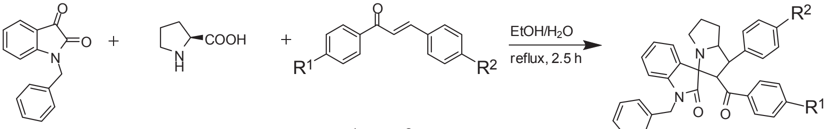
Amides and amines play a central role in the control and modulation of virtually all biological processes. On the other side the inflexibility of the quaternary carbon of spirocycles locks the adjoined ring into a fixed 3-dimensional conformation such that it must receive some responsibility for its interaction with given receptors.

Currently we have engaged ourselves in project aimed to define a one-pot protocol for the synthesis of highly functionalized spiro-oxindoles starting from corresponding *α,β*-enones, N-protected isatins andproline as well.

We chose to synthesise the indolin-3 containing spirocycle, which provide a template for use in combinatorial chemistry. We have been able to demonstrate the versatility of **4a,b** by derivatising the scaffold at each of its functional groups by use N-protected isatin **1,** proline **2**, and *α,β*-enones.



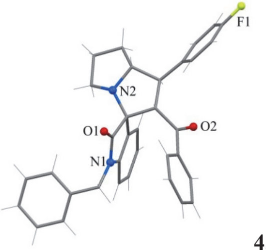
**1**

**2**

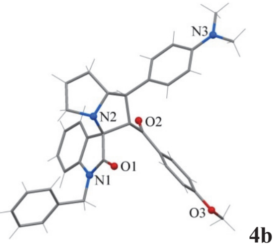
**3a**: $R^1$=H, $R^2$=F
**3b**: $R^1$=$OCH_3$, $R^2$=$N(CH_3)_2$

**4a**: $R^1$=H, $R^2$=F
**4b**: $R^1$=$OCH_3$, $R^2$=$N(CH_3)_2$

In this report we demonstrate the stereoselectivity of [2+3] addition and crystal structure of two main products obtained by single crystal X-ray method.



**4a**



**4b**

Compounds **4a** and **4b** crystalize in centrosymmetric space groups, thus represent racemats. Space group and unit cell parameters for **4a** are *P*-1, *a*=9.8449(7) *b*=12.552(1) *c*=12.6961(9)Å, *α*=115.561(8), *β*=97.134(6), *γ*=101.279(7)º, *V*=1348.9(2)Å$^3$ and for **4b** *P*2$_1$/*n*,*a*=11.6456(7), *b*=11.6090(5), *c*=22.6398(9) Å, *β* =93.820(4)º, *V*=3054.0(2) Å$^3$.

**Acknowledgements.** The authors are grateful for the funding offered by the National Agency for Research and Development of the Republic of Moldova under the project **15.817.02.17A.**

**P142**

# SYNTHESIS OF ENATIOMERICALLY PURE HIGHLY FUNCTIONALISED SPIRO-[INDOLIN-3,3'-PYRROLIZIN]-2-ONES

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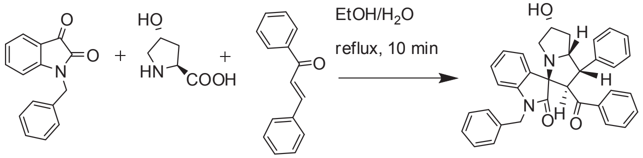
Number of spiro-derivatives of isatin has biological activity and some have been isolated from natural sources. A cycloaddition reaction of unsaturated molecules with parts of the other molecule, can serve as versatile building blocks of a number of important and often novel bioactive compounds.

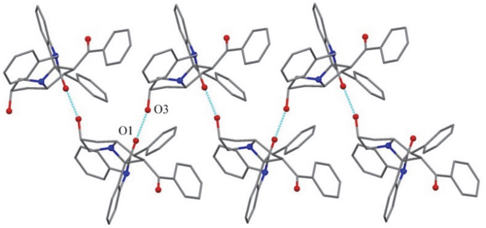
In presentation will include methodology enhancement for generation of novel spiro-indolin-3,3'-pyrrolizin]-2-onesscaffolds and application to the synthesis and study of enatiomerically pure indolin-3,3'-pyrrolizin]-2-ones **4**.



**1** **2** **3** **4**

Methodology has included N-benzylisatine **1**, *trans*-4-hydroxyproline **2** and chalcone **3**. The results of the modeling and NMR study of the compounds will also be discussed.

The structure of **4** has been confirmed by single crystal X-ray method. Compound crystalizes in orthorhombic non-centrosymmetric space groups $P2_12_12_1$, thus represent pure enantiomer, $a$ = 9.1612(6), $b$ = 10.5824(8), $c$ = 28.393(2) Å, $V$ =2752.7(3) Å$^3$. Bond distances O1-1 1.215(5) and O2-C 1.208(6)Å unambiguously indicates double bonds while O3-C 1.411(5) single one. The sum of bond angles at N1 atom equals 360.1° and shows planar configuration whereas the sum of bond angles at N2 atom equals 343.2° and indicates some degree of its pyramidality.



In the crystal O3-H…O1 2.982Å hydrogen bonds unite molecules of 4 in infinite left-handed helix along crystallographic axis *a*.

**Acknowledgements.**The authors are grateful for the funding offered by the National Agency for Research and Development of the Republic of Moldova under the project 19.80012.80.07A.

**P143**

# SYNTHESIS AND CHARACTERIZATION OF NEW COPPER(II) COMPLEX WITH DRIMANE THIOSEMICARBAZONE LIGANDS

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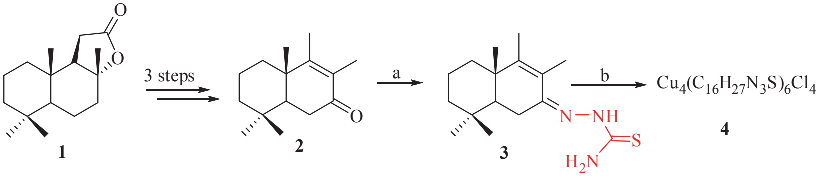
Thiosemicarbazones have attracted attention for many years due to their pharmacological utility as therapeutic agents and versatility as ligands allowing them to give rise to a wide variety of coordination modes [1]. In this connection, we used in coupling reaction with tiosemicarbazide drimenone (**2**), which is the degradation product of commercially available sclareolide (**1**).

The synthesis of the target compounds was done according to the Scheme:



**Reagents and conditions:***a.*$NH_2NHCSNH_2$, EtOH, Δ, 24h, 83%; *b.*$CuCl_2 \cdot 2H_2O$, MeOH, 50°C, 30 min,67%.
**Scheme**

As starting material for the synthesis of named compounds lactone (**1**) was used, which was transformed in three steps in drimenone (**2**), with an 51% overall yield (Scheme) [2].

Drimenone (**2**) was coupled in ethanol with thiosemicarbazide in a molar ratio 1:1, to afford drimane thiosemicarbazone (**3**). Subsequently, the complexation of the ligand (**3**) with Cu(II) salt in the molar ratio 1,5:1 (L:M), was developed [3].

The structure of obtained compounds have been established using modern methods of analysis (ATR-FTIR, $^{1}H$, $^{13}C$ and $^{15}N$ NMR, MS and XRD).

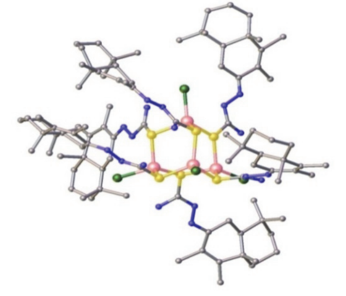


**Figure**. Molecular structure of compound **4**.

According to X-ray crystallography compound (**4**) crystalize in chiral P1 space group of triclinic system. The crystal has a molecular crystalline structure, the asymmetric part of which includes two asymmetric crystallographic complexes having the formula: [$Cu_4L_6Cl_4$], where $H_3L$ is the neutral ligand (**3**). The hexanuclear cluster has an adamantanoid structure enhanced by four $Cl^-$ terminal ions and six molecule of (**3**) as bidentate ligands. Each copper atom has a $S_2Cl_2$ coordination having a weakly distorted tetrahedral geometry and an oxidation number +1. The positive charge of the copper atoms is offset by the negative charge of the four chlorine ions so that the load balance corresponds to the formula [$Cu_4L_6Cl_4$].

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**P144**

# COMPARATIVE STUDY OF THE PRODUCTIVITY OF CALLUS BIOMASS AND CELL AGGREGATES OF *R. ROSEA IN VITRO*

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Golden root (*Rhodiola rosea* L.) is a well known species of plants, which has been used medicinally for decades, but studies of its pharmacological effects and of the compounds responsible for it use still continue [1]. Unfortunately, lately due to the intensive collection, the distribution area of this species has been substantially reduced. The attempts of industrial cultivation of the species did not produce the desired results.

Cell culture of *R. rosea* represents an alternative method and a model for investigation of the influence at the biological level of organization on the ability of plants to accumulate *secondary metabolites*. In addition, this method offers the possibility to study the influence of physical and chemical factors under controlled conditions on the accumulation processes. There is information in the literature demonstrating that in some cases the accumulation of *secondary metabolites* in an *in vitro* culture is more efficient in a liquid medium (no agar) compared to a solid culture medium (containing agar). Considering this, our studies have been conducted on the influence of these factors on both callus cultures and on aggregates of *R. rosea* cells grown in a liquid medium [2]. This paper, reports the results of the extraction of the active components from callus and cell aggregates of *R. rosea*, which represent the amount of substances extracted with different solvents from cell culture cultivated in solid and liquid medium (Table).

**Table.**The results of extractions from callus biomass and cell aggregates of *R. rosea*with hexane and methanol at the end of the cultivation period (on day 40 and 20, respectively).

| Sample | Sample mass, g | Hexane extracts (HE) | | Methanolic extracts (ME) | | Mass of non-extractable components, g |
|---|---|---|---|---|---|---|
| | | Weight, g | Productivity, % | Weight, g | Productivity, % | |
| Callus | 0.5622 | 0.0053 | 0.27 | 0.0357 | 6.35 | 0.5260 |
| Cell aggregates | 0.1517 | 0.0024 | 0.12 | 0.0464 | 30.59 | 0.1054 |

The total content of substances extracted from the mass of cell aggregates obtained in the liquid medium is approximately five times higher thanin the biomass of callus.At the same time, the content of extracts with lipophilic properties (HE) is higher in callus cells. Thus, the content of substances of phenolic origin (ME) is significantly higher in cell aggregates grown in a liquid medium.

Given that the active principles of *R. rosea* are mainly represented by phenolic compounds, it becomes clear the priority of cultivating cell aggregates in the liquid medium.

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**P145**

# FUNCTIONALIZATION OF CHITOSANE WITH POLIFENOLS AND USE OF THOSE COMPLETED IN CANCEROGENESE

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Functionalized polymers are widely applied in the biomedical field as tools in diagnosis and treatment of diseases [1]. Polymer particles can be adsorbed or loaded with multiple drugs and can more effectively control drug release in the body. Chitosan is a natural polymer that is abundant in nature. Due to its good physico-chemical properties and unique biological properties, chitosan is applied in many industries [2].

Polyphenols are well known for their antioxidant properties, they are natural compounds with one or more phenolic groups. They have a major influence on many diseases [3].The functionalisation of maleic anhydride to chitosan was performed in the first step according to the scheme presented in Figure 1.

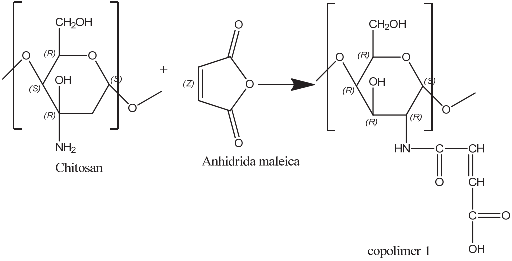

**Fig. 1.** The reaction mechanism of chitosan grafting to copolymer I

After purification of copolymer I by sedimentation, it was added in the dimethylformamide, subjected to quercetin grafting according to the scheme presented in Figure 2.

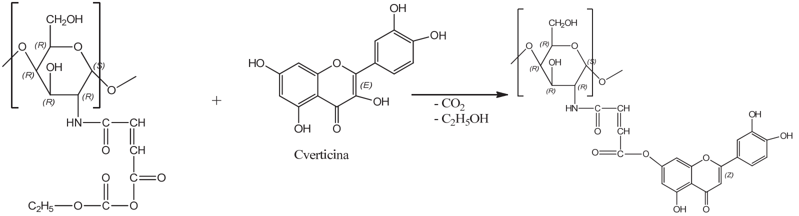

**Fig. 2.** The reaction mechanism of chitosan grafting to copolymer II

The chitosan-quercetin copolymer was synthesized by chitosan functionalization in the first step with maleic anhydride, then in step II the copolymer I was treated with ethyl chloroformate and triethylamine, after which in step III the obtained copolymer II was functionalized with quercetin. At every step for all copolymers the IR spectra were obtained.

Was determined antioxidant activity by the ABTS and DPPH methods. It was found thatchitosane functionalized with quercetin has stronger antioxidant activity than thepure quercetin of the same concentration.

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**P146**

# FUNCTIONALIZATION OF CHITOSANE WITH CARBOXYL ACIDS AND THEIR USE IN THE INHIBITION PROCESS OF *N*-NITROSAMINS IN CANCER FORMATION

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Cancer is a major health problem and is the second leading cause of death in the world. DNA oxidation can cause mutations and can therefore play an important role in the initiation and progression of carcinogenesis. For this reason, the imbalance between antioxidants and the levels of reactive oxygen species leads to oxidative alterations, which can occur at molecular levels. These processes can cause toxicity, mutations, and induction of cancereenose [1]. The role of oxidative stress in initiating and promoting cancer justifies the functional antioxidant approach in the prevention and treatment of cancer by developing inhibition methods in the carcinogenic *N*-nitrosoamines formation by the functionalization of chitosan with carboxylic acids, especially with dihydroxyfumaric acid.

The functionalisation of chitosan was performed according to the scheme presented in the Figure. The anti-oxidant activity of the functionalized chitosan was determined by theDPPH test and it has been established that the antiradical power of the functionalized copolymer is 2.5 times higher than pure dihydroxyfumaric acid. These composites are to be used to inhibit the formation of N-nitrosamines in drug-nitrosation.

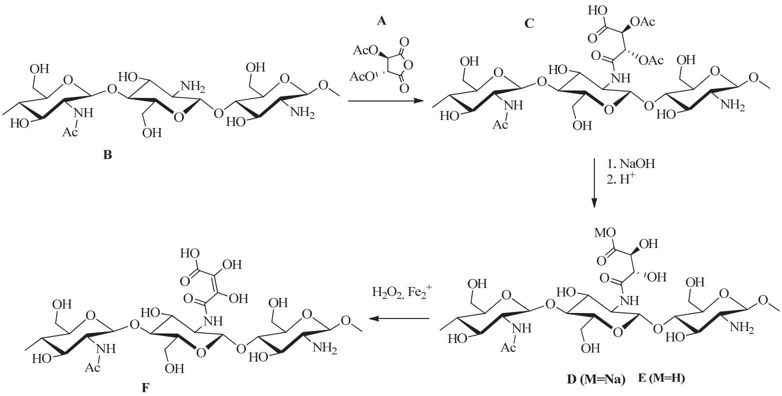

**Figure.** The reaction mechanism of chitosan grafting to dihydroxyfumaric acid.

It has been developed a functionalization of chitosan with dihydroxyfumaric acid. The antiradical power of the functionalized copolymer was determined. Intermediate and final compounds have been demonstrated by IR, UV and H1-NMR spectra.

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**P147**

# SQUALENE BASED POLYMERIC NANOCARIERS FOR GENES DELIVERY: *IN VITRO* STUDIES

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Due to the lack of therapeutic treatments for genetic and acquired disorders, in the last decades the attention of researchers was focused on gene therapies. The emergent need for innovative treatments is due to the fact that existing therapies are outdated and nonspecific [1]. Gene therapies using non-viral vectors have shown promising behaviours, after viral vectors, in treating different types of melanoma[2]. The use of non-viral approaches has some advantages and disadvantages compared with viral therapies, *in vitro* testing on different types of cells proved that non-viral carriers exhibit low cytotoxicity with different degree of transfection efficiency depending on components used in vectors synthesis [3]. The most explored components are cationic compounds, especially polycationic compounds which showed a significant efficiency in delivering of nucleic acids (branched and linear polyethyleneimine) [4].

In this context, our studies were focused in obtaining non-viral vectors with improved transfection efficiency and low cytotoxicity by using combinatorial chemistry. Previously studies by our group in this field showed that the most suitable components to fulfil the desired properties are: squalene (a natural biocompatible lipid), benzene-1,3,5-tricarboxaldehyde (TA) (multifunctional core), branched polyethylenimine with low molecular weight (PEI) (positively charged polymer) and polyethylene glycol (PEG) (biocompatible polymer) which are connected together by reversible imine bonds [5,6]. The main aim of this study was to observe the influence of PEG from its composition on transfection efficiency. For this purpose, we used PEG of three molecular weights in different molar ratios. TEM and DLS studies showed that in aqueous media this type of systems adopts a core-shell structure forming hydrophobic/hydrophilic assemblies. The formation of the polyplexes between plasmid nucleic acid and non-viral vectors was proved by agarose gel electrophoresis assay, showing that, the obtained systems are able to bind the plasmid nucleic acid. The efficiency in transfection and cytotoxicity were tested *in vitro* on HeLa cell line and results showed that the type and content of PEG in obtained polyplexes possess a crucial role in delivering genetic material.

**Acknowledgements.**This work was supported by Horizon 2020 WIDESPREAD 2-2014: ERA Chairs Project no 667387 and a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PN-III-P1-1.1-TE-2016-1180, within PNCDI III.

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**P148**

# RECYCLABLE CATALYSTS BASED ON *N*-HYDROXYPHTHALIMIDE FOR SELECTIVE OXIDATION OF POLYSACCHARIDES

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Chemical derivatization of pullulan, such as oxidation, etherification, esterification, and hydrogenation have been reported since many years. Particularly, the oxidation of pullulan to carboxypullulan is an important direction to functionalization the hydroxyl groups in the maltotriose unit of pullulan. The introduction of carboxylic groups in the pullulan backbone provide anionic polymers, able to interact more effectively with other charged compounds. Thus, pullulan can be readily oxidized at primary hydroxyl groups to the carboxylic moiety by using free nitroxyl radicals, such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and a primary oxidant, like sodium hypochlorite (NaOCl). In this process the nitrosonium salt is the key species resulting from the conversion of the nitroxyl radical in the presence of NaBr/NaOCl.

According to the current trends in catalysis, attempts have been made to immobilize *N*-hydroxyphthalimide (NHPI) into solid support in order to obtain easy separable and reusable catalyst.

In this work, we would like to propose a convenient route for the selective conversion of the primary OH groups in the water soluble pullulan, using a new catalytic polymer-supported *N*-hydroxyphthalimide (NHPI) immobilized on polystyrene via amide or ester bonds.

All reactions were carried out at room temperature, atmospheric pressure and pH=10. The characterization of the catalysts and oxidized products has been done using NMR and FTIR methods. The analyses of the oxidized pullulans reveals that in all samples, the primary alcohol groups were selectively oxidized into carboxyl groups. The possibility of recovery and recycling of the polymer-supported NHPI catalyst was tested for up to four cycles, since the morphological analyses performed on the catalysts using SEM, revealed no significant changes.

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**P149**

# SYNTHESIS OF 1,2,3-TRIAZOLES FROM (1R,3R,4R,6S)-4-AZIDO-4,7,7-TRIMETHYLBICYCLO[4.1.0]HEPTAN-3-OLE

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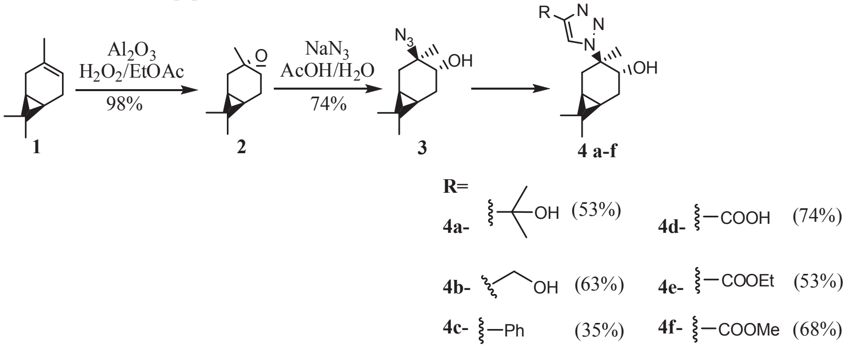
Since Huisgen dicovery of the use of Cu (I) salts as catalyst in reactions of 1,4-substituted 1,2,3-triazoles construction by cycloaddition of azides and terminal alkynes, this ddirection has been widely developed in organic chemistry. In present, a large number of Cu(I) complexes have been proposed as catalysts for this reaction.

Our intention was to prepare 1,2,3-triazoles functionalized (1R,3R,4R,6S)-4,7,7-trimethylbicyclo[4.1.0]heptan-3-oles from bicyclic monoterpene(+)-3-carene **1** *via* initial formation of epoxide **2** with a system $\alpha$-$Al_2O_3/H_2O_2$[1]. Transformation of **2** to azidoalcohol **3** was confirmed by independent experiments, where aqueous acetic acid solution of it was treated with sodium azide [2].



We have studied reactions of azidoalcohol **3** with substituted alkynes aimed on developing synthetic approaches to potentially bioactive polysubstituted 1,2,3-triazoles structures. Treatment of optically active azidoalcohol **3** with monosubstituted alkynes utilizing the CuI/DIPEA or ($CuSO_4$/ sodium ascorbate) under mild reaction conditions afforded the corresponding enatiomeric pure 1,2,3-triazoles functionalized (1R,3R,4R,6S)-4,7,7-trimethylbicyclo[4.1.0]heptan-3-oles **4a-4f** in good yields.

**Acknowledgements.**The authors are grateful for the funding offered by the National Agency for Research and Development of the Republic of Moldova under the project 15.817.02.17A.

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**P150**

# NEW 1,4-SUBSTITUTED 1,2,3-TRIAZOLES FROM (1S,3S,4S,6R)-4-AZIDO-4,7,7-TRIMETHYLBICYCLO[4.1.0]HEPTAN-3-OLE

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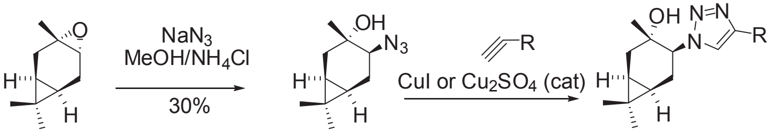
Recently we found a simple approach to configurationally stable, enantioenriched aminoalkylated aziridines from natural (+)-3,7,7-trimethylbicyclo[4.1.0]hept-3ene [1].

As part of our continuing interest on preparation of bicyclo[4.1.0]heptan-3-oles with useful properties we describe here the synthesis of a new trimethylbicyclo[4.1.0]heptan-3-oles having an 1,2,3-triazolesat C-3.

The precursor **2** was prepared from3,4-epoxicarane **1** [2] by refluxing with sodium azide/$NH_4Cl$ in MeOH (Scheme).



**1**

**2**

**3** R=$CO_2Me$ (68%)
**4** R=$CO_2Et$ (53%)
**5** R=$CO_2H$ (74%)
**6** R=$CMe_2OH$ (53%)
**7** R=$CH_2OH$ (63%)
**8** R=Ph (35%)

Synthetic strategy and methodology applied to creation of new targets **3-8** are discussed in further details and with additional examples.

**Acknowledgements.** The authors are grateful for the funding offered by the National Agency for Research and Development of the Republic of Moldova under the project 15.817.02.17A.

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4. Macaev F., Curlat S.; Logina L.Moldova Patent, № 4364, BOPI, №8, 24 (2015).

**P151**

# SYNTHESIS AND CHARACTERIZATION OF PYRAZOLE-CONTAINING CARBOXYLIC ACIDS AS NOVEL DITOPIC ORGANIC LIGANDS FOR POROUS COORDINATION POLYMERS

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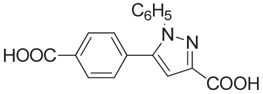
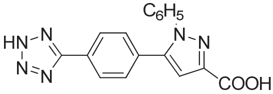
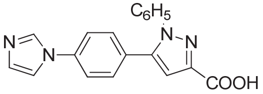
The majority of organic ligands used to build porous coordination polymers feature a rigid, hydrocarbon-based central core that is substituted with coordinating functional groups (*e.g.*, carboxylate) or have nitrogen heterocycles (imidazole, tetrazole, etc) as coordinating sites. Organic linkers having a heterocycle-based central unit have been underemployed for the generation of coordination polymers, and their use has been largely limited to commercially available compounds. This contribution aims at introducing three novel rigid, ditopic, carboxylate or hybrid ligands **1**–**3** having a pyrazole in the central core, useful for the preparation of porous coordination polymers.



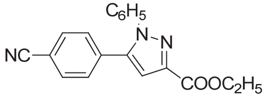
**1**



**2**



**3**



**4**

The reaction sequence leading to the desired ligands starts with the Claisen-like condensation between of diethyl oxalate with an acetophenone *para*-substituted either with cyano or with 4-(1*H*-imidazol-1-yl), followed by the reaction of the resulting 2,4-dioxobutanoate with phenylhydrazine. Next, simultaneous transformation of the nitrile and ester function in intermediate **4** under harsh hydrolysis conditions (KOH, water, reflux, 48 h) produces ligand **1**, whereas ring closure of tetrazole leading to ligand **2** is performed by reacting the cyano group in intermediate **4** with $NaN_3$. Ligand **3** is efficiently obtained through the mild hydrolysis (LiOH, THF–MeOH–water, rt, overnight) of the ester function in the corresponding imidazole-substituted analogue of **4**. The structures of the intermediates and the target compounds have been established by $^{1}H$- and $^{13}C$-NMR spectroscopy, and they are in agreement with the proposed structures. In addition, the structure of ligand **2** has been determined by single crystal X-ray diffraction experiments. Compound **2** crystallizes in space group $P2_{(1)}2_{(1)}2_{(1)}$ of orthorhombic system, with one neutral molecular unit of $C_{17}H_{12}N_6O_2$ in the asymmetric part, and unit cell parameters $a = 5.8614(8)$ Å, $b = 8.8381(10)$ Å, $c = 28.489(4)$ Å.

**Acknowledgements.** The financial support of European Social Fund for Regional Development, Competitiveness Operational Programme Axis 1 - POCPOLIG (ID P_37_707, Contract 67/08.09.2016, cod MySMIS: 104810) is gratefully acknowledged.

**P152**

# CHEMICAL COMPOSITION OF ESSENTIAL OIL AND ANTIMICROBIAL ASSESSMENT OF EXTRACT FROM *LONICERA JAPONICA*

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Japanese honeysuckle (*Lonicera japonica* Thumb.) is a species belonging to *Caprifoliaceae* family. These are creeping plants native to Asian countries (China, Japan and Korea), known more for their decorative properties. More than 212 chemical compounds have been isolated from the plants of this species, which primarily include organic acids, flavonoids, iridoids, triterpenoids and other volatile terpenic components [1-3]. Pharmacological studies have shown that *L. japonica* possess antibacterial, antiviral, anti-inflammatory, antipyretic, liver and gall bladder-protective, anti-oxidative, anti-fertility, hypolipidemic, anti-allergic and immuno-regulatory effects [4]. The GC-MS analysis of *L. japonica* oil of Moldavian origin resulted in identification of twenty-seven components (Table), which represent 99.47% of the total oil constituents.

**Table.** Phytochemical composition of *L. japonica* essential oil

| *No.* | *RT* (min)* | *Component* | *%* | *No.* | *RT* (min)* | *Component* | *%* |
|---|---|---|---|---|---|---|---|
| ***1*** | 5.450 | 6-Methyl-5-heptene-2-one | 0.517 | ***15*** | 19.603 | Elemol | 0.331 |
| ***2*** | 6.997 | (*Z*)-3-Octen-1-ol | 0.636 | ***16*** | 19.888 | (*E*)-Nerolidol | 0.790 |
| ***3*** | 8.172 | Linalool | 39.415 | ***17*** | 20.097 | (*Z*)-Hexenyl benzoate | 1.155 |
| ***4*** | 8.232 | Nonanal | 0.465 | ***18*** | 20.261 | Hexyl benzoate | 0.468 |
| ***5*** | 12.186 | Nerol | 0.685 | ***19*** | 22.025 | $\alpha$-Cadinol | 0.612 |
| ***6*** | 13.242 | Indol | 2.722 | ***20*** | 22.948 | (2*Z*, 6*E*)-Farnesol | 0.292 |
| ***7*** | 13.990 | Cyclohexane, (1-methylethyl)- | 1.299 | ***21*** | 23.303 | (2*Z*, 6*E*)-Farnesal | 0.583 |
| ***8*** | 14.476 | Antranilic acid methyl ester | 5.151 | ***22*** | 23.483 | Farnesol | 27.580 |
| ***9*** | 15.957 | (*Z*)-Jasmone | 1.622 | ***23*** | 23.884 | Farnesal | 0.961 |
| ***10*** | 17.252 | Geranyl acetone | 0.588 | ***24*** | 24.460 | Benzyl benzoate | 0.483 |
| ***11*** | 17.996 | Germacrene D | 7.147 | ***25*** | 25.912 | Farnesyl acetate | 3.306 |
| ***12*** | 18.361 | $\gamma$-Elemene | 0.348 | ***26*** | 30.777 | Geranyl linalool | 0.808 |
| ***13*** | 18.704 | Buthylated hydroxytoluene | 0.746 | ***27*** | 31.955 | Heneicosane | 0.350 |
| ***14*** | 18.978 | (-)-$\beta$-Cadinene | 0.411 | | | | |

**RT - retention time.*

The *in vitro* assessment of ethanolic extract from *L. japonica* plants have shown medium antibacterial activity against both non-pathogenic Gram-positive/Gram-negative (*Bacillus subtilis* and *Pseudomonas fluorescens*) and phytopathogenic (*Xanthomonas campestris*, *Erwinia amylovora*, *E. carotovora*) bacteria in the range of concentrations of 0.03-0.06%. Its antifungal properties against *Candida utilis* are higher at lower concentrations of 0.03%.

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**P153**

# RADICAL PERFLUOROALKYLATION OF *ENT*-KAURENOATE DERIVATIVES

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Atom transfer radical addition (ATRA) to alkenes provides a useful tool to create C-C and C-X bonds in a single synthetic step [1-3]. It offers some attractive routes to synthesize the pharmaceutically important molecules. Reductive ATRA represents one of the mildest procedures for a formal alkene carbohydrogenation. We report the application of a mild and convenient reductive ATRA procedure [5], in order to generate a series of methyl *ent*-kaurenoate **1** fluorinated derivatives **2**-**6** (Figure).

Carbohydrogenation of methyl *ent*-kaurenoate **1** was performed with several iodo-radical precursors under very mild conditions, in the presence of triethylborane and oxygen (open air) as radical initiators and 4-methoxycatechol as a reducing agent.

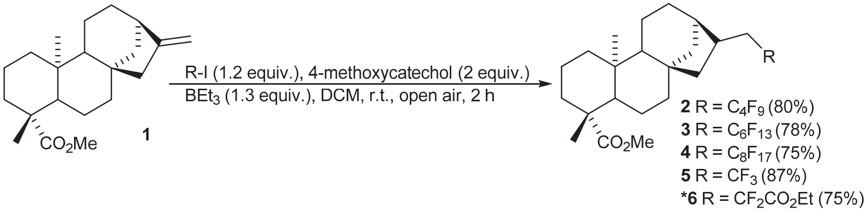

**Figure.** Carbohydrogenation of *ent*-kaurenoate ester.
(**tert*-butylcatechol (TBC) was used)

Hydroalkylation of *ent*-kaurene derivatives with perfluoroalkyl iodides as radical precursor afforded the fluorinated compounds **2**-**6** in very good yields (75-87%). These compounds will be tested for biological activity in the following studies towards implementation in medicine or radiology.

**Acknowledgments.** We are grateful to the Swiss National Science Foundation and University of Bern for support of this research.

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**P154**

# RADICAL TRANSFORMATIONS OF *ENT*-ISOCOPALIC DITERPENES

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Spongiane diterpenoids are natural compounds isolated form sponges, corals and marine mollusks. Most of them play a key role as physiological mediators and are of interest for potential applications as therapeutic agents. These diterpenoids possess biological properties including antifungal, anti-inflammatory, cytotoxic and anti-HIV activities [1, 2].

Methyl *ent*-isocopalate, the tricyclic diterpene of the spongian family is used as a good precursor in the total synthesis of natural compounds [3]. It was obtained in 61% overall yield, starting from sclareol, a commercially available and inexpensive compound. Carboazidation of methyl *ent*-isocopalate with ethyl iodoacetate and phenylsulfonyl azide under DTBHN initiation conditions resulted in the formation of azide **2** in 55% yield (Figure). The relative stereochemistry of azide **2** was determined based on NOESY NMR data.

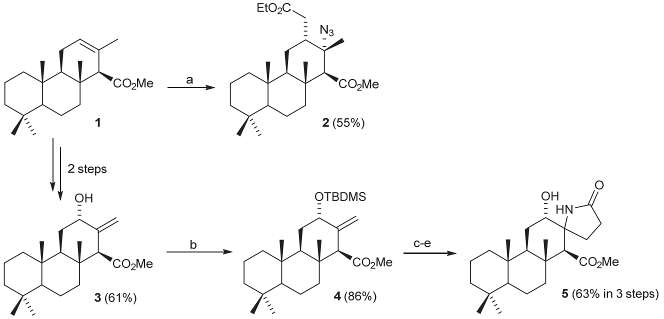

**Figure.** Radical carboazidation of diterpenes.

***Reagents and conditions:*** a. $ICH_2CO_2Et$ (2 equiv.), 3-$PySO_2N_3$ (3 equiv.), $Bu_6Sn_2$ (1.5 equiv.), DTBHN (0.03 equiv.), benzene, 10 h, Δ; b. imidazole (4 equiv.), TBDMSCl (2 equiv.), DMF, r.t. overnight; c. $ICH_2CO_2Et$ (2 equiv.), $PhSO_2N_3$ (3 equiv.), $Bu_6Sn_2$ (1.5 equiv.), DTBHN (0.03 equiv.), benzene, 10 h, Δ; d. TBAF (3 equiv.), THF, r.t., overnight. e. $H_2$, Pd/C, EtOAc, r.t., 48 h.

The 12α-hydroxy-*ent*-isocopal-13(16)-en-15-oic acid **3** was synthesized from isocopalic ester **1** according to the known procedure [4]. Then, compound **3** was transformed *via* the TBDS ether **4** into lactam **5** over 3 steps in a 63% total yield. The key step in this sequence was the carboazidation of the exomethylenic double bond, followed by reduction of the azide moiety, which triggered a spontaneous lactamization. The introduced heteroatomic functional groups represent new structural motifs integrated into the isocopalic framework and their effect on the biological properties is currently under investigation.

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**P155**

# MOLECULAR INHIBITOR OF HL-60 CANCER CELLS' PROLIFERATION BASED ON 2-{[2-(PROP-2-EN-1-YLCARBAMOTHIOYL)HYDRAZINYLIDENE]-METHYL}PYRIDINIUM NITRATE

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Cancer is a group of diseases commonly found in the world, being one of the main causes of mortality. Chemotherapy is often used for cancer treatment. Substances that are used to treat cancer have some shortcomings, including high toxicity and low selectivity. Many substances with antiproliferative properties have low solubility in aqueous solutions, which reduces the possibility of their application in medical practice. Thiosemicarbazone class of organic substances attracts constant scientific interest due to its anticancer activity. Therefore, the study of new derivatives of N$^4$-substituted thiosemicarbazones, which exhibit selective anticancer activity and increased solubility in water, is of interest from both theoretically and practically points of wiew.

The aim of this work is to find the conditions of synthesis and to determine the structure and antiproliferative properties of 2-{[2-(prop-2-en-1-ylcarbamothioyl)hydrazinylidene]-methyl}pyridinium nitrate ($HL\cdot HNO_3$).

$HL\cdot HNO_3$ was obtained by reaction between 2-formylpyridine, $N^4$-allyl-3-thiosemicarbazone (HL) and nitric acid. The structure and purity of $HL\cdot HNO_3$ were determined by $^1$H and $^{13}$C NMR spectroscopy. The NMR data correspond to these from the literature for compounds with the protonated pyridine nitrogen atom. The peaks of pyridinic hydrogen atoms have higher chemical shifts compared to the same hydrogen atoms in corresponding thiosemicarbazone HL.

Single crystals of the $HL\cdot HNO_3$ were obtained by recrystallization from ethanol.

Empirical formula $C_{10}H_{13}N_5O_3S$; space group P $2_1$/C; cell lengths [Å]: a = 5,1190(5); $b$ = 16,353(2), c = 15,968(2); cell angles: $\alpha$ = 90°, $\beta$ = 90,081(9)°, $\gamma$ = 90°.

The solubility of $HL\cdot HNO_3$ is 5.0 mg/mL (18 mM) that is 35 times higher than the solubility of initial thiosemicarbazone HL. The molar conductivity of the $10^{-3}$ mol/L solution of $HL\cdot HNO_3$ in water corresponds to an electrolyte of type 1:1.

It was studied the antitumor activity of synthesized substances on human leukemia HL-60 cells. The obtained $IC_{50}$ value for $HL\cdot HNO_3$ is 0.1 μmol/L, but the $IC_{50}$ for the initial thiosemicarbazone HL is 0.38 μmol/L. Thus the obtained salt is 3.8 times more active than HL and also 2 times more active than doxorubicin that is used in medical practice.

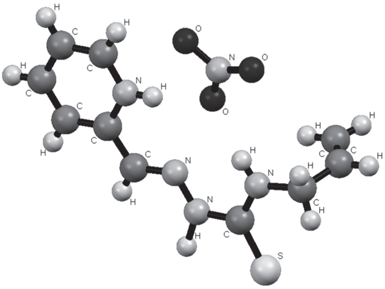

**Figure.** Crystal structure of $HL\cdot HNO_3$

**P156**

## SYNTHESIS OF SOME GUANIDINE DITERPENOIDS

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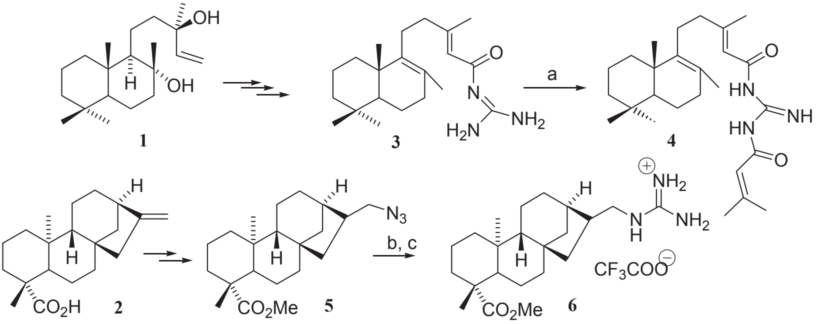
Guanidine compounds represent a large group of biologically active secondary metabolites [1, 2]. Several of them, despite their low content in the source, have been intensively explored as new promising agents against various cancer cell lines [3, 4] and in the infectious diseases treatment [5]. Taking into consideration all the data explored in the literature it seemed attractive and necessary to synthesize guanidine containing diterpenoids and to study their biological activity.

In this communication we present convenient approaches for the synthesis of some polycyclic nitrogen containing diterpenoids, starting with accessible (-)-sclareol (**1**) and *ent*-kaur-16-en-19-oic acid (**2**), according to the scheme given below.



***Reagents and conditions:***(a) Senecioic acid, NMP, CMPI, 2 h, then (**3**), NMP, DIEA, 52%, (b) $H_2$, Pd/C, 1,3-di-boc-2-(trifluoromethylsulfonyl)guanidine, EtOAc, 98%; (c) TFA/DCM, 95%.

**Scheme**

As result, a series of guanidine diterpenoids, N-labd-8(9),13(E)-dien-15-oyl guanidine (**3**), N-labd-8(9),13(E)-dien-15-oyl-N′-senecioyl guanidine (**4**) and metil-(16R)-17-guanidin-*ent*-kauran-19-oat (**6**), were obtained. All compounds were characterized by NMR spectroscopy.

### Acknowledgements

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**P157**

# OENOLOGY MYCOTOXINS REMOVAL USING CATIONIC CLAYS

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Bentonite is a hydrated aluminum silicate of volcanic origin. It consists of minerals from the smectite group, mostly of montmorillonite. The crystal structure of this mineral adsorbent is built of $SiO_2$ tetrahedrons and $Al_2O_3$ octahedrons, which are interconnected and build a three-layer plate with a negative charge, while the edges of the lamellae have positive charge [1]. This clay contains interchangeable cations Na, K, Ca, and Mg. From an oenological point of view, the composition and structure of bentonites have been studied and related to their adsorption capacities. Nevertheless similar studies regarding micro and trace elements release to wine have not been done so far except for those of rare earth elements.This mineral adsorbent increases the hardness and strength of pellets and it adsorbs some mycotoxins, such as: aflatoxins, ochratoxin A, zearalenone, citrinin, patulin, and fusarium. Mycotoxins can be defined as toxic secondary metabolites produced under appropriate environmental conditions by filamentous fungi, mainly *Aspergillus, Penicillium*, and *Fusarium*. Their presence can evoke a broad range of toxic properties including carcinogenicity, neurotoxicity, as well as reproductive and developmental toxicity. These compounds are produced by particular species of fungi [2]. Patulin and ochratoxin A are mycotoxins that have been reported in grapes and grape products such as wine. Patulin is produced most notably by the fruit-rotting fungus, *Penicillium expansum*, whereas ochratoxin A is associated with *Penicillium verrucosum* and *Aspergillus ochraceus*. Patulin causes gastrointestinal problems, skin rashes, and is known to be mutagenic. Ochratoxin A is carcinogenic and is considering imposing regulatory limits in wine. Bentonite is used in oenology to improve the clarity and stability of wine and to predict the formation of deposits in the bottle. Exchangeable cations in these lamellar structures strongly influence certain properties, such as surface area, exchange capacity and adsorption behavior [3].

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**P158**

# BIOMARKERS OF GEORGIAN PETROLEUM

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Relict hydrocarbons after deposition in rocks, retained the identity or underwent insignificant change in composition and structure of carbon skeleton of the original biomolecules that participated in the processes of crude oil formation. These relicts are considered to be the most important biomarkers or geochemical labels. Any regularity of their concentration distribution in the samples are geochemical criteria and allow us to judge the nature and origin of the source of raw materials in this region of sedimentation, its age, degree of decomposition and catagenetic maturity. This information is used to carry out various geochemical correlations, genetic and chemical typifications of oils and solving various problems of crude oil geochemistry. The most important biomarkers are normal and isoprenoid alkanes, $C_{19}$-$C_{35}$ sterane and terpenehydrocarbons of sesqui-, di- and triterpene series, terpenoids, steroids, porphyrins and little-studied aromatic hydrocarbons of the relict type structure. Currently, more than 1000 different representatives of them are identified in crude oils and organic matter of rocks. Biomarkers along with carbon isotope composition are the main carriers of information about the life of the ancient periods of the Earth. The relict hydrocarbons of some Georgian oils, the genetic and geochemical aspects of their chemical composition, and the main geochemical criteria allowing for various genetic correlations to be considered have been studied.

The saturated portions of the 50–200°C, 200–350°C, 200–420°C and > 420°C fractions of oils from the main oil and gas region of Eastern Georgia were studied using GLC on highly efficient capillary columns, MS and GC/MS methods.

As a result of the study, Georgian crude oil was identified as belonging to various chemical types: B1, B2, A1 and A2. It has been established that, despite the difference in chemical composition, the studied crude oils belong to a single genetic type. A characteristic feature of Georgian oils was revealed – high concentrations of isoprenoid alkanes, such as pristane ($iC_{19}$) and phytane ($iC_{20}$) with a large predominance of pristan, therefore the ratio $iC_{19}/iC_{20}>1$.

In the middle boiling fractions of Taribani, Satskhenisi, Norio and Teleti crude oils were identified polymethylsubstituted decalines, relict type hydrocarbons having $C_{14}$-$C_{16}$ composition that most likely are related to significant triterpene relicts – hopanes. In high-boiling fractions > 420°C, large tetra- and pentacycloalkane ($C_{27}$-$C_{33}$) molecules were identified – steranes and triterpenes with predominance of hopans belonging to the 17α(H)-hopan ($C_{30}H_{52}$) series, which was present at maximum concentration. The main mass of steranes is made by thermodynamically more stable isosteranes. The degree of catagenetic transformation of crude oils was determined by the ratios $\Sigma nC_{13}$-$nC_{15}/\Sigma nC_{25}$-$nC_{27}$, $\Sigma iC_{19}$-$iC_{20}/\Sigma nC_{17}$-$nC_{18}$, $\alpha$-isosteranes, etc. The highest degree of conversion was determined for Samgori crude oil, and the least degree – for Shromis-Ubani crude oil.

Studies of Georgian crude oils revealed the presence of well-known relic structures, peculiarities in composition, quantitative and relative distribution of certain biomarkers, various geochemical indicators, which give reason for carrying out a more thorough study of the genetic code of Georgian Petroleum.

**P159**

# SYNTHESIS OF NEW POTENTIAL ACTIVE HOMODRIMANE SESQUITERPENOIDS WITH 1,3,4-THIADIAZOLE UNITS

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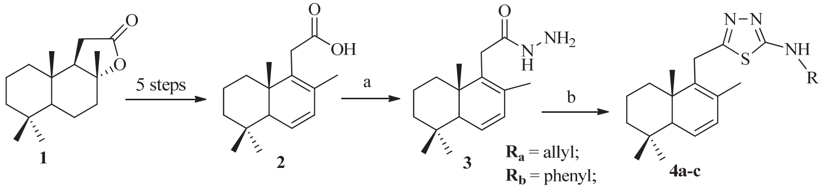
Sesquiterpenoids, especially those with a homodrimane skeleton, are natural compounds with a wide range of pharmaceutical and biological activities [1]. The 1,3,4-thiadiazole and its derivatives are considered interesting heterocycles since they possess important pharmacological activities [2].

As starting material for the synthesis of new title compounds 11-homodrim-6,8-dien-12-oic acid **2** was used. It was obtained before from commercially available sclareolide **1**in 5 steps, with an overall yield of 47%, as depicted in Scheme [3]. After that coupling reaction of acid **2** with hydrazine hydrate was performed. Subsequently, was used *one-pot* method, that includes the interaction of the hydrazide **3** with a series of substituted isothiocyanates, without isolation of the intermediate compounds. This reaction was carried out in the presence of triethylamine ($Et_3N$) in water, giving desired homodrimane compounds bearing 1,3,4-thiadiazole units in 72-78% yields [4].



**R**$_a$ = allyl;
**R**$_b$ = phenyl;
**R**$_c$ = 4-methyl-phenyl.

**Reagents**: *a*. $NH_2$-$NH_2$·$H_2O$, EtOH, Δ, 5h, 85%; *b*. R-NCS, $Et_3N$, $H_2O$, Δ, 18h, 72-78%.
**Scheme.**Thesynthesis of homodrimane sesquiterpenoids with 1,3,4-thiadiazole units.

The structures of compounds **4a-c** were fully confirmed based on their $^{1}H$, $^{13}C$, $^{15}N$ and 2D NMR data.

**Acknowledgements.** The financial support from the STCU (Ukraine) Project No 6330 is acknowledged.

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**P160**

# SYNTHESIS OF NEW ACTIVE NITROGEN AND SULFUR CONTAINING NORLABDANIC COMPOUNDS

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The synthesis of hybrid terpeno-heterocyclic compounds is a recent concern of researchers in the field of natural products. Several papers describing the synthesis and biological activity of terpenic compounds bearing diazine [1,2], carbazole [2], triazole [2,3], oxadiazoleand thiadiazole [4] units have been recently published. It should be noted that the intermediates of terpeno-heterocyclic compounds often exhibit biological activity. This communication confirms this fact and presents last-minute results. We report the synthesis of new di- and trinorlabdane thiosemicarbazides **1** and **2**, tetranorlabdane 2-iminothiodiazole **3** and diacyl hydrazide **4**, obtained in 60%-82% yields Figure 1. The structures of compounds **1**-**4** were fully confirmed by $^1$H, $^{13}$C and 2D NMR analysis.

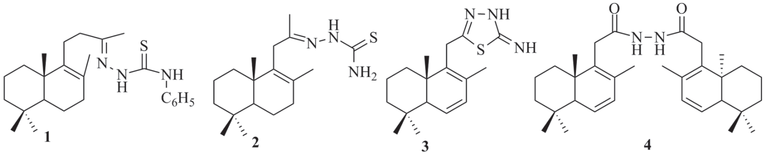

**Figure.** New nitrogen and sulfur containing bioactive norlabdanes.

Compounds **1**-**4** were tested *in vitro* for antifungal and antibacterial activity on five strains of fungi and both Gram-negative and Gram-pozitive bacteria (Table 1).

Compound **3** have shown the best antifungal and antibacterial activity at (MIC) of 0.125 µg/mL and 2.5 µg/mL, respectively. Compounds **1**, **2** and **4** possess activity comparable with reference compounds Caspofungin and Kanamycin (4 µg/mL).

**Table.** Results of *in vitro* testing of antibacterial and antifungal activity of compounds **1**-**4**.

| Compound | MIC (µg/mL) | | | | | | |
|---|---|---|---|---|---|---|---|
| | *Aspergillus niger* | *Fusarium* | *Penicillium chrysogenum* | *Penicillium frequentans* | *Alternaria alternata* | *Bacillus sp.* | *Pseudomonas aeruginosa* |
| **1** | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 4 | 4 |
| **2** | 0.19 | 0.19 | 0.19 | 0.19 | 0.19 | 3 | 3 |
| **3** | 0.125 | 0.125 | 0.125 | 0.125 | 0.125 | 2.5 | 2.5 |
| **4** | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 | 3 | 3 |
| **Caspofungin** | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | - | - |
| **Kanamycin** | - | - | - | - | - | 4 | 4 |

**Acknowledgements**. The financial support from the STCU (Ukraine) Project No 6330 is acknowledged.

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**P161**

# THE INFLUENCE OF *CIS*-METHYL 5'-CHLORO-2'-OXOSPIRO[CYCLOPROPANE-1,3'-INDOLINE]-2-CARBOXYLATE ON THE ACTIVITY OF SOME PHYTOPHOTOGENIC VIRUSES

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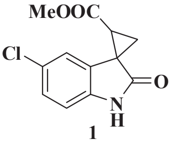
The unique structural features of spirooxindoles together with the diverse biological activities have made them privileged structures in new drug discovery. According to a large number of publications, such spiro compounds have different biological properties [1]. Among them are activities against numerous viruses. Previously, we and other authors have reported about spiro compounds that can potentially be used as anti-HIV agents, or in veterinary medicine against Bovine Viral Diarrhoea Virus (BVDV) [2,3,4].

Nowadays, compound **1** is being tested for its ability to inhibit the action of the tobacco mosaic virus- TMV, tomato spotted wilt virus-TSWV and cucumber mosaic virus-CMV.



**1**

TSWV infects a variety of hosts, contributing to its global economic impact on crops. There are over a thousand of different hosts for TSWV. The host range of TSWV includes economically important crops like tomatoes and tobacco. TMV is known as one of the most stable viruses. It has a very wide survival range. As long as the surrounding temperature remains below approximately 40 degrees Celsius, TMV can sustain its stable form.

The effect of the tested compoundsagainst TSWV is studied on the tomatoes of Emir variety. Studies on the effects of the same compounds against CMV are conducted on Rodnichok cucumbers.

The effect of the preparations is also tested under conditions of artificial infection of the susceptible variety of tomatoes Elvira with the TMV under controlled conditions (in the climate chamber-POL-ECO-APARAT).

**Acknowledgements.** The authors are grateful for the funding offered by the National Agency for Research and Development of the Republic of Moldova under the project 19.80012.80.07A.

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**P162**

# MULTICOMPONENT SYNTHESIS AND NMR CHARACTERIZATION OF BENZO[*f*]PYRROLO[1,2-*a*]QUINOLINE DERIVATIVES

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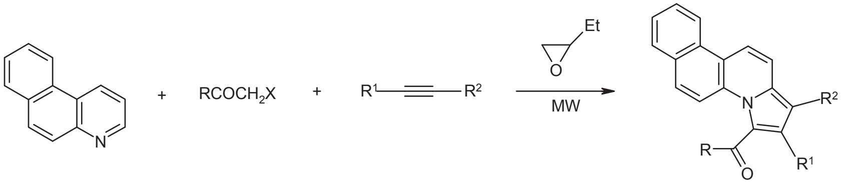
Benzo[*f*]pyrrolo[1,2-*a*]quinoline is a fused ring system with a bridgehead nitrogen atom structurally similar to the steroid skeletonand its derivatives show potential biological activity and interesting features of dyes.

Benzo[*f*]pyrrolo[1,2-*a*]quinoline derivatives have been prepared *via* multistep synthesis from 1-hydroxy-8-methoxybenzo[*f*]quinoline, by 1,3-diploar cycloaddition reactions of benzo[*f*]quinolinium *N*-ylides with acetylenic dipolarophiles,or by the cascade reactions of *N*-(naphthalen-2-yl)pent-4-ynamides with arylacetylenes under microwave irradiation in the presence of $AuBr_3$-$AgSbF_6$ catalyst system.

We present an efficient one-pot, three component microwave-assisted synthesis of a range of novel benzo[*f*]pyrrolo[1,2-*a*]quinoline derivatives,which has the advantages of considerable shorter reaction time, reduced solvent consumption, operational simplicity and minimal impact on the environment.



**1**

**2**

a: R=3-$MeOC_6H_4$, X=Br
b: R=3,4-$(MeO)_2C_6H_3$, X=Br
c: R=4-$MeC_6H_4$, X=Br
d: R=4-$NO_2C_6H_4$, X=Br
e: R=3-$ClC_6H_4NH$, X=Cl
f: R=2,6-$Et_2C_6H_3NH$, X=Cl
g: R=4-i-$PrC_6H_4NH$, X=Cl

**3**

a: $R^1$=H, $R^2$=COPh
b: $R^1$=H, $R^2$=COMe
c: $R^1$=$R^2$=$CO_2Me$
d: $R^1$=H, $R^2$=$CO_2Et$

**4-12**

**Acknowledgements**

This work was supported by the Ministry of Research and Innovation, CNCS - UEFISCDI, project ERANET-INCOMERA-2018-BENDIS, within the PNCDI III and EU H2020 programs.

**P163**

# COMPOSITION, ANTIOXIDANT AND ANTIFUNGAL ACTIVITY OF WILD OREGANO (*ORIGANUM VULGARE*) ESSENTIAL OIL

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Nowadays, there is a continuous interest in the research of antimicrobial, antifungal and antioxidant potential of essential oils and extracts from various plants. This tendency being mainly attributed to the incoming outbreaks of food poisoning worldwide, along with the negative consumers'perception against artificial food additives. Wild oregano (*Origanum vulgare*) is an aromatic herb belonging to the *Lamiaceae* family and being commonly spread throughout Asia, Europe and northern Africa [1]. The aim of the present study was to evaluate the chemical composition, total polyphenols (TPC) and flavonoids (TFC) content and to investigate the antioxidant and antifungal properties of the wild oregano essential oil (WOEO) of Romanian origin against three fungi species with high incidence on food products (*Aspergillus flavus, Penicillium expansum* and *Fusarium oxysporum*).

In all the experiments a commercial WOEO was used. The chemical composition of WOEO was determined by gas-chromatography coupled with mass spectrometer detector triple quadrupole (GC/MS-Triple Quad). The TPC and TFC have been quantified by Folin-Ciocalteu and $AlCl_3$ respectively methods [2]. The antioxidant activity of WOEO was evaluated using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2'-azino-bis 3-ethylbenzthiazoline-6-sulfonic acid (ABTS) radicals based methods [2]. The evaluation of the WOEO antifungal activity was performed using the puncture inoculation method [3].

The results showed that WOEO had high content of oxygenated monoterpenes (84.05%) of which carvacrol was the most abundant (73.85%) followed by β-linalool (3.46%) and thymol (2.29%). The high content of oxygenated monoterpenes had beenin accordance with TPC (6.71±0.73 mg of gallic acid equivalent/g oil) and TFC (46.5±4.8 μg quercetin equivalent/g oil) respectively. The required concentration to scavenge 50% of the total DPPH free radicals was 0.76±0.13 mg/mL. Moreover, WOEO had significantly inhibited the growth of selected pathogenic fungi species. Thus, it was observed an inhibition of growth up to 75% by exposure of *Aspergillus flavus* and *Fusarium oxysporum* to 1μL and of *Penicillium expansum* to 2 μL of WOEO, respectively. This study demonstrates that the antioxidant and antifungal activity of wild oregano essential oil is well correlated with total polyphenols and oxygenated monoterpenes hydrocarbons content. It can be concluded that wild oregano oil could be used in food preserving in some food products in which *Aspergillus flavus*, *Penicillium expansum* and *Fusarium oxysporum* couldgrow and have potential to produce health hazardous mycotoxines.

**Acknowledgements.** The study was supported by UEFISCDI, INTERA project contract no. 13PCCDI/2018.

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## P164

# SYNTHESIS OF A C12-FUNCTIONALIZED NORSCALARANE FROM SCLAREOL

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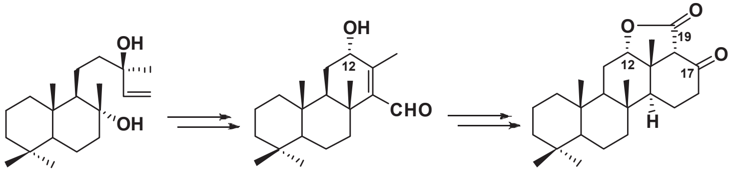
Scalarane sesterterpenoids emerged as interesting bioactive natural products which have been isolated basically from marine sponges and shell-less mollusks [1]. Some representatives isolated from plants are also known [2,3]. A range of scalarane sesterterpenoids displayed a wide spectrum of interesting biological properties, such as antifeedant, antimicrobial, antifungal, antitubercular, antitumor, cytotoxicity, anti-HIV, stimulation of nerve growth factor synthesis, as well as anti-inflammatory activity [1,3,4].

Due to their important biological properties, many efforts have been undertaken for the construction of this framework [5-7]. The main synthetic difficulty lies in their challenging structures, many chiral centers and different functional groups attached, especially the oxygenated functional group at the C12 position that is a prerequisite for the biological activity of many investigated scalaranes. The current work is dedicated to solving this problem.

The synthesis of C12-functionalized norscalarane was performed *via* an isocopalic derivative using (-)-sclareol as accessible starting material (Scheme). The tetracyclic lactone framework was build following an addition strategy, which includes intramolecular Michael reaction of a tricyclic acetoacetic ester derivative and intramolecular aldol condensation as key synthetic steps.



(-)-Sclareol

12$\alpha$-hydroxy-*ent*-isocopal-13(14)-en-15-al

17-oxo-20-norscalaran-12$\alpha$,19-*O*-lactone

**Scheme**

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**P165**

# SYNTHESIS AND SELF-ASSEMBLY BEHAVIOR OF AMINO ACID-BASED RANDOM COPOLYMERS

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Self-assembly of polymeric materials into organized nano/microstructures has gained a considerable attention in nanoscience due to their versatile properties and morphologies, their relationship to biological structures, as well as their fundamental importance in many fields, such as biomedical, microelectronic, photoelectric and optical materials [1,2]. Among these, block copolymers with narrow polydispersities were widely used due to their excellent self-assembly behaviours [3], although the formation of assemblies in random copolymers is possible despite their indistinct structure caused by the broader dispersion arising from the random distribution of hydrophilic and hydrophobic segments throughout the polymer chains. Moreover, random polymers are readily synthesized (one-step copolymerization or one-pot post-polymerization treatment [4]) in comparison to block copolymers. Organized assemblies of different shape and size are obtained in solutions at a threshold concentration called critical aggregation concentration (CAC). Accordingly, a variety of poly(acrylamide)s and poly(methacrylamide)s containing different amino acids have been synthesized to study their structure and properties, as well as their characteristic polymerization behaviour [5]. The main processes that trigger their behaviour relies on the fact that these amphiphilic polymers undergo intra- or interpolymeric hydrophobic associations, that lead to the achieving of secondary structures in the form of micelle-like clusters, which show a higher compatibility with the biological systems, characteristic that can be exploited in the attaining of hydrophobically modified amino acid-based optically active polyelectrolytes.

In this context, the aggregation behaviour of two types of random copolymers with *D/L*-phenylglycine moieties in the side chains was studied. The structures, thermal and optical properties of these polymers synthesized through free radical polymerization were investigated by spectral analyses (FT-IR, $^{1}$H NMR, $^{13}$C NMR), gel permeation chromatography, thermal analyses (TGA and DSC) and optical measurements. The self-assembly process can be monitored by using surface tension, fluorescence spectroscopy and transmission electron microscopy (TEM). The specific rotation values recorded for the two copolymers with dextro and levo enantiomeric forms have suggested a good correlation between the obtained experimental data, their direction of rotation being the same as in the starting monomers. The synthesized copolymers were explored in order to establish the potential applicability field of the polymeric aggregates.

**Acknowledgement**
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**P166**

# SYNTHESIS OF CYCLOALKYLPHENOL MANNICH BASES

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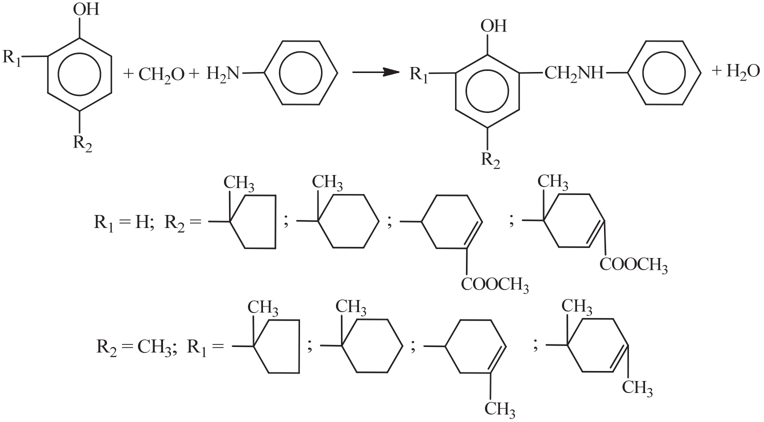
The synthesis of Mannich bases is simple and facile. High reactivity and great possibility for practical application allow us to increase its variety and realize diverse chemical conversions [1,2].

This paper presents the results of studies cycloalkylation of phenol and p-cresol with 1-methylcyclopentene, 1-methylcyclohexene, diprene and dipentene in the presence of a catalyst – zeolite-Y impregnated with phosphoric acid to produce cycloalkylphenols. Based on the synthesized cycloalkylphenols, 2-hydroxy-3 (5) -cycloalkylbenzylphenylamines were obtained.

The reaction of phenols interaction with 1-methyl cyclopentene, 1-methyl cyclohexene, diprene and dipentene has been studied at temperature 60-130°C, reaction duration 2-6 hours, phenol to cyclone mole ratio 0.5-h 1:3, catalyst amount 5-20% of taken phenol. Under the established optimum conditions the main products acceptable yield is 73.4-89.6%.

The reaction of 2-hydroxy-3(5)-cycloalkylbenzylphenyl amines synthesis was performed by cycloalkylphenols interaction with formaldehyde and aniline at temperature 75-90 °C. In that case the main products yield amounted to 73.4-88.6%.

After 3-hydroxy-3(5)-cycloalkylbenzylphenyl amines treatment their chemical structure has been confirmed by IR and MR spctroscopic methods.



The cycloalkylbenzylphenyl amines synthesized have been tested as an additive to motor oil. The oil stability has been studied in accordance to GOST 11063-77 at temperature 200°C, duration 10-20 hours, additive amount 0.5-1.0%.

The results of the researches carried out show that cycloalkylbenzylphenyl amines synthesized may be used as an efficient antioxidative additives to motor oils.

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**P167**

# COPOLYMERS FROM MONO- AND POLYHYDROXIPHTHALOCIANINE OF ZINC FOR THE PREPARATION OF SEMICONDUCTOR COATS

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The development of organic polymer semiconductor layers is addressed at the contemporary stage for optoelectronics and especially for the development of photovoltaic devices [1,2]. In this paper the synthesis of new metallophthalocyanine (Pc-Me) derivatives, including zinc, cobalt and copper hydroxyphthalocyanines, zinc tetrahydroxiphthalocyanines and other Pc-Zn derivatives is discussed. Their synthesis allowed solving one of the common difficulties in the properties of composites - low solubility in organic solvents.

The obtained metallophthalocyanines demonstrated solubility in chloroform and in other solvents of tens of times greater than the solubility of Pc-Zn (Aldrich).

Basing on the synthetized phthalocyanines and polyepoxipropylcarbazole compositions, thin layers with an HO-Pc-Zn content of 10 to 80 mass % have been made. These layers were deposited on a polyethylene terephthalate support coated with a thin optically transparent chromium layer.

Investigation of the photosensitivity of the layers was carried out by means of a special installation by the method of plotting the potential deposited on the surface of the layer of HO-Pc-Zn- carbazolic polymer, both in full illumination and wave-length $\lambda$=700 nm. The most useful properties have been demonstrated by the photosensitive layers of carbazole polymer with metallo phthalocyanine and with 2,4,7-trinitrofluorenone added. Layers that do not contain HO-Pc-Zn are sensitive only in the $\lambda$=560-650 nm range, and those with metallophthalocyanine are sensitive across the visible and near infrared range $\lambda$=700-800 nm. Thus, these polymeric layers with a content of 50-80 mass % of metallophthalocyanine can be used for production of some photovoltaic devices, including photovoltaic cells.

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**P168**

# SYNTHESIS OF NOVEL AMIDE DERIVATION OF DEHYDROABIETIC ACID

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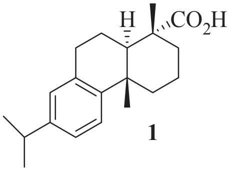
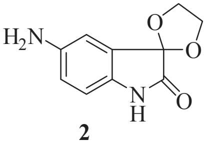
The numerous of natural and synthetical substances are represented by isatines and oxindoles. It is known, that the biological activity depends of space structure of chiral compound performing the fundamental role, therefore, the obtaining of active pure enantiomer is a hard challenge. Some reasons when isatines are used as initial compound are accessibility both the original structure with biological activity.

We have proposed and realized the synthesis of new compound **4** based on classical reaction of amidation between chloride of natural material – dehydroabietic acid **1** and 5-aminospyrodioxalane **2** followed by deprotection of dioxalane cicle.

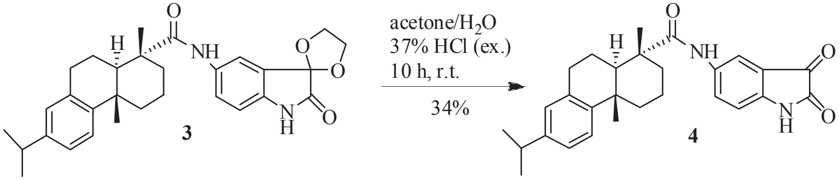


**1**



**2**

The selective extraction from turpentine succeeding by uneasy processes led us to pure [1] dehydroabietic acid **1**. Next, it was transformed into chloride by interaction with oxalylchloride in dry chloroform in 5 hours yielded 97%. The famous isatine was used as initial compound in three-stage synthesis of 5-aminospyrodioxalane **2** by two different approaches [2, 3], but the difference in yields varied only 11%. Initially, the compound **3** was synthesized by interaction between 5-aminospyrodioxalane **2** and dehydroabietic acid chloride with equimolar amount of $Et_3N$, but the ultimate deprotecting essay took part in aqueous acetone (1:1) catalyzed by excess of 37% hydrochloric acid leading to enantiomeric pure desired product **4**. The target compound was isolated by column chromatography and its structure was proved by NMR.



**Acknowledgements.** The authors are grateful for the funding offered by the National Agency for Research and Development of the Republic of Moldova under the project 19.80012.80.07A.

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**P169**

# THE FIRST EXAMPLE OF SPIROCYCLOPROPANEOXINDOLE FUNCTIONALIZED BY DEHYDROABIETIC ACID

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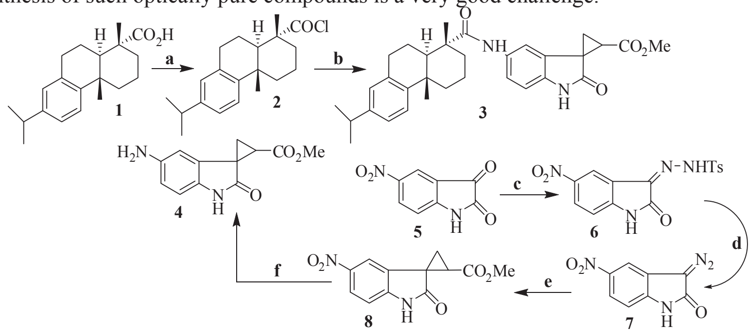
Oxindolic fragment is an often part of many natural compounds having various useful biological properties such as antiviral, anti-cancer, antimicrobial etc. It is worth noting and different spirooxindoles, because the presence of spirocycle in its molecules, its scale and variety of substitutes in spirocycles lead us to a huge amount of substances with potential biologic activity. It is known, that spirocyclopropaneoxindoles possessing anti-HIV activity, that is why, the synthesis of such optically pure compounds is a very good challenge.



Reagents and conditions:
**a)** 1,2 eq. oxalylchloride, dry $CHCl_3$, 5 h, r.t. (97%), **b) 4**, 1 eq. $Et_3N$, dry $CHCl_3$, 12 h, r.t. (50%),
**c)** $NH_2NHTs$, MeOH, reflux, 5 h (86%), **d)** 0,2 M NaOH, $50^0C$, 3 h (97%), **e)** 3 eq. $CH_2CHCO_2Me$,
reflux, 8 h (72%), **f)** $H_2$, 10% Pd/C, MeOH/THF, 6 h, r.t. (73%).

Initially, the selective extraction from turpentine succeeding by uneasy processes leads us to pure [1] dehydroabietic acid **1**, but the next interaction with oxalylchloride in dry chloroform gave us chloride **2** in quantitative yield practically. The synthesis of cyclopropaneoxindole **4** resulted in four stages [2, 3] (see scheme), but the final conversion was realized by classical amidation reaction between chloride **2** and oxindole **4** in dry chloroform with equimolar amount of $Et_3N$ and led us to new functionalized spirocyclopropaneoxindole **3**. The target compound was isolated by column chromatography and proved by NMR.

**Acknowledgements.** The authors are grateful for the funding offered by the National Agency for Research and Development of the Republic of Moldova under the project 19.80012.80.07A.

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**P170**

# TOTAL CAROTENOID CONTENT EVALUATION OF FUNCTIONAL FOOD PRODUCTS WITH ROSEHIP POWDER *(ROSA CANINA)*

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In this paper, the antioxidant capacity and physico-chemical characteristics of lipid-soluble extracts of rose hips wereevaluated. It was performed the analysis of the impact of biologically active compounds on the physico-chemical characteristics of oily extracts and the investigation of their oxidative stability. The results obtained by high performance analysis methods have allowed the argumentation of the importance of replacing synthetic antioxidant compounds with natural antioxidants in the process of producing food products with a high content of lipids.

The comparative analysis of the rose hip extract and the treated vegetable oil showed significant differences for several quality indices studied. The rose hip extract is characterized by lower peroxide values (1.86 ± 0.20 mEq $O_2$/kg) and acidity values (0.07 ± 0.001 KOH/g) compared to the values obtained for the treated vegetable oil samples. This may be explained by the antioxidant action of the biologically active compounds of the rose hip that contribute to the oxidative process slowdown.

Following the optimization of the extraction methods, it has been established that the extraction of a high content of biologically active liposoluble compounds can be carried out by ultrasonography at 45°C. The content of carotenoids extracted is 4.8 ± 0.12 mg/L and the ascorbic acid content is 12.00 ± 0.19 mg/L.

The antioxidant capacity of the rose extract compared to the treated oil sample and the content of the biologically active compounds - vitamin C, polyphenols, β-carotene were measured after 3 months of storage. The antioxidant action of the biologically active compounds, which essentially stagnate the oxidation of the oil, is argued.

This research demonstrates the possibility of using liposoluble extracts of rose hip in the production of high lipid content foods. Of particular interest, it is the opportunity to substitute synthetic antioxidants with natural ones obtained from indigenous horticultural sources in order to provide consumers with stable and safe food for consumption.

**Acknowledgements**

This work was benefited from support through the 16.80013.5107.22/Ro project, “The substitution of synthetic food additives with bioactive components extracted from natural renewable resources”, funded by Governmentof Moldova.

**P171**

# THIOPHENE ORGANOELEMENT FRAMEWORKS ON THE GLASS AS PRECURSORS FOR BIOCHIP TECHNOLOGIES

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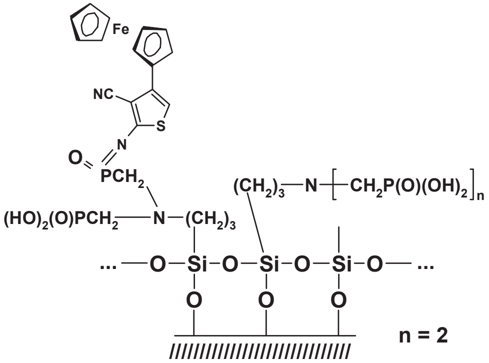
Biochip (diagnostic sensor) is a microarray or a matrix covered by protein molecules, nucleic acids, biomacromolecules or biostructures using for a large number of simultaneous tests in one sample. The supportsfor biochips are polydimethylsiloxane and polymethyl- methacrylate, but these polymers are often not suitable for application in any organic medium.

Currently, glass is usually common used for biochips manufacturing. The relative chemical inertness and the possibility of chemical modification do glass a convenient material and allow the molecule to consolidate on its surface. The immobilization of biomolecules on glass surface is possible after its chemical modifications – the formation of free silanol groups, followed the treatment with organic compounds to form reactive functional groups on the surface.

The generation of micro-, nano- and macromolecular structures from organic substances with active functional groups (including organosilicon compounds) on the polymer surface allow to control the desired molecular structure and properties of surface layers [1, 2].



The method of obtaining thiophene-phosphorus-nitrogen frameworks on a glass was developed. It was shown that such modifications exhibit hydrophilic properties compare the original surface. The obtained structure was studied by X-ray photoelectron spectroscopy and IR-spectroscopy.

**Acknowledgements**. The study was financially supported by the Russian Foundation for Basic Research (project no. 18-03-00892).

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**P172**

# SYNTHESIS OF SOME NEW DRIMANE COMPOUNDS WITH 1,3,4-OXADIAZOLE FRAGMENT

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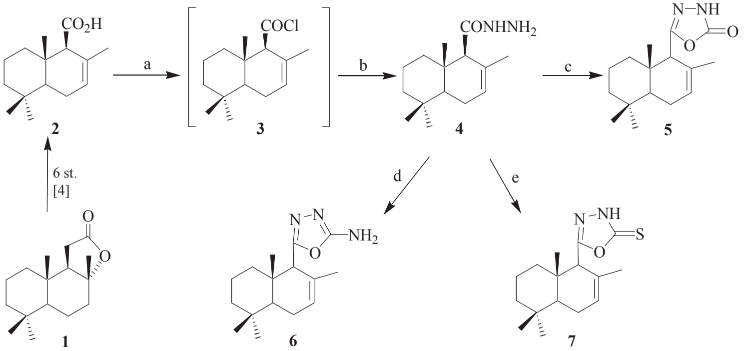
Many drimane sesquiterpenoids exhibit various biological activity [1]. In continuation of our investigation of the synthesis of nitrogen-containing drimane and homodrimane sesquiterpenoids [2, 3], herein, we describe the synthesis of 5-drimenyl-1,3,4-oxadiazol-2(3H)-one (**5**), 2-amino-5-drimenyl-1,3,4-oxadiazol (**6**), and 5-drimenyl-1,3,4-oxadiazol-2(3H)-thione (**7**) from commercially available norambreinolide (**1**) according to the scheme:



Reagents and conditions: a) $(COCl)_2$, $C_6H_6$, 20°C, 1 h, Δ, 1 h; b) $N_2H_4 \cdot H_2O$ (98%), $CH_2Cl_2$, 20°C, 10 h, 71%; c) CDI, $Et_3N$, THF, 20°C, 20 h, 95%; d) BrCN, $NaHCO_3$, dioxane, 20°C, 12 h, 90%;e) TMTD, DMFA, Δ, 1.5 h, 72%.

The structures of the newly obtained compounds were proved by IR-, $^1$H- and $^{13}$C NMR-spectroscopy, and mass-spectra.

**Acknowledgements.** The financial support from the STCU (Ukraine) Project No 6330 is acknowledged.

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## P173

# SYNTHESIS OF SOME NEW HOMODRIMANE SESQUITERPENOIDS WITH 1,3,4-OXADIAZOLE FRAGMENT

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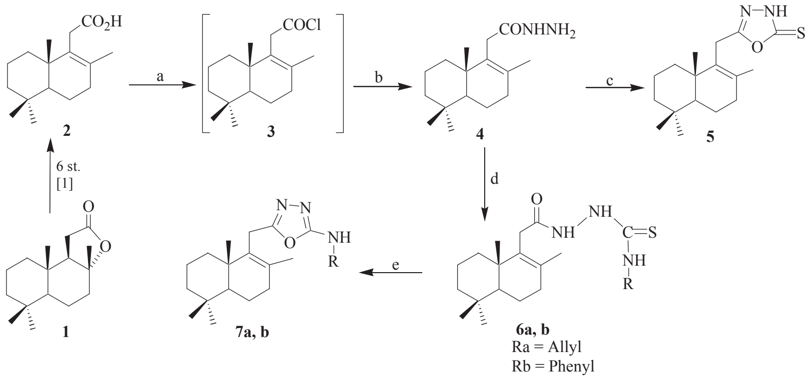
For the purpose searching of new biologically active compounds, herein, we describe the obtaining of 5-($\Delta^{8,9}$-bicyclohomofarnesenyl)-1,3,4-oxadiazol-2(3H)-thione (**5**), 2-allylamino-5-($\Delta^{8,9}$-bicyclohomofarnesenyl)-1,3,4-oxadiazole (**7a**), and 2-phenylamino-5-($\Delta^{8,9}$-bicyclohomofarnesenyl)-1,3,4-oxadiazole (**7b**) from commercially available norambreinolide (**1**), according the scheme.



Reagents and conditions: a) $(COCl)_2$, $C_6H_6$, 20°C, 1 h, Δ, 1 h; b) $N_2H_4 \bullet H_2O$ (98%), $CH_2Cl_2$, 20°C, 2 h, Δ, 6 h, 65%; c) TMTD, DMF, 90°C, 1.5 h, 70%; d) R-NCS, EtOH, 20°C, 4 h, 80-90%; e) DCC, $CH_3OH$ – $CH_3COCH_3$ (1:1), Δ, 5 h, 56-76%.

The structures of the newly obtained compounds were proved by IR-, $^1$H- and $^{13}$C NMR-spectroscopy and mass-spectra.

**Acknowledgements.** The financial support from the STCU (Ukraine) Project No 6330 is acknowledged.

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**P174**

# SYNTHESIS, STRUCTURE AND SOME PROPERTIES OF 4-HYDROXYMETHYLPYRIDYNIUM HEXAFLUOROSILICATE

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Caries is one of the most common diseases, and in childhood, this pathology ranks first among chronic diseases. In recent years, ammonium hexafluorosilicates have been the objects of extensive studies as novel promising anti-caries and hyposensitive agents. In order to enhance the use of ammonium hexafluorosilicate as anti-caries agents, we conducted a synthesis, studied the structure and some properties of 4-hydroxymethylpyridinium hexafluorosilicate (**I**).

Synthesis of hexafluorosilicate was carried out by interacting the methanol solution of 4-hydroxymethylpyridine with 45 % $H_2SiF_6$ in the molar ratio of components1 : 3. The resulting reaction product is characterized by elemental analysis, mass spectrometry, IR spectroscopy and X-ray diffraction. According to the X-ray diffraction, the geometry of the $SiF_6^{2-}$ anion in **I** is a distorted octahedron: the Si–F bond lengths are in a range 1.6780(11)–1.6877(11) Å. The difference in the Si–F bond lengths is explained by the involvement of fluorine atoms of the anions in H-bonds NH···Fand NH···Oof different strength with H-donor moieties of the cations.

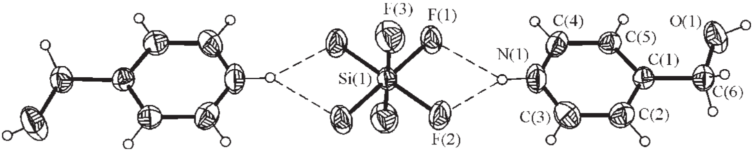

**Figure.** Formula unit of compound **I** with hydrogen bonds

In the three-term formula unit $(LH)_2SiF_6$ the hexafluorosilicate anion is located in the inversion center; the organic cation occupies a general position, being practically in the anion plane. The intense absorption bands at 738cm$^{-1}$ [ν(SiF)] and 482 cm$^{-1}$, 423 cm$^{-1}$, 403 (shoulder) cm$^{-1}$ [δ($SiF_2$)] in the IR spectrum of **I** are assigned to the $SiF_6^{2-}$ anion vibrations.

An essential factor for a medicinal substance, which significantly affects its bioavailability, is the solubility of the compound in water. The solubility of the complex in water and organic solvents: very easily soluble in water, easily soluble in DMSO, poorly soluble in methanol and ethanol (96 %). The calculated degree of hydrolysis α of salt **I** in the $1\cdot10^{-4}$ M aqueous solution is expectedly high, being 87.3 % which indicates a high degree of $SiF_6^{2-}$ ion conversion in diluted solutions with the formation of silicon dioxide and the release of fluoride ions:

$$SiF_6^{2-} + 4H_2O \rightleftarrows Si(OH)_4 + 6F^- + 4H^+.$$

The latter is important in the context of clarifying the prospects for using **I** as a carioprotective agent. This hexafluorosilicate has good solubility, a high degree of hydrolysis in a dilute aqueous solution, and can serve as a potential target for further biological research.

**P175**

# ALKYLPYRAZINES SYNTHESIS OVER ZN/AL MIXED OXIDE OBTAINED BY MECHANOCHEMICAL METHOD

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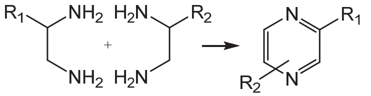
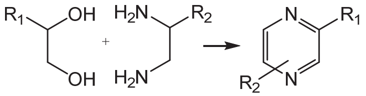
This study emphasizes the use of different types of reactants to obtain compounds belonging to the same class, alkylpyrazines. The mechanism of these reactions is cyclo-dehydrogenation [1] on the surface of a mixed oxide catalyst, which is obtained from a layered double hydroxide (LDH) [2]. LDHmaterials are part of a class having $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}]\cdot mH_2O$ general formula. In our case, $M^{2+}$ is Zn, and $M^{3+}$ is Al. The LDH material prepared by a mechanochemical method has been subsequently calcinated at 450C for 18 h, affording the mixed oxide as a catalyst for the reactions that were further studied.

Different types of cyclo-dehydrogenation reactions have been performed, using diamines, hydroxiamines or a diamine and a diol. The raw materials used and the various reaction parameters like temperature, space velocity and molar ratio of the reactants exert a significant influence in the conversion and selectivity values.



$R_1$ = H, $-CH_3$, $-CH_2CH_3$, $R_2$ = H, $-CH_3$



The reactions between diamines tend to give a small percentage of secondary products, mainly superior alkylpyrazines, the desired product being obtained almost exclusively. In the case of hydroxyamines the quantity of secondary products is influenced by the nature of -OH moieties, being lower for secondary alcohols. Regarding the reaction between a diamine and a diolthe outcome is more complex, the diamines can react with themselves, altough the catalyst favours the cyclization between a diamine and a diol. Evaluation of the process efficiency and also characterization of the synthesized compounds will be detailed.

## Acknowledgments

Financial support: Complex Projects CDI, no 70PCCDI/2018 – MAUS, Executive Agency for Higher Education, Research, Development and Innovation (UEFISCDI)

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**P176**

# DIASTEREOMRIC SEPARATION OF THE DERIVATIVES OF POTENTIAL ANTI-HIV AGENTS

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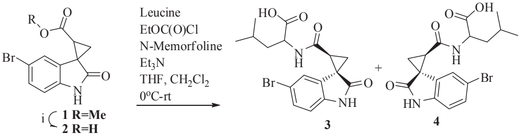
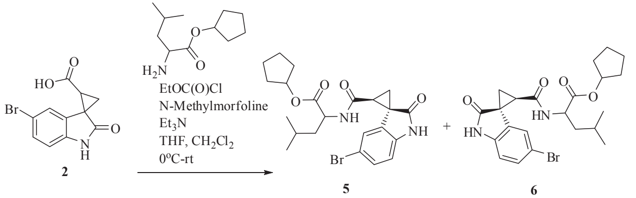
Some spirooxindole derivatives have been demonstrated earlier to inhibit HIV reverse transcriptase [1]. This ability is manifested at concentrations close to the concentrations of active drugs ($EC_{50}$ = 50 nM). Previously, we have also shown that such spirooxindoles have significant activity against another retroviral enzyme - integrase [2].

However, it should be mentioned that none of the individual enantiomers were tested for their biological properties, but rather their racemic mixtures. Usually only one of the enantiomers is active, that is why one can expect that the use of pure enantiomers will increase the activity twice, will reduce the dosage and, consequently, diminish the toxicity.Therefore, the hit compound **1** was purposely derivatized to form diastereomers. Leucine was chosen as an asymmetric fragment, which formed a peptide bond with the carboxyl group of **2** (Scheme 1). However, the resulting mixture of diastereomers could not be separated.



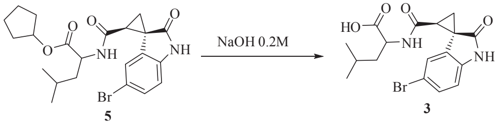
**Scheme 1**. The synthesis of compounds **2, 3, 4** (i: NaOH 0.2M**).**

Leucine was replaced by its cyclopentyl ester. The resulting mixture of **5** and **6** was chromatographically inseparable, but one of the products could be crystallized (Scheme 2).



**Scheme 2**. Synthesis of the compounds **5** and **6.**

The resulting ester **5** was hydrolyzed, which led to the target product **3** (Scheme 3).



**Scheme 3**. Synthesis of the compound **3.**

**Acknowledgements.** The authors are grateful for the funding offered by the National Agency for Research and Development of the RM under the project 19.80012.80.07A.

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**P177**

# PRELIMINARY EVALUATION OF THE CHARACTERISTICS OF SOME VEGETAL EXTRACTS FROM SPONTANEOUS FLORA IN MOLDOVA AREA (ROMANIA) WITH POTENTIAL BIOINSECTICIDE ACTIVITY

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An insufficiently studied and exploited direction today is the use of plant active principles in the agricultural area, in the field of weed and pest management of crops and seed in warehouses. Although conventional synthesis pesticides (chemical compounds) are showing satisfactory results, their repeated use leads to pest-resistant phenomena, which demands higher concentrations and increasingly complex compositions. The result is the temporary reduction of pest attacks, but variable amounts of related chemical compounds are found on treated plants or seeds, in agricultural soil and other adjacent crops, untreated with these substances. This ultimately results in the deterioration of the quality of the vegetal raw materials and even the animals for the food industry, respectively the deterioration of the quality of the foodstuffs with the health condition of the population.

In order to avoid this aspect, in the concept of promoting an ecological and sustainable agriculture, vegetal extracts / volatile oils obtained from different plants were studied to prevent and treat the effects of pest and crop pest attacks on warehouses. Various biologically active compounds from plant sources have been shown to exhibit high efficacy, multiple mechanism of action, low toxicity to mammals, which has increased the interest in using them as biopesticides in a stabilized and easy to handle form.

The aim of the herein reported investigation was to obtain some vegetal extracts using plants from spontaneous flora in the geographical area of Moldavia and Bucovina (Romania) for the production of non-toxic vegetal extracts, which show vermifug, repellent and / or germicidal effect on the field pests using two classical methods: heat reflux extraction and maceration.The obtained extracts were preliminarily characterized by sensory analysis, determination of physical constants and chemical compounds together with physical-chemical analysis by drawing and exhaustive interpretation of the UV-VIS and FTIR spectra.

**P178**

# NON-FULLERENIC ACCEPTORS BASED ON FUSED RING SYSTEM FOR SINGLE MOLECULAR ORGANIC SOLAR CELLS

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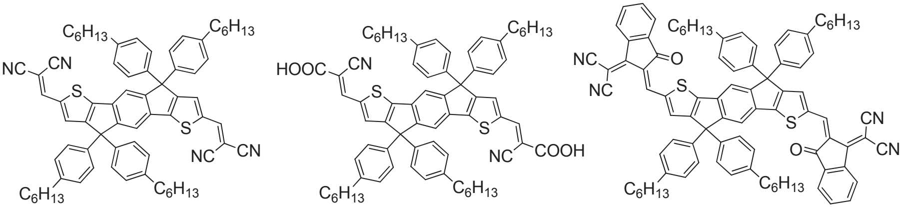
The indaceneditiophene (IDT) block is known in the literature as the central building unit to synthetize small [1,2] and polymer [3,4] acceptor molecules for organic solar cells [5,6]. The compounds presented below **1-3** are A-D-A acceptors, based on IDT as donor block (D) and different acceptor moieties (A), malononitrile for the compound **1**, 2-cyanoacetic acid for the compound **2** and 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile for the compound **3** (Figure 1). Due to their strong intramolecular charge transfer, A-D-A systems typically exhibit strong and broad absorption bands that can be easily extended to the near-infrared (NIR) and hence substantially improve photocurrent generation and eventually allow the design of semitransparent devices. To tune the solubility and film morphology, hexyl side-chains were introduced on the central fused-ring block. Our work focuses on the synthesis and investigation of A-D-A acceptors adequate by modified (Figure 1) to be connected to molecular donors for the synthesis of single molecular organic solar cells (SMOSCs).



**1** **2** **3**

**Figure 1.** The chemical structure of the target compounds **1-3.**

The target compounds **1-3** were obtainedusing a multi-step strategy and their structure was confirmed by high resolution mass-spectrometry (HR-MS), $^{1}$H and $^{13}$C NMR spectroscopy. In addition, investigation of their electrochemical and absorption properties showed that our compounds are suitable for being used as non-fullerene acceptor unit in SMOSCs.

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**P179**

# POLYMERIC MATERIALS BASED ON *α*-POLYGLYCANS WITH ANTIBACTERIAL PROPERTIES

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This work presents the results of extensive research of*α*-polyglycans based polymers using antibacterial substances of the nitrofuran class, such as furacilin, isofural and others in order to keep an accentuated prolongation effect and to reduce or to avoid the toxicity of these antibacterial substancesfrom utmost to completely [1,2]. The synthesis of conjugated *α*-polyglycan was performed by using ethyl chloroformate in the presence of triethylamine according the general scheme.

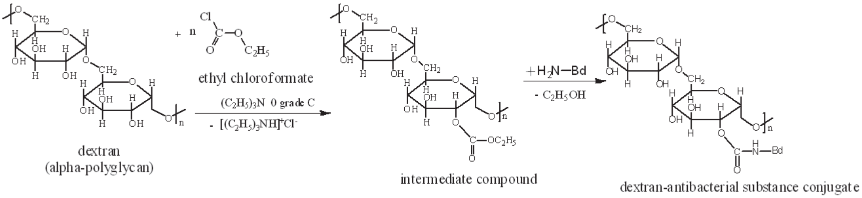

**Figure.** The general scheme of synthesis ofconjugated*α*-polyglycan.

The concentration of antibacterialsubstancesanddextranrangedfrom 10 to 50 mol%. The obtained polymers were purified by reprecipitation from hexane and next diethyl ether. The final structure of compound was confirmed by IR- and UV-VIS spectroscopy. According to IR-spectra, there are new absorption bands at 3419.18, 1680.60 and 1573.88cm$^{-1}$, which confirm the presence of -CO-NH- functional group.

Also, the concentration of antibacterial substances in the dextran macromolecules mixtures, confirmed by using IR and UV-VIS spectroscopy, is correlated with the theoretical value. For example, the dextran concentration in the dextran:benzocaine:isofural conjugate is 61% (the polymer conjugate was synthesized in the 50:30:20 mol% ratio).

The synthesized polymersare active against *S. Aureus, E. Coli* and especially *Pr. Vulgaris*. Polymeric materials with antibacterial properties can be recommended for clinical testing and medical practice.

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**P180**

# SYNTHESIS OF HALOGENATED DERIVATIVES OF *ENT*-KAUR-16-EN-19-OIC ACID

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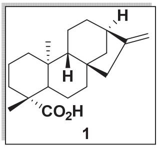
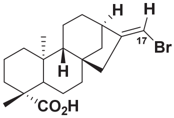
Halogenated terpenoids generally are discovered in many marine organisms, including plants and invertebrates. A substantial number of these interesting compounds demonstrated not only cytotoxic, antimicrobial, antibacterial, enzyme inhibitory activity [1-3], but also relevant ecological functions, such as antifeedant, insecticidal, antifouling and allelopathic activities [1].

For all the foregoing reasons, a series of halogenated compounds with *ent*-kauranic skeleton was obtained. The *ent*-kaur-16-en-19-oic acid (**1**) previously isolated from the sunflower *Helianthus annuus* L. dry waste [4, 5] was used as a starting material.

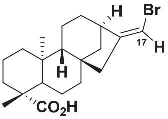
Thus, the one step functionalization of acid (**1**) catalyzed by LiBr and mediated by an hypervalent iodine oxidant [6] has generated new brominated and acetoxy-brominated compounds (**2**) - (**5**) (Figure).



**1**



**2**



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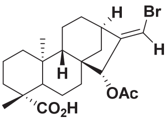

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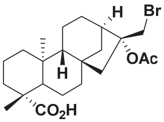

**5**

The structure and stereochemistry of the synthesized diterpenoid compounds (**2**)–(**5**) was established basing on their spectral data (IR, $^{1}H$- and $^{13}C$-NMR).

The preliminary biological activity evaluation of the diterpenic acids (**4**) and (**5**) has shown a selective inhibition of HeLa, BxPc-3 and RD tumor cells.

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**P181**

# KINETICS MODEL OF PEROXIDATION PROCESS IN NANOCOMPOSITE BIOSYSTEM SUCH AS MITOCHONDRIAL MEMBRANE OF CELL

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Currently, the widespread use of the physical measurement methods in all domains of bioscience has greatly enhanced the capabilities of biochemical methods of analysis and has caused the intensive growth of biotechnology. Thus, the large-scale studies of processes and phenomena in the natural composite biosystems, stimulate not only the study of their properties and structural features, but also the elaboration and creation of various artificial biocomposite materials with the desired properties, which is extremely important for the development of medicine and pharmacology. One of the most extensive classes of the natural composite biosystems are the cell membranes (CM) of animals and plants, as well as their artificial analogs based on the lipid mono- and bilayers, having a flat or spherical shape. According to this model, the CM on its surface and inside its structure contains a mosaic of disordered inclusions of various protein molecules (performing the transport, signaling, channel-forming and catalytic functions). In addition, the lipid bilayer, which consists of various saturated and unsaturated lipids, being the supporting base of the CM, is also a disordered mosaic system of nanoscale fragments that have a liquid crystalline structure and vary in size and composition. Thus, a biosystem of this kind can be considered as an amorphous compound representing a chaotically coupled set of the various nanoscale fragments.

The given work is devoted to the modeling of the peroxidase activity of the cytochrome *c* (Cyt) and cardiolipin (CL) complexes, due to which the process of lipid peroxidation (LPO) occurs in the mitochondrial membranes (MMs). The formation of the Cyt-CL complexes that manifest a quite high peroxidase activity, both *in vivo* (in the MMs) and *in vitro* (in the artificial analogs of CMs based on the lipid mono- and bi-layers) has been proven experimentally (details on the composition, the structure and causes of the peroxidase activity of Cyt-CL complexes are presented in the review [1]). Also in this work, the influence of lipid antioxidants(by the example of α-tocopherol and its homologs) on the kinetics of LPO was taken into account. The system of the differential equations relative to the concentrations of reagents was composed following the analysis of the general model reaction scheme consisting of 22 reactions [1] that go on two reaction pathways: enzymatic and non-enzymatic. By performing the numerical simulation and comparing of the yields of the lipid oxidation products, the obtained system of equations allows to determine and compare the effectiveness of the action of various lipid antioxidants on the LPO process; to find the unknown rate constants for some reactions, using the existing experimental data; to evaluate the peroxidase activity of the Cyt-CL complexes including the different types of cardiolipin.

**Acknowledgments.** This work was supported by the CSSDT of the Academy of Sciences of Moldova, Institutional Projects 15.817.02.03A.

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**P182**

# C-H FUNCTIONALIZATION OF BRASSINOSTEROIDS

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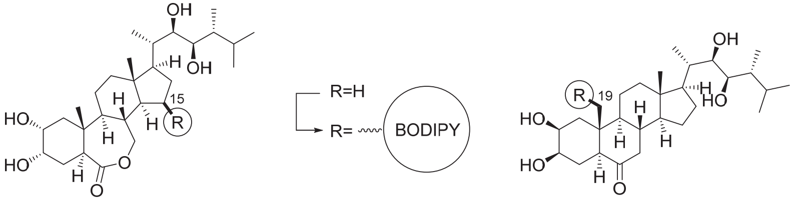
Brassinosteroids are hormones that regulate numerous biological processes in plantsincluding growth, reproduction and resistance to stresses [1]. These steroids are available only synthetically and their preparation is a laborious task. Nevertheless, such brassinosteroids as 24-epibrassinolide and 24-epicastasterone are used in agrochemistry and efficient protocols for their preparation on kilograms scale have been developed. Conjugates of brassinosteroids with fluorescent dyes are demanded in chemical biology for visualization of biochemical processes. An important issue in the design of the conjugates is that after the chemical modification, biological activity of a modified steroid should be similar to that of the parent molecule. As far as functional groups in brassinosteroids are responsible for biological activity, we decided to prepare conjugates in which a linker would be connected to the hydrocarbon skeleton of the molecule. Although total synthesis of steroids with a modified core still remains a challenging task, significant progress in the regioselective modification of complex molecules by means of direct C-H bond functionalization has been achieved recently [2]. Two regioselective C-H activation-based methods for derivatization of readily available 24-epibrassinolide and 24-epicastasterone will be presented in the current communication. Our first approach is based on the rhodium-catalyzed C-H amination that enabled the preparation of C15-functionalized brassinosteroids [3]. An alternative method of hydroxyl-directed 1,5-hydrogen atom transfer was utilized to prepare C19-modified 24-epicastasterone. All of the obtained derivatives of brassinosteroids were successfully transformed to the conjugates with BODIPY dyes.



24-epibrassinolide and its C15-conjugate

24-epicastasterone and its C19-conjugate

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**P183**

# THE FIRST SYNTHESIS OF 2-TERT-BUTYL-3-(1*H*-1,2,4-TRIAZOL-1-YL)-2*H*-CHROMENE-2-OL

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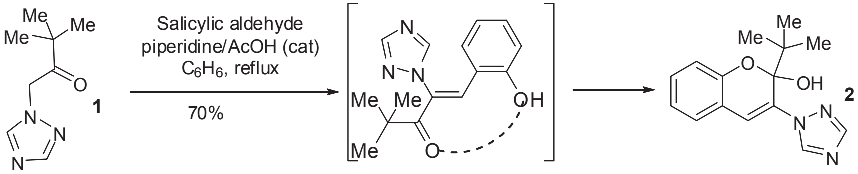
It is well known that the derivatives of 1,2,4-triazole posses fungicidal and regulating plant growth activity [1]. As the result of our studies, it was found that aldol condensation between N-vinyltriazolyl ketones and derivatives of salicylic aldehyde follows by two paths: 1) the final product of desired N-vinyltriazolyl ketone IS *E*- or *Z*-isomer, 2) the formation of unsaturated 1-benzopyran, also known as chromen [2] that forms through the subsequent cyclization of N-vinyl-triazolyl ketone. The reaction direction depends from the nature of substituent in initial triazolyl ketone and salicylic aldehyde.

Recently, the synthesis of chromenes from initial bromylsulfonylbenzene and phenolic substrate using cesium carbonate as a catalyst was described [3]. Herein, we present the first example of the interaction between 1,2,4-triazolil ketone **1** [4] and salicylic aldehyde resulting a "hybrid" compound **2** with 1,2,4-triazole and 2*H*-chromene moieties. The reaction is conducted with catalytic amount of piperidine and acetic acid inboiling benzene followed by azeotropic water removal, resulted desired compound **2** (see scheme).



The structure of compound **2** is confirmed by elemental analysis, IR-, NMR-spectroscopy and X-ray.

**Acknowledgements.** The authors are grateful for the funding offered by the National Agency for Research and Development of the Republic of Moldova under the project **15.817.02.17A.**

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**P184**

# THE FORMATION OF 2H-CHROMENES UNDER THE REACTION OF CYCLOCONDENSATION BY THE DEPENDENCE OF SUBSTITUENT'S NATURE

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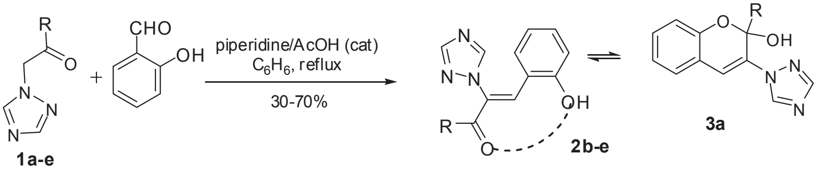
In recent years, 1,2,4-triazole derivatives have entered confidently the list of drugs for medical practice. On the other hand, many natural compounds contain chromenes and being the object of close attention from scientists like substances exhibiting biological activity as well, as their synthetic analogs [1]. To furnish, so-called, the "hybride" compound with some units from different classes is a very interesting challenge.

The aldol condensation of 1,2,4-triazolyl ketone **1a** with salicylic aldehyde leads to *N*-vinyltriazolyl ketone but the subsequent cyclocondensation does compound **3a** [2] – a "hybride" substance with 1,2,4-triazole and *2H*-chromene moieties.



R=*t*-Bu, **3a** (70%)
R=2,4-diCl$C_6H_3$ ,**2b** (60%)
R=$C_6H_5$, **2c** (60%)
R=4-Cl-$C_6H_4$, **2d** (71%)
R=4-Me-$C_6H_4$, **2e,3e**(30%)

It is worth noting, that the presence of an electron-donating group in initial triazolyl ketone contributes the formation of *N*-vinyltriazolyl ketone (see scheme), but to generate the succeeding cyclocondensation, unfortunately, is not enough. If there is an electron-withdrawing group, the same reaction does the mixture of products. The identification of such obtained compounds was carried out by NMR-spectroscopy. The signal of carbonyl group in $^{13}C$ spectra ranged 190-200 ppm for vinyltriazolyl ketones and signal ranged 95-105 ppm for hydroxyl in *2H*-chromenes clearly indicate the structure of synthesized compounds.

**Acknowledgements.** The authors are grateful for the funding offered by the National Agency for Research and Development of the Republic of Moldova under the project **15.817.02.17A.**

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