

Ministry of Education and Research  
Institute of Chemistry

**Scientific seminar**

# **ECOLOGICAL CHEMISTRY ENSURES A HEALTHY ENVIRONMENT**

*Dedicated to the 50<sup>th</sup> anniversary from the founding of the Laboratory of Mineral Resources and Water Chemistry, 30 years since organization of the Laboratory of Ecological Chemistry and commemoration of the remarkable chemist and ecologist, doctor Valeriu ROPOT*

## **Book of Abstracts**

September 16, 2022  
Chisinau, Republic of Moldova

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## Scientific seminar “*ECOLOGICAL CHEMISTRY ENSURES A HEALTHY ENVIRONMENT*”

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

*Dear Colleagues, Friends and Guests,*

*It is our pleasure to welcome You all the participants of the virtual Scientific seminar „ECOLOGICAL CHEMISTRY ENSURES A HEALTHY ENVIRONMENT”, organized by the Laboratory of Ecological Chemistry, Institute of Chemistry, Chisinau. The current event is dedicated to the 50<sup>th</sup> anniversary from the founding of the Laboratory of Mineral Resources and Water Chemistry, 30 years since organization of the Laboratory of Ecological Chemistry and commemoration of the remarkable chemist and ecologist, doctor Valeriu ROPOT (20 years of upon passing away).*

*The main aim of the seminar is active promoting in society of the scientific results obtained in the field of ecological chemistry, environmental protection and population health.*

*The seminar is addressed to a broad circle of researchers, including young licence, master and PhD students from different fields with tangential activities to the topics of the seminar and also to specialists from research and development areas of enterprises / organizations with a profile in environmental protection.*

*We are delighted to announce participation of distinguished colleagues from national and international research institutions and laboratories who kindly accepted our invitation to provide oral presentations. We express our gratitude and appreciate your contributions.*

*Acad., Dr. habilitate, Prof. Tudor LUPASCU  
Director of the Research Center of Ecological  
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## THE MAIN SCIENTIFIC RESULTS OBTAINED DURING 50 YEARS

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In the oral communication, the main results obtained by the personal reporter, as well as with the scientific researchers from the Mineral Resources and Water Chemistry Laboratory as well as from the Ecological Chemistry Laboratory of the Institute of Chemistry during 50 years of activity, are presented.

The results of studies of the interaction processes of textile dye ions in aqueous solutions are presented. It has been demonstrated that the value of the association factor of dye ions is dependent on the possibility of forming intra- and extramolecular hydrogen bonds. The sorption processes and mechanisms of organic pollutants (dyes, detergents, amines, humic substances, etc.) on different activated carbons were studied. It has been demonstrated that the degree of utilization of carbon sorbent pores is a function of the ratio between the size of the adsorbent pores and the adsorbate ions or their associations. The research results of textile dye adsorption processes in dynamic conditions on a column with a length of 10.5 meters are also presented. The research results showed that the length of the adsorption layer under dynamic conditions must be at least 3.2 meters. The results of scientific research were the basis for the design and implementation of the waste water treatment plant at the Steaua Rosie factory from Chisinau.

The scientific results related to the study of processes and mechanisms of carbonization and activation of secondary products from the processing of fruits and vines (peach pits, plums, apricots, grape seeds) are highlighted. The optimal parameters of the production technology of activated carbons from vegetable raw material have been established. The developed and patented technology was implemented at the activated carbon factory from Stefan Voda. Carbosan-E and Carbosan H enterosorbents were developed and patented on the basis of activated charcoal obtained from fruit pits and were used for detoxification of the human body.

The results of the studies of the oxidation processes and mechanisms of activated carbons are also presented. The quality and quantity of the functional groups on the modified carbon adsorbents were determined. The immobilization processes and mechanisms of heavy metals on oxidized activated carbons were studied. The structural and catalytic properties of the carbon catalysts were obtained and studied. The processes and mechanisms of heterogeneous catalytic oxidation of  $S^{2-}$ ,  $NO_2^-$ ,  $NH_4^+$ ,  $Fe^{2+}$ ,  $Mn^{2+}$  ions in model solutions and in real groundwater containing these pollutants were studied. The research results were used for the development of groundwater potable technologies. The developed technology was patented and tested in Bulboaca commune, Anenii Noi district and town Hancesti and implemented in Sculeni commune, Ungheni district.

In the oral communication, the results of studies of processes and mechanisms of depolymerization and oxidation of tannins obtained from grape seeds are highlighted. As a result of these processes, a new product was obtained which was patented under the name Enoxil. The antioxidant, antibacterial, antifungal, regenerative, toxic properties of the Enoxil preparation were investigated. The obtained results demonstrated that the preparation exhibits enhanced pharmaceutical properties and is not toxic. Based on the biologically active substance Enoxil, pharmaceutical preparations have been developed in the form of lotions and ointments. Preclinical *in vitro* and *in vivo* tests of the mentioned pharmaceutical preparations were carried out. Based on the results obtained, pharmaceutical monographs and



technological regulations for the production of the biologically active substance Enoxil and pharmaceutical products based on this active substance were elaborated. It is mentioned that the pharmaceutical compounds obtained based on the biologically active substance Enoxil were tested in 4 republican clinics. The results obtained are very good. Currently, the technical-normative documentation for the industrial production of the pharmaceutical preparations based on the biologically active substance Enoxil is being developed.

The chemical, physico-chemical and microbiological properties of tannins obtained from sawdust from oak wood, walnut and oak leaves were obtained, chemically modified and investigated.


The results of research related to the obtaining of the new construction materials based on local raw materials, which were patented and implemented at SRL "Monolit", are also presented.

A new process of depolymerization of tannins, through their halogenation, is described. The mechanism of the process was studied and the physico-chemical and microbiological properties of the new products obtained were investigated. The aim of these researches was to obtain biologically active substances with antifungal and antibacterial properties, which can be used as biodegradable pesticides for plant protection.

*I bring thanks to my colleagues: dr. hab. Mihail Ciobanu, dr. Victor Botan, dr. Nina Timbaliuc, dr. Raisa Nastas, dr. Oleg Petuhov, dr. Lucian Lupascu, dr. Irina Ginsari, dr. Maria Sandu, dr. Tatiana Goreacioc, sci. res. Tatiana Mitina et al.*

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## VALERIU ROPOT SCIENTIST DEVOTED TO THE STUDY OF MINERAL DEPOSITS AND WATERS IN THE REPUBLIC OF MOLDOVA

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In 1972, the young Doctor in Chemistry Valeriu Ropot founded at the Institute of Chemistry of the Academy of Sciences of Moldova the Laboratory of Water Chemistry and Mineral Resources. At the initiative of the ecologist Valeriu Ropot in 1992, due to the need to solve the environmental problems that were intensifying in the world, including in Bassarabia, the laboratory is re-profiled in the Laboratory of Ecological Chemistry.

The protection of the environment requires the implementation of a complex of social, economic, scientific research and technical measures, which guarantee the preservation and improvement of the state of the natural environment useful for society. These measures can have both a global character, touching the vital interests of the entire population of the earth, and a local character, for solving ecological problems.

The main scientific objectives of the institute new structure were aimed at the evaluation of natural minerals, the research and establishment of the formation laws of the quality of surface and underground waters and highlighting the processes and mechanisms of transformation of natural and anthropogenic pollutants in aquatic systems. Scientist Valeriu Ropot paid special attention to the development of high-performance technologies for making surface water potable, as well as those for purifying waste water from economic activities in the Republic of Moldova.

In the scientific research carried out under the direction of dr. Valeriu Ropot, the mechanism of pollutant immobilization through mineral absorbents, the role of active centres in the migration and transformation processes of pollutants in the aquatic environment was highlighted. Thus, the initial field of research was the evaluation of natural minerals (clays) used for the purification of waste water from the winemaking industry [2, 3, 6-8].

There were deep researches on the quality of surface and underground waters, being organized by the scientist Ropot Valeriu many scientific expeditions from the source to the Black Sea, the Dniester and Prut rivers and many small rivers in the Republic of Moldova. The obtained results of the scientific researches were presented in various scientific publications (about 200), presented at various national and international scientific conferences [1, 5] and used in the development of the National Strategic Action Program in the field of environmental protection, years 1995-2010-2020 [4].

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## OXIDATION/MINERALIZATION OF ANIONIC SODIUM DODECYL BENZENESULFONATE SURFACTANT BY FENTON REAGENT

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Surfactants are the main ingredients of synthetic detergents. It is widely used in soap, toothpaste, cleaning detergents and shampoo. They also have numerous applications in industrial products, in cosmetics, medicines, textiles, food, paper, oil technology, paints, polymers, pesticides and mining. The composition of wastewater includes anionic and nonionic surfactants, which are the most difficult to biodegrade in natural waters, thus spilled into surface and underground waters, cause negative influences on the self-purification process. The global production of surfactants is 13 million tons per year, and anionic surfactants constitute the largest part of the total STAs used. The toxicity of linear alkyl sulfonates (ASLs) to fish and humans is quite high, since ASLs even at low concentrations (1 mg/L) can cause toxicity to aquatic organisms, which increases in proportion to the total carbon content of the alkyl chain. Therefore, due to their resistance to biodegradation, they can accumulate in aqueous environments and influence the quality of natural waters. In this context, the development of waste water decontamination methods is a fairly current issue. Various technological processes are used for the removal or degradation of surfactants, including the use of anaerobic fluidized bed reactors, chemical methods, electrochemical oxidation, membrane technology, chemical precipitation, and catalytic and photocatalytic degradation. However, the limitations of using biological methods and difficulties in using other technologies (such as membranes) require us to develop and use new methodologies to deal with these problems. Thus, advanced oxidation processes (AOPs) [1] are recommended for wastewater pre-treatment or tertiary treatment, when wastewater contaminants have high chemical stability and/or low biodegradability.

By reason of scientific research, it was found that the degradation/mineralization performance of the anionic surfactant sodium dodecylbenzenesulfonate (SDBS) depends on physico-chemical parameters such as pH value, hydrogen peroxide and catalyst concentration, and reaction time.

As a result of the experimental studies, the degradation conditions of SDBS were determined. It was established that at optimal conditions of homogeneous oxidation ( $[\text{H}_2\text{O}_2]_0=1 \cdot 10^{-3} \text{ molL}^{-1}$ ,  $[\text{Fe}^{2+}]_0=1 \cdot 10^{-3} \text{ molL}^{-1}$ , and pH value 3), the concentration of anionic surfactant in the system decreases from 20 mg/L to 7 mg/L, and the degradation performance can reach up to 74.4%. The reaction rate ( $\Delta c/\Delta t$ ) of oxidation/mineralization is determined by the concentration of OH radicals formed on the surface of the catalyst and by the probability that OH radicals interact with surfactant molecules. So, the reaction rate of SDBS can reach  $2.89 \cdot 10^{-7} \text{ molL}^{-1}\text{s}^{-1}$ , and the rate constant  $k=0.76 \cdot 10^{-3} \text{ s}^{-1}$  under optimal conditions.

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## DISTRIBUTION OF SOLUBLE AND INSOLUBLE SPECIES OF METALLIC IONS AS A RESULT OF SLUDGE APPLICATION ON THE SOILS

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Applying sludge to agricultural land is reasonable as it improves some soil properties such as pH, organic matter content and nutrients. But the use of sludge and biosolid on forested and agricultural land is restricted by heavy metal content. Long-term use of sludge leads to the accumulation of heavy metals in the soil. Even after a short-term application, the content of heavy metals can increase considerably. The application of sludge affects the salinity of the soil and consequently the availability of metals to plants increases [1]. To evaluate the potential impact of sludge application on agricultural land it is necessary to know the mobility and bioavailability of heavy metals in soil. The solubility of metals is controlled by adsorption/desorption, precipitation/dissolution and complex formation reactions. Although metal solubility is initially reduced by sorption reactions, long-term solubility is controlled by chemical forms/species that may vary over time. Knowledge of metal distribution and speciation in solution is essential to understanding the chemistry of the soil solution–metal ion system.

The thermodynamic evaluation of soluble and insoluble species of *Cu* (II) in soils treated with sludge from domestic wastewater treatment processes was carried out, based on experimental data regarding the typical chemical composition of soil solutions from the Republic of Moldova. The choice of copper is conditioned by its high content in native soils. Thermodynamic calculations of *Cu* (II) ion speciation in sludge-treated soil solutions were performed. The developed thermodynamic model was used for chemical speciation in homogeneous monophasic and heterogeneous biphasic systems as a function of a series of thermodynamic parameters [2]. As a result, expressions to calculate the domains of thermodynamic stability of *Cu* (II) species in the analyzed systems were deduced. One of the most important advantages of using the developed thermodynamic model, which is based on computer calculations, is the possibility to predict the distribution of metal ion species in sludge. The results of this study suggest that as soil pH decreases, the availability and mobility of copper ions increases due to the soluble chemical species in which this ion is present in soil solutions.

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## ACTIVATED CARBON - A KEY FOR A HEALTHY ENVIRONMENT

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The problem of soil and water pollution has accelerated with the development of organic synthesis technologies, which has led to the appearance of considerable quantities of non-biodegradable substances and materials: fertilisers, pesticides, pharmaceutical products, phosphates, petroleum substances, detergents, polychlorinated biphenyls, etc. The removal of many pollutants from water, soil and air presents a problem at the global level, and the increase in the concentration of toxic substances in the environment leads to the appearance of diseases in all systems of living organisms.

An environmentally friendly solution to pollutant removal is the process of adsorption, and in particular adsorption on activated carbons. Activation is one of the processes for modifying carbonaceous materials and consists in the partial oxidation of carbonized from the layers of its structure, using steam, carbon dioxide, hydroxides or alkali metal carbonates as activating agents. During this process, the surface and porosity of the carbonized organic material increases, as a result, activated carbons are obtained - the most widespread adsorbent, having the widest uses.

The Laboratory of Ecological Chemistry has a rich history and experience in the synthesis, regeneration and study of carbon adsorbents. The first activated carbons in the laboratory were obtained in the early 90s using chemical activation methods. At the moment, in the Laboratory of Ecological Chemistry, various processes are developed and used to obtain carbonic adsorbents: chemical activation, classic physico-chemical activation with water vapor, microwave treatment, hydrothermal and fluidized bed activation. For more than 30 years, activated carbons have been obtained from local agricultural waste, but also from non-biodegradable materials such as used polymers and tire pyrolysis residues. The synthesized carbon adsorbents have been used in water treatment processes, in the pharmaceutical field and as catalysts.

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## THE INFLUENCE OF GLUTATHIONE ON THE SELF-PURIFICATION CAPACITY OF AQUATIC SYSTEMS

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Removing the impact of chemical substances on the aquatic systems has become very topical and fits into the concept of ecological chemistry which consists of the formation of the chemical composition of the environment, appropriate to a biological value of habitation. Glutathione (GSH) is a substance from the thiol class, of biogenic origin, with strong reducing properties, respectively it actively participates in redox processes in natural waters. To determine the influence of GSH on the *self-purification* process of aquatic systems, several systems were modeled using the radical trap, PNDMA (p-nitroso-N,N-dimethylaniline), which allows the determination of the *inhibition capacity* and stationary concentration of OH radicals in the modeled systems. For this purpose, the following systems were modeled: *GSH-H<sub>2</sub>O<sub>2</sub>-PNDMA-hv*; *GSH-H<sub>2</sub>O<sub>2</sub>-PNDMA-Cu(II)-hv*; *GSH-H<sub>2</sub>O<sub>2</sub>-PNDMA-Fe(III)-hv*. All model systems were irradiated with polychromatic lamp DRT-400 and Solar Simulator, Oriel Model 9119X (SS) [1,2].

From the obtained results, it was found that increasing the concentration of GSH in the system leads to an increase in the *inhibition capacity* and a decrease of the OH radicals concentration, for the systems irradiated at all sources. It was determined that the *inhibition capacity* values in the presence of GSH, which was added in concentrations  $(0.33-3.33) \cdot 10^5$  M, are of order  $10^6-10^5$  s<sup>-1</sup>. According to the *inhibition capacity* parameter, the systems are classified as highly polluted and polluted waters. So, in the presence of GSH, in aquatic systems, the intensity of *self-purification* processes decreases considerably and depends on the concentration of GSH as well as the emission spectrum and the intensity of solar rays.

When Cu(II) ions and more obviously Fe(III) ions are introduced into the system, the *self-purification capacity* of aquatic systems suddenly worsens, which is manifested by increasing the values of the *inhibition capacity* and decreasing the concentration of OH radicals. The values of the *inhibition capacity* in the presence of Cu(II) ions increase by 1.3-3.5 times, and in the presence of Fe(III) ions by 1.5-5.3 times and depend on the concentration of GSH, as well as the source of irradiation. So it was confirmed that GSH binds Cu(II) and Fe(III) ions in complexes of the form:  $(\text{GSH})_2\text{Cu}^+$  and  $(\text{GSH})_2\text{Fe}^{2+}$ , which have a much higher reactivity towards OH radicals compared to systems where GSH is present and lead to their consumption. As a result of the given research, it was demonstrated that GSH, having a strong reducing character, leads to the consumption of oxidative equivalents in aquatic systems on the one hand, and on the other hand excludes Cu(II) and Fe(III) ions (which have an important role of catalysts in oxidation-reduction processes in natural waters), thus diminishing the intensity of the *self-purification* processes of aquatic systems.

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## SOME CONSIDERATIONS OF NITRITE IONS ADSORPTION ON ACTIVATED CARBONS. THE SUGGESTED MECHANISMS

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Activated carbons are efficient adsorbent materials for removing pollutants from water. The physical-chemical nature of the activated carbons surface plays an important role in the process of adsorption and should be considered when selecting or preparing activated carbon for application purposes in adsorption and/or oxidation. Based on the obtained results regarding the characterization of carbonaceous adsorbents surface chemistry as well as the nitrite adsorption capacity as function of pH value, mechanisms of pollutants adsorption were proposed [1].

For the *initial activated carbons*, which are poor in functional groups on the surface, in the adsorption process  $C_\pi$  sites participate. These sites or adsorption centers ( $C_\pi$ ) are strongly influenced by the solution pH value, in the acidic domain, protons ( $H^+$ ) are concentrated on  $C_\pi$  sites and the positively charged graphitic structure of activated carbon attracts the nitrite ions (Figure 1). For the *modified activated carbons (modified with chlorine ions)*, adsorption proceeds via the mechanism of protonation of hydroxyl groups ( $-OH$ ) on the activated carbon surface. On the surface of initial activated carbons, with a weak basic surface, there are few hydroxyl groups from alcohols and phenols, while on the surface of oxidized activated carbons there are more hydroxyl groups from alcohols, phenols and carboxylic acidic. In the basic domain,  $OH^-$  ions are competitive with the nitrite ions, the graphitic surface of activated carbon becomes negatively charged and, consequently, rejects the nitrite ions [2].

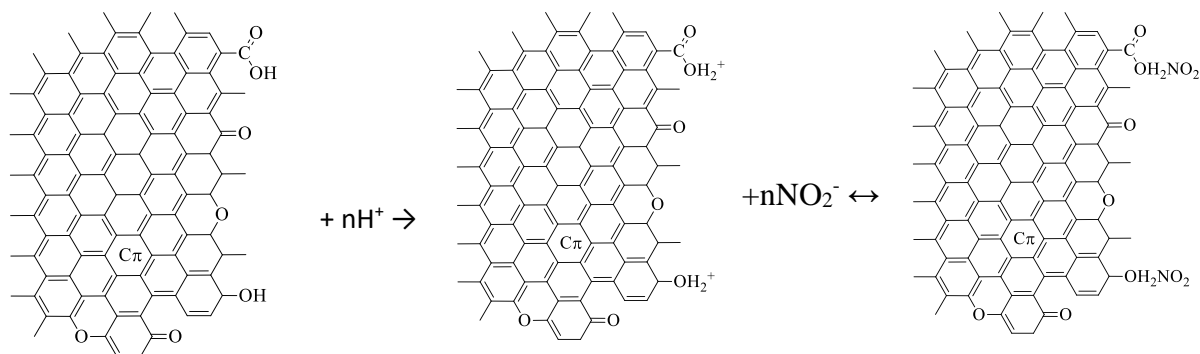


Fig. 1. Schematic presentation of the nitrite ions adsorption on the surface of the modified activated carbon. (1) - protonation of functional groups on the surface of activated carbon; (2) - adsorption of nitrite ions by electrostatic interaction [1].

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## POPs CONTAMINATED SITES IN REPUBLIC OF MOLDOVA: PROBLEM DEFINITION AND POSSIBLE SOLUTIONS

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The soil is an important and non-renewable natural resource which is a base for life and for supporting livelihoods. Healthy soil is an essential component of the agriculture production with the capability of supporting the ecosystems on which economic activities and livings rely (<https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52006PC0232> [1] <http://www.ipes-food.org/pages/CommonFoodPolicy> [2]). However, soils are under increasing environmental pressure across the globe, and the associated soil degradation is raising extreme values in Europe due to a high population density and its related activities, such as industrial activity, inappropriate agricultural and forestry practices, tourism or urban development ( <https://esdac.jrc.ec.europa.eu/themes/soil-contamination> [3]). The aim of this study is an evaluation of the status of contaminated sites in Republic of Moldova and problems of their management for the sustainable agriculture production. The 16 POPs contaminated sites were studied in 2020 year for the actualization of the current situation after the inventory project in 2009 – 2010 years. More detail risk assessment procedure was realized for the studied sites for the evaluation of possible impact to nearest ecosystems, agriculture production and human health. The obtained results showed that the situation from the past inventory (2009) is not changed essential for POPs contaminated sites. The high level of contamination was identified for the majority of sites, the level and spectrum of pollutants have not changed significantly. All studied sites have high environmental and public health risks. The remediation actions are required for all of them. These actions can include the utilization of in-site remediation technology and dumping of contaminated materials at the site. Several projects were made for the testing of in-situ remediation technologies like bio- and phytoremediation. The POPs degradation and microbiological properties of contaminated soils have been investigated in the application of the phytoremediation experiment and DARAMEND technology. The activation of soil microorganisms in the complex with “Green Chemistry” approach leads to the destruction of POPs in soil and decreasing of hazards from high polluted soil in the conditions of Republic of Moldova. The special requirement should be elaborate and later adopt regulation for each site based on guides of the European Union, and other actors in the field. The other important factor is to elaborate and approve environmental quality standards that indicate the admissible concentrations of hazardous substances in the soil based on the type of land use: agriculture, residential, commercial, and industrial. One of the most important strategies for the achievement of sustainable development is the promotion of a legislative system coherent with current requirements at the international level. The conclusion is that possible remediation action should to be developed after the complex study of pollution spectrum and geotechnical conditions for every polluted site by the complex approach.

**Acknowledgements.** This work was carried out within the Moldovan State Program (2020-2023), project number 20.80009.7007.20.

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## ADSORPTION OF WATER SOLUBLE VITAMINS ON AUTOCHTHONOUS ACTIVATED CARBONS

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The continuous and increasing pollution of water is one of the most pressing environmental problems in the world. A special type of contaminants are pharmaceutical products, that are ever more discovered in the environment, significantly affecting the quality of life. The increasing use of human and veterinary pharmaceutical products, accompanied by their infiltration into the aquatic and terrestrial environment, requires urgent solutions for the immobilization and removal of this category of pollutants. Adsorption is one of the most effective and practical techniques for removing pollutants from water. The use of carbonic adsorbents in water treatment technologies is justified by the fact that activated carbons are able to remove almost entirely a very wide spectrum of pollutants.

In the Ecological Chemistry laboratory of the Institute of Chemistry, using different methods and conditions of activation, a set of activated carbons was obtained in order to identify samples with potential of use for the immobilization and removal of pollutant substances from aquatic systems. In this research were studied the adsorption parameters of vitamins B3 (Nicotinic acid,  $C_6H_5NO_2$ , MM 123.11) and B6 (Pyridoxine,  $C_8H_{11}NO_3$ , MM 169.18) on four samples of autochthonous activated carbon (CAS-23, obtained from peach kernels; CAN-8, obtained from walnut shells; AC-MR, obtained from apple wood, AC-C, obtained from apricot kernels). The influence of initial concentrations of adsorbates, contact time, temperature, granulometric composition and surface parameters of carbons on the adsorption process were investigated. The research of the influence of the granulometric composition of carbon adsorbents on the adsorption capacity of vitamins showed a considerable increase (about 30%) of the adsorption power value with the decrease of the carbon particle size (from 800-2000  $\mu m$  to 90-125  $\mu m$ ). The adsorption kinetic curves were determined in a time interval between 10-300 minutes at 25°C. The obtained data shows that the amount of immobilized vitamins on investigated carbon adsorbents grows with increasing contact time between vitamins solution and carbon adsorbent surface. It was found that the equilibrium of the adsorption process was achieved after 3 hours of stirring/contacting. The adsorption isotherms of vitamins on local carbon adsorbents were determined at three values of temperatures (25°C, 35°C and 45°C). According to the obtained data the increase of the temperature is accompanied by the decrease of the amount of immobilized adsorbate for all studied carbon samples. The adsorption capacity of the autochthonous carbon adsorbents towards investigated vitamins was determined from their adsorption isotherms. The obtained results are in accordance with the method of obtaining of researched carbons and their structural parameters, being obvious the advantage of samples AC-MR and AC-C, which showed the highest adsorption values: about 0.9 mmol/g. The adsorption values of CAN-8 and CAS 23 samples indicated near 0.65 mmol/g.

The realized research shows that pharmaceuticals such as vitamins B3, B6 can be effectively removed from aqueous solutions using autochthonous activated carbon, obtained from the local vegetable raw materials.

**Acknowledgements.** The research leading to these results has received funding from the institutional project DISTOX, number 20.80009.7007.21.

## ASSESSMENT OF ACCUMULATION OF POTENTIALLY TOXIC ELEMENTS IN MOSSES COLLECTED IN THE REPUBLIC OF MOLDOVA

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The moss biomonitoring technique was used for the assessment of air pollution in the Republic of Moldova, in the framework of the UNECE ICP Vegetation Programme. The content of 11 chemical elements (Al, V, Cr, Fe, Ni, Zn, As, Sb, Cd, Cu, and Pb) was determined by neutron activation analysis and atomic absorption spectrometry in samples collected in spring 2020. Distribution maps were built to identify the most polluted sites. The highest concentrations of elements in mosses were determined in the north-eastern, central, and western parts of the country. The main element associations were identified using factor analysis. Three factors were determined, of which one of mixed geogenic–anthropogenic origin and two of anthropogenic origin. A comparison of the data obtained in 2020 and 2015 [1,2] showed a significant decrease in the concentrations of Cr, As, Sb, Cd, Pb, and Cu in 2020. The state of the environment was assessed using Contamination Factor and Pollution Load Index values, which characterized it as unpolluted to moderately polluted. Possible air pollution sources in the Republic of Moldova are resuspension of soil particles, agricultural practices, vehicles, industry, and thermal power plants.

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## STUDY OF THE ADSORPTION OF *BACILLUS SUBTILIS* AND *BACILLUS CEREUS* ON DIFFERENT FRACTIONS OF ACTIVATED CARBONS OBTAINED FROM APPLE WOOD

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The paper presents the results of scientific research related to the study of adsorption processes of *Bacillus subtilis* and *Bacillus cereus* bacteria on activated carbon obtained from apple wood. The activated carbons used have a specific BET area of about 2018 m<sup>2</sup>/g and a total sorption volume of the pores equal to 1.573 cm<sup>3</sup>/g. The study of the kinetics of the adsorption processes of the *Bacillus subtilis* and *Bacillus cereus* bacteria showed that the value of the maximum adsorption for the fraction 630-800 μm is established within 90 and 70 min, respectively. The maximum adsorption capacity for the *B. subtilis* bacteria is 0.54-0.55 McF\*10<sup>8</sup>/g, higher than activated charcoal obtained from apricot stones that has the values of 0.375-0.385 at 27°C. For the *B.cereus* bacteria the maximum adsorption was attested at the value of 0.45 McF\*10<sup>8</sup>/g, also higher than the adsorption capacity of the activated charcoal obtained from apricot stones, that has the value of 0.33 McF\*10<sup>8</sup>/g at 27°C. An example of a peak adsorption after 90 minutes of the contact for the *B.subtilis* bacteria is presented in the figure below:

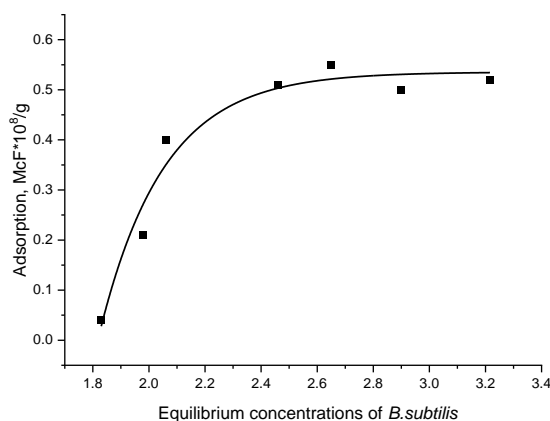


Fig. Adsorption isotherm of *B. subtilis* bacterium on AC-apple, fraction 630-800 μm at 27°C.

The kinetics of the adsorption processes of activated carbon obtained from apple wood (fraction 800-2000 μm) for the same bacteria were evaluated at 27°C. The main sorptive properties were attested after 90 to 120 minutes of contact. The adsorption values were in the range of 0.21-0.25 McF\*10<sup>8</sup>/g for *B. subtilis* and 0.26-0.28 McF\*10<sup>8</sup>/g for *B. cereus* depending on the contact time, lower than in the case of the fraction 630-800 μm.

Thus, we can conclude that the sorption capacity of the activated carbon of the fraction 630-800 μm obtained from apple wood is approximately 2 times higher than in the case of the 800-2000 μm fraction of the same carbons for both bacterial species taken into study.

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## PRELIMINARY STUDIES REGARDING THE ADSORPTION OF PHENAZONE AND CADMIUM IONS ON COMMERCIAL ZEOLITE

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One of the main problems of modern medicine is intoxication of a human organism, as a result of the direct impact of the negative state of the environment. The scientific results have shown that the detoxification of the organism can be performed by enterosorbents for removal of various toxic substances from the organism, both that enter in it from the environment or form in the organism itself [1,2].

Here we present the preliminary results obtained for adsorption of phenazone (marker of hepatic enzyme drug metabolizing activity) and cadmium ions (endocrine disruptor) on commercial zeolite from water solutions in order to develop new composites-enterosorbents.

Batch adsorption experiments were carried out by contacting the same amount of the zeolites with the phenazone, cadmium ions solutions and the mixtures of these two adsorbates. The solution pH (3.0 and 5.5) was maintained by using acetate buffer solutions and the suspensions were vigorously shaken at 35 °C. The phases were separated by filtration and the residual phenazone and cadmium ions were determined by UV-Vis and AAS spectroscopies.

Summarizing the preliminary results, it was found that,

- (i) the adsorption capacity of the zeolite for phenazone is higher than for cadmium ions, being approx. 7 and 4 mg/g, respectively;
- (ii) as the pH value rises from 3 to 5.5, the adsorption capacity of the zeolite for both adsorbates decreases, up to approx. 5mg/g for phenazone and approx. 0.3 mg/g for Cd ions;
- (iii) in the case of the adsorption of phenazone and cadmium ions from the mixture on zeolite, at both pH values, the behaviour is similar as in the case of the adsorption of these adsorbates from individual solutions;
- (iv) for adsorption from the mixture, the adsorption capacity of the zeolite decreases with the increase of the pH value (5.5), for phenazone from approx. 6 mg/g at approx. 3.5 mg/g and for cadmium ions from approx. 6 mg/g to 0.6 mg/g;
- (v) by comparing the results obtained for the adsorption of adsorbates from individual solutions and the mixture, it is observed that, in the case of adsorption from the mixture, the adsorption capacity of phenazone decreases slightly, whilst for the adsorption capacity of cadmium the insignificant increase has been registered, for both pH values.

**Acknowledgements.** This research was performed with the financial support of the Project “Reducing the impact of toxic chemicals on the environment and health by using adsorbents and catalysts obtained from local raw materials”, DISTOX, 20.80009.7007.21, within Moldovan State Program 2020-2023.

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## MONITORING THE CONTENT OF THIOLS IN THE RIVER RAUT (PERIOD OF THE YEARS 2019-2021)

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The Raut River is the main right tributary of the Dniester River on the territory of the Republic of Moldova and has a total length of 286 km [1]. In turn, the Dniester River represents the main source of drinking water supply for the large cities located along its course [2]. The water of the Raut directly influences the quality of the waters of the Dniester river after the discharge of the tributary near the village of Ustia, Dubasari district. This shows the importance of protecting the Raut River as a living environment and the continuous monitoring of its ecological state.

The ecological well-being of natural waters is ensured by the presence of active forms of dissolved oxygen, called oxidative equivalents, especially hydrogen peroxide, which together with reducing equivalents, of which thiols are also a part, form the redox balance of the waters [3]. The redox state of the water can be estimated by the content of hydrogen peroxide or by the content of reducing equivalents. Thus, the purpose of the research is to determine the content of thiols in the waters of the Răut River during the years 2019-2021.

The content of thiols in the water samples taken was determined by the Ellman method [4]. The annual averages of thiol content varied within  $10^{-5}$ - $10^{-6}$  M, the highest concentration being observed in 2019 ( $1.25 \cdot 10^{-5}$  M), and the lowest in 2021 ( $1.82 \cdot 10^{-6}$  M), while the average for the year 2020 is  $5.42 \cdot 10^{-6}$  M. Compared to other data on the content of thiols in surface waters, the recorded values are high [5]. Taking into account that thiols are also of natural origin, their concentration must undergo a seasonal variation, reaching maximum values in summer when the biological activity is maximum and, respectively, in autumn and spring, minimum concentrations. Thus, natural seasonal variation was recorded only during 2021. In summer, the content of thiols was maximum ( $2.43 \cdot 10^{-6}$  M), and in spring and autumn, the content was minimum ( $1.52 \cdot 10^{-6}$  M).

Therefore, the thiol compounds were determined during the entire monitoring period, the concentration of which varied within the limits of  $10^{-5}$ - $10^{-6}$  M, being characterized as high contents for surface waters. The lack of natural seasonal variation of thiols in the years 2019 and 2020, with the maximum concentrations in autumn, indicates the pollution of the river especially with degradable organic substances.

**Acknowledgements.** This research was supported by the *research project: 20.80009.5007.27*.

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## CHANGES OVER TIME IN PERSISTENT ORGANIC POLLUTANTS CONCENTRATIONS IN SOILS IN LOWER DNIESTER REGION, REPUBLIC OF MOLDOVA

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Dniester hydrographic district covers approximately 60% of the Republic of Moldova territory ensuring 63% of the annual water quantity and it encompasses ~80% of country's underground waters. Soils, more precisely, agricultural lands and the practices applied on them serve as a source of point pollution of groundwater and surface waters, in addition to other sources such as the household sector, the food industry, the agricultural sector, the energy sector and other sources of continuous pollution.

Moldova is considered an agrarian country whose main resource and wealth are fertile soils. Substances from the group of persistent organic pollutants (POPs) pose a particular danger to the health of the population and to environmental factors. During the seventies of the last century, organochlorine compounds from this group were widely used in agriculture as insecticides and fungicides. Considering that the impact of the environment on the human body is inevitable, it is necessary to monitor the content of POPs in soils in the Republic of Moldova, aimed at reducing the risk of toxic substances by reducing their impact on living organisms.

The study aims to identify the changes over time of POPs concentrations in the soils from 16 sites along the Dniester River. Results of the research done in 2010 were compared with the investigations in 2020 of the same sites. Random sampling was used, and complex samples were collected from the depth of 0-10 cm. Gas Chromatography coupled with mass spectrometry was used for POPs identification and quantification according to EPA and ISO methods. The degradation status of DDTs was assessed using the ratio (DDE + DDD)/DDT, which ranged from 0.052 to 0.472 in 2010 and from 0.045 to 8.78 in 2020. These reports show old sources of DDT pollution, indicating that DDT residues were significantly transformed into their degradation products in these areas.

The distribution of HCH isomers varied between soil samples. This may be associated with the isomerization of HCH during the soil transformation process, as well as with differences in physicochemical properties and degradation rates. The value of the  $\beta/(\alpha + \gamma)$  isomers ratio was used for the identification of aged sources of pollution. In the present study, in 53% of the results from 2010 and for 69% of the analysed soils in 2020 the ratio of  $\beta/(\alpha + \gamma)$  isomers was  $> 1$ . Thus, it can be concluded that in these regions the source of pollution is the past use of technical HCH (the share of samples in which the  $\beta/(\alpha + \gamma)$  isomers ratio was  $> 1$  is greater than 50%). The value of the  $\alpha$ -HCH/ $\gamma$ -HCH ratio varied from 0.12 to 7.8 (2010) and from 0.0 to 8.3 (2020), indicating that there is a slight increase in the HCH transformation under natural conditions and that both lindane and technical HCH were sources of HCH contamination. In conclusion, the study has shown that the contamination level has not changed significantly over time, subsequently there is a need for the remediation of the studied sites.

**Acknowledgements.** The research was carried out within the National Project no. 20.80009.7007.20 "Study and management of pollution sources for the elaboration of recommendations for the implementation of measures to reduce the negative impact on the environment and the health of the population".

## ASSESSMENT OF THE IMPACT OF BIOCHEMICAL PROCESSES AT THE SEDIMENT-WATER INTERFACE IN AQUATIC ECOSYSTEMS IN THE BIOSPHERE RESERVE „PRUTUL DE JOS” ON BIODIVERSITY IN THE CONTEXT OF CLIMATE CHANGE

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Conservation of biological diversity in ecosystems, species, populations and genes is one of the main concerns of mankind in the third millennium. The problem is that with the advancement of technological progress and the intensive use of natural resources, the anthropogenic impact on biological diversity has considerably increased, significantly reducing the number of species and varieties of living organisms that populate the Earth. Assessing the impact of biochemical processes at the sediment-water interface in aquatic ecosystems in the Biosphere Reserve „Prutul de Jos” on biodiversity in the context of climate change is important in that it includes biochemical research at the sediment-water interface, including the establishment of properties surface area and influence of the organic-mineral complex, amorphous phase, interstratular material of clay minerals, determination of mineralogical features, changes in the cation exchange complex, spatial dynamics of heavy metals in sediments, their chemical partition in particle constituents and their mobility in aquatic ecosystems, such as and evaluation of the complex influence of abiotic factors on water quality, establishing the kinetic characteristics of biochemical transformations of nitrogen in aquatic ecosystems, consumption of dissolved oxygen in water, self-purification capacity of the aquatic ecosystem, use of the model for ru biochemical simulations and for practical purposes, for modeling and forecasting ecological crisis situations in the water basins of the Biosphere Reserve „Prutul de Jos” and assessing the impact of these processes on the biodiversity of the aquatic ecosystem as a whole.

Climate change, changes in water circulation, intensification of water evaporation processes, eutrophication of water basins are becoming a concern for the environment and human health. That is why it is important to detect, monitor and evaluate the impact of different metabolites eliminated in the aquatic environment following the processes at the sediment-water interface and the impact on aquatic flora and fauna.

The object of study is the „Prutul de Jos” Biosphere Reserve (Republic of Moldova) located in the southwest part of the country. This biosphere reserve includes the Prut River and several floodplains. Two thirds of the area is occupied by Lake Beleu. A wetland stretches along the Prut River, covering a mosaic of water ecosystems, meadows and forests. The reservation was established by Law no. 132/2018 on the founding of the „Prutul de Jos” Biosphere Reserve, and was included in the UNESCO World Network of Biosphere Reserves [1]. The aquatic ecosystems from the „Prutul de Jos” Biosphere Reserve have an impact on the Danube - Black Sea river basin .

This study addresses and integrates existing recommendations in a series of European Directives on water and biodiversity, and obtained results contribute to the scientific substantiation of the development of recommendations for the harmonization of the methods used and the improvement of water management exploited on the national territories of the Republic of Moldova and Romania.

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## THE FLAGEL CALLED ALUMINUM

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In recent decades, the world's population, especially the West, has begun to suffer the reverse of "technological progress": pollution of soil, air and water with noxious substances, pesticides, heavy metals, etc. This boomerang return is directly proportional to the increase in allergies, food intolerances, autoimmune and neuro-degenerative diseases. It is about aluminum, more precisely the toxicity of some of its forms used in food, medicine and cosmetics.

The aim of this project is to inform, raise awareness and popularize the risks of using antiperspirants containing aluminum for human health. After an intense documentation we determined the aluminum content of some antiperspirants using complexometric titration. I also chose some recipes for obtaining deodorants from natural products that I obtained in the chemistry laboratory.

Working on this project, I gained a lot of knowledge about the content of deodorants and the health hazards to which we are exposed. At the same time, we made natural deodorants that can successfully replace the commercial ones. Baking soda, starch and coconut oil are among the best known ingredients that fight against the unpleasant odors eliminated by our body. To this combination was added lemon juice and essential oils to create the desired smell.

Do we continue to use products that we know nothing about or do we know could hurt us? Or, are we looking for natural, safe alternatives?

There are a number of natural deodorants on the market that claim to have 100% safe ingredients. However, it is safest to produce our deodorant at home, from as few ingredients as possible, which we also tried in this project.

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## ADSORPTION OF *BACILLUS SUBTILIS* AND *BACILLUS CEREUS* BACTERIA ON ENTEROSORBENT OBTAINED FROM VEGETAL RAW MATERIAL

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One of the main problems of modern medicine of this century is intoxication of a human organism as a result of the direct impact of the negative state of the environment on a human. Enterosorption is one of the safest and most effective methods for removing toxic substances, based on oral administration of drugs that can absorb various toxic substances of endogenous and exogenous origin in the lumen of the gastrointestinal tract without entering into chemical reactions with them [1].

Are presented the results of adsorption of 2 species of gram-positive bacteria, such as: *Bacillus subtilis*, *Bacillus cereus* on enterosorbent AC-A obtained from vegetal raw material. The mentioned bacterial species were isolated from soil samples and grown on nutrient agar for the accumulation of the biomass. The adsorption of bacteria was studied as a function of temperature (26 and 36°C) and the pH of the solution (1.97-4.05).

The equilibrium of the adsorption process of *B. subtilis* bacteria is established after 75 minutes of stirring, and in the case of *B. cereus* bacteria the equilibrium is established in 90 minutes. The analysis of the adsorption isotherms of the bacteria allow to conclude that the adsorption process of the bacteria is an exothermic one, *i.e.* with the increase of the temperature, the adsorption value decreases.

The pH value of the solution has a different influence. In the case of *B. subtilis*, the decrease in pH leads to an increase in the amount of immobilized bacteria per unit area of carbon adsorbent, and in the case of *B. cereus* bacteria the effect is the opposite, a decrease in pH leads to a decrease in the number of immobilized bacteria on the carbon enterosorbent.

Using Scanning Electron Microscopy (SEM), it has been shown that the immobilization of bacteria takes place on the outer surface of the carbon adsorbent. The studied bacteria are adsorbed on the outer surface of the carbonic enterosorbent. This is explained by the fact that the length of the bacteria is within the dimensions of 1-6  $\mu\text{m}$ , a size that exceeds several times the diameter of the macropores of the carbon adsorbent.

**Acknowledgments.** This research was performed with the financial support of the Project "Reducing the impact of toxic chemicals on the environment and health by using adsorbents and catalysts obtained from local raw materials", DISTOX, no. 20.80009.7007.21.

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## WATER QUALITY IN SOME WATER SUPPLY SOURCES IN COȘERNIȚA AND COJUȘNA VILLAGES

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This work describes the results of the research of underground water from artesian wells, wells and rills from the villages Coșernița and Cojușna of the Republic of Moldova. In spring, 2022, 2 samples of water from artesian wells, 1 sample from wells and 3 samples from rills were taken from Coșernița. At the same time, 1 sample of water from artesian wells, 4 samples of water from wells and 2 samples from rills were taken from Cojușna. All the sampled wells are important sources of drinking water for population. Water quality assessment for use as a drinking water was done according the criteria set by the national regulation – Law 182/ 19/12/2019. All samples were analyzed for various chemical parameters, such as hydrogen sulfide and dissolved sulfides, ammonia and ammonium ions, nitrites, nitrates, total hardness, sodium ions, iron ions, fluorides, sulfates, chlorides, permanganate index, total dissolved solids. None of the water samples from Coșernița met water quality requirements by one or more parameters, and only two water samples from Cojușna met the requirements of the Law 182/ 19/12/2019 by the analyzed parameters. As an objective criterion of water quality assessment, we took the ratio of the concentration of each parameter in mg/L to its maximum allowable concentrations ( $C_i/mac$ ) where  $C_i$  is the concentration of each parameter in mg/L,  $mac$  is the maximum allowable concentrations for the parameter in mg/L. Table 1 shows the values of the maximum allowable concentrations for those indicators, max detected concentrations, not meeting those values and the values of exceeding the  $mac$  for water samples from artesian wells. The concentration of nitrites, chlorides and permanganate index did not exceed the maximum allowable concentration in any of the analyzed samples.

*Table 1. Values of exceeding the maximum allowable concentration for water from the villages Coșernița and Cojușna.*

Parameter	the maximum allowable concentrations, mg/L	$C_i/mac$ (max)
H <sub>2</sub> S	0,1	21
NH <sub>4</sub> <sup>+</sup>	0.5	8
NO <sub>3</sub> <sup>-</sup>	50.0	4
total hardness max	7 mol/m <sup>3</sup>	4.4
Na <sup>+</sup>	200	1.48
Fe (total)	0.2	4.35
F <sup>-</sup>	1.5	1.14
SO <sub>4</sub> <sup>2-</sup>	250	3.6
TDS	1500	1.57

The present research detected a major problem with water quality in the Republic of Moldova and showed the need for modern technologies of water purification for solving this problem.

**Acknowledgments.** This research was performed with the financial support of the Project "Reducing the impact of toxic chemicals on the environment and health by using adsorbents and catalysts obtained from local raw materials", DISTOX, no. 20.80009.7007.21.

## EVALUATION OF CATALYTIC ACTIVITY OF DIFFERENT CATALYST SAMPLES

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The catalytic activity of different samples of catalysts known in the field literature and obtained by us in the laboratory, through the decomposition of hydrogen peroxide at the laboratory installation, was studied. The catalytic activity of following catalysts Centaur, Quantum DM1-65, AC-Mn1, AC-Cu1, AC-Co1, AC-Mn2, AC-Mn1+KMnO<sub>4</sub>, AC-Mn2+KMnO<sub>4</sub> was evaluated at different mixer speeds and different particle size of the catalyst. It was found that the sample AC-Mn1 + KMnO<sub>4</sub> (22.86ml O<sub>2</sub> /5min) has the highest catalytic activity, followed by Centaur (7.7ml O<sub>2</sub> /5min) and AC-Co1 (6.8ml O<sub>2</sub> /5min). The other samples have a lower catalytic activity. Grinding the Centaur catalyst to dust resulted in altered catalytic activity. The speed of mixing is also of great importance, which can lead to the destruction of the catalyst and to the reduction of its catalytic activity. The fastest kinetic process of decomposition of hydrogen peroxide occurs on the AC-Mn1 + KMnO<sub>4</sub> sample.

Next steps will include the study of the evaluation of the centers responsible for the catalytic activity of the samples AC-Mn1 + KMnO<sub>4</sub>, AC-Co1- catalysts obtained in the laboratory of Ecological Chemistry. The Centaur catalyst is well known in field literature, as one of the best catalysts, which oxidizes hydrogen sulphide from deep waters and has a wide application in making these categories of water potable.

The best catalysts will be tested for removing of pollutants, which exceed the maximum admissible limit in the deep waters of the Republic of Moldova.

**Acknowledgments.** This research was performed with the financial support of the Project "Reducing the impact of toxic chemicals on the environment and health by using adsorbents and catalysts obtained from local raw materials", DISTOX, no. 20.80009.7007.21.

## FLOTATION PROCEDURES WITH PARTICIPATION OF NITROGEN- AND SULFUR-CONTAINING COMPOUNDS

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The flotation process of organic residues from wastewater treatment is explained by the formation of micro-bubbles of molecular nitrogen or nitrous oxide with the decrease in the density of suspended particles. A large difference in the size of micro-bubbles, formed in suspension in the vicinity of organic particles and those formed during the denitrification process in the aqueous part of the dispersed system with the release of large amounts of molecular nitrogen or N<sub>2</sub>O, has been established. The formation of gas bubbles in solution is a spontaneous and intensive process that generates a destructive agitation of the float, by dispersing and fragmenting the suspended system. Thus, it is necessary to regulate the formation of micro-bubbles and stop the process of spontaneous denitrification in the separation water. Depending on the formation and control of micro-bubbles on the flotation process, three types of flotation systems have been identified.

The first type consists of combining primary sediment (PS) and activated sludge (AS) in certain proportions. For the WWTP Chisinau, where the flotation process has optimal indices, this ratio is in the ranges of 15%-20% SP and 85%-80% NA. The optimal temperature range is 41 – 45 °C, an intermediate temperature range between the mesophilic and thermophilic process, therefore characteristic for the mesothermophilic process. It should be noted that the preparations used in the technology of the aforementioned station to reduce the smell of organic residues, have an effect of suppressing the flotation process. The use of preparations to stop the sulphate-reduction process, *i.e.* to capture hydrogen sulphide (H<sub>2</sub>S) and mercaptans (R-SH) in PS and return the centrifugation water leads to the loss of the flotation effect. The experiments carried out prove that the odor reduction preparations suppress the effect of micro-bubble formation following the denitrification process, the protein sulfur in the AS granules having a regulatory role.

The second type of float occurs with old AS. The aging period is about 7-11 hours, when the remaining dissolved oxygen is consumed and a process of denitrification or combining the amount of remaining ammonium with nitrite and nitrate ions is still possible. The latter become a source of oxygen both for the oxidation of ammonium and for the reduction of nitrites and nitrates due to decomposing organic matter.

A third type of flotation occurs when using preparations to suppress sulfur reduction and capture sulfur sulfide (H<sub>2</sub>S) and mercaptan (R-SH). The sulfur fixation process initially occurs in the liquid part of the dispersed system. Then there is the formation of gas micro-bubbles, generated and regulated due to the sulfur in the bacterial proteins fixed in the AS granules.

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## ULTRASOUND ASSISTED EXTRACTION OF BIOLOGICALLY ACTIVE COMPOUNDS FROM WASTES OF THE CANNED FOOD INDUSTRY

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In the last decades waste generation and management is one of the main concerns of the canned food industry. The waste generated in the food sector is generally rich in water and organic compounds and therefore these by-products can cause environmental problems. The manufacturers face additional costs for the adequate disposal or treatment of their residues. However, food waste could be a potential raw material for the extraction of valuable products. It is cheap and produced in large quantities as by-products. In this aspect, more comprehensive studies related to valorisation of waste could lead to economic and environmental benefits. The processes of manufacturing of canned vegetables, juices, tomato paste, oil, wines, etc., generate large amounts of solid wastes as marc, seeds, epidermis, and stems that contain valuable components. These wastes are a source of high value-added products and can be processed with the aim to extract various biologically active compounds that can be used as food components or pharmaceutical preparations.

Tomato and pepper seeds contain biologically active compounds that refer to the group of steroidal glycosides. It was found out that these glycosides exhibit antimicrobial, antioxidant, anticancer, and fungicidal properties. Tomatoside – steroidal glycoside extracted from seeds of tomato *Lycopersicon esculentum* Mill. – exhibits antiviral properties and is more effective than interferon. Capsicoside extracted from seeds of pepper *Capsicum annum* L. and tomatoside extracted from tomato seeds can be used as growth stimulators of agricultural crops. Biologically active compounds from pepper seeds (capsicosides) prevent accumulation of lipids in adipocytes and can be promising for application as an effective remedy for prevention and treatment of obesity.

We have accomplished comprehensive studies of the influence of ultrasonic treatment on the processes of extraction of biologically active compounds from canned industry wastes – tomatoside from tomato seeds and capsicoside from pepper seeds.

It was shown that application of ultrasonic cavitation treatment during extraction reduces the duration of the extraction process of biologically active compounds by a factor of 9 and the temperature of the process to 35-55 °C. The action of ultrasound considerably accelerates the swelling of the seeds' walls and induces the cell destruction. This leads to an intensive release of biologically active compounds and their diffusion into the solvent, in our case 70% ethanol was used. Ultrasound assisted technique for extraction of biologically active compounds from tomato seeds accelerate the process and allows one to increase the yield of the end product by a factor of 1.5. During of the extraction of biologically active compounds from tomato and pepper seeds using ultrasonic cavitation treatment at a temperature of 55 °C the changes of the chemical composition of the extracted substances was not registered.

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## ADSORPTION OF BENZENESULFONATE AND DODECYLBENZENESULFONATE BY ACTIVATED CARBON OBTAINING FROM WOOD CHARCOAL

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Among the most common chemicals used in household and industrial applications are surfactants. Due to widespread use surfactants are often found in the domestic and industrial wastewater as these may not be completely utilized in the application. Obviously, part of surfactant discharged could be degraded naturally. However, biodegradation alone is not sufficient when the surfactant is present in large concentration. The surfactants have an impact of the humans if these enter into the food chain. Their presence can also affect the treatment efficacy of the wastewater treatment plants.

The surfactants are widely used in detergent, shampoos and cosmetics. Surfactants increase solubility of organic compounds in water and hence presence of surfactants can lead to enhancement in carcinogenic potential and dermatitis as reported in literature [1]. Considering environmental and health impacts, permissible limits for surfactants is 1 mg/L in water intended for domestic purposes and still low at 0.5 mg/L for potable water [2].

Adsorptive separation of commercial sodium benzenesulfonate (SBS) and sodium dodecylbenzenesulfonate (SDBS) was investigated in the present work using activated carbon obtaining from wood charcoal by different methods. In the case of activated carbons from wood charcoal obtained by the fluidized layer method (CAML-SF) more effective results were obtained than in case of charcoals obtained by the classical method (CAML-MC). The samples were stirred at the speed of rotation 150 rpm, amplitude 4 and the temperature of 298 K. Kinetic study yields important information about the rate of removal and time required to achieve equilibrium. Rapid adsorption rate of SDBS from solution on both CAML-SF and CAML-MC samples was observed in first 15 min which decreased and became negligible after 120 min. Around 91% SDBS removal was achieved in initial 15 min from solutions having an initial concentration as 0.5 mmol/L on CAML-SF samples which continued to 97 % at 240 min. In the case of CAML-MC samples approximately 51 % were removed in the first 15 minutes and respectively until 62 % at 240 min.

The effect of temperature conditions on extent of SBS removal has been studied. Adsorption isotherms of SBS at different temperatures namely: 298 K, 308 K and 318 K were measured. Initially stock solutions of SBS and SDBS having 5 mmol/L were prepared. The required solutions having different initial concentration for experiments were obtained after appropriate dilution. BET surface area of adsorbents and the pore size distribution have been analyzed based on the Brunauer-Emmett-Teller (BET) method using the Autosorb-1 instrument based on N<sub>2</sub> adsorption-desorption.

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## THE VISIBLE LIGHT PHOTOCATALYTIC ACTIVITY OF HYBRID PHOTOCATALYST TiO<sub>2</sub> /DIATOMITE IN DEPENDENCE OF THE SYNTHESIS CONDITIONS

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Wastewater treatment is one of the urgent tasks of environmental protection. Among the various methods of water purification from toxic contaminants, especially those that are difficult to decompose, photocatalytic methods have been developing in recent decades. They provide not only the removal of impurities, but also their conversion into safe compounds - water, carbon dioxide, etc. Titanium dioxide in the form of nanosized anatase is very often used as a photocatalyst because of its properties. TiO<sub>2</sub> is a cheap, non-toxic, easily obtainable material capable to mineralize a wide range of organic pollutants to harmless compounds. However, there are several disadvantages of using nanosized anatase in a slurry-type photocatalytic reactor: a high tendency to particle agglomeration, leading to a decrease in photocatalytic activity and even to its complete disappearance, difficulty in separating the catalyst after the photodegradation process, and a wide bandgap of anatase, which requires ultraviolet light source. The first disadvantage can be overcome by using a support on which nanoscale titanium dioxide is fixed.

An increase in the photoactivity of titanium dioxide in visible light can be achieved by doping it with various atoms and ions.

The hybrid photocatalyst TiO<sub>2</sub> /diatomite was obtained by low-temperature hydrolysis of titanium tetrachloride in the presence of diatomite as a substrate. Sensitivity to visible light was provided by doping with nitrogen.

The synthesis parameters of hybrid catalysts have been determined which affect their photocatalytic properties in visible light: the content of titanium dioxide (anatase), nitrogen concentration in the samples and the method of adding the reagents during the synthesis.

Adsorption and photocatalytic degradation performance of the composite were assessed using aqueous methylene blue (MB) solution as a model pollutant.

It was shown, that:

- The adsorption value and the degree of decomposition of MB by all samples under the action of visible light exceed those in the dark by about 30% and reaches 75% compared to 52% adsorption.
- The amount of anatase in the samples has an extreme dependence: the degree of MB decomposition increases up to 20% of the anatase content in the composite, then it decreases and becomes minimal at 75% TiO<sub>2</sub>, and the DTD20 samples were used for further manipulations.
- The synthesis method with urea as the nitrogen precursor in the potassium hydroxide precipitation process is more efficient than using ammonium chloride by 25%.
- The N/Ti = 6 ratio in the DTD20 samples with the ammonium chloride nitrogen source and N/Ti = 3 ratio with urea showed the highest degree of AM dye removal in visible light conditions.

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## FINE ORGANIC SYNTHESIS APPROACHES FOR OBTAINING MONASTROL BY GREEN CHEMICAL METODOLOGIES

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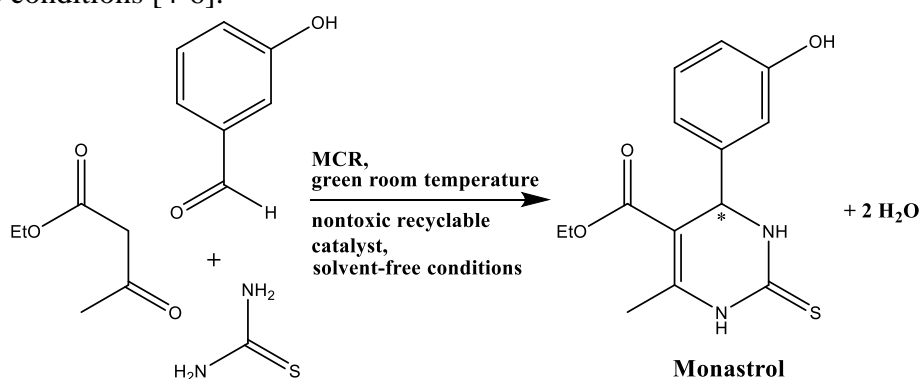
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Monastrol (M) is an important target molecule for organic chemists in virtue of its remarkable biological properties, *e.g.* antitumoral activity [1] and inhibition of the motility of the mitotic motor protein kinesin Eg5, thus serving as a particularly useful tool for study of mitotic mechanisms [2].

The most useful and smart method actually applied for M synthesis is the Biginelli multicomponent reaction (MCR), discovered in 1891 by Pietro Biginelli [3]. MCRs have the advantage of performing the reaction in a one-pot version, thus avoiding waste from multi-step purifications and residue generation. Moreover, MCR adducts include in their structures almost all atoms (atom economy), the common by-product being water.

Current communication will present some recent advances described in the literature, regarding the convenient synthesis of M, based on the environmentally benign methods in sustainable conditions [4-6].



*Schematic representation of Biginelli reaction applied for the preparation of (+/-)-Monastrol in eco-friendly conditions*

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