

Ministry of Education and Research
Moldova State University
Institute of Chemistry

Scientific seminar

**ADVANCED MATERIALS TO
REDUCE THE IMPACT OF TOXIC
CHEMICALS ON THE
ENVIRONMENT AND HEALTH**

Book of Abstracts

September 21, 2023
Chisinau, Republic of Moldova

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Scientific seminar “ADVANCED MATERIALS TO REDUCE THE IMPACT OF TOXIC CHEMICALS ON THE ENVIRONMENT AND HEALTH”

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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 ADVANCED MATERIALS TO REDUCE THE IMPACT OF TOXIC CHEMICALS ON THE ENVIRONMENT AND HEALTH, organized by the Laboratory of Ecological Chemistry, Institute of Chemistry of the Moldova State University.

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

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
Dr., Assoc. Prof. Raisa NASTAS*

UDC: 661.183.2:502/504

ACTIVATED CARBONS – EFFICIENT ADSORBENTS FOR THE PROTECTION OF THE ENVIRONMENT AND HUMAN HEALTH

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The present work presents the results of scientific research obtained over several years in the field of the development of the synthesis procedures of activated carbons from renewable autochthonous raw material, the application of these carbonic adsorbents in the processes of purification of waste water, potability of natural water, as well as for the detoxification of the human body.

Activated carbons are carbon adsorbents, which have a developed porous structure obtained through different activation processes of carbonized and non-carbonized raw material as a result of chemical, physical-chemical and mixed treatment of the raw material. Activated carbons due to the increased amount of micropores and mesopores have a specific surface of up to 3000 m²/g. Due to this fact, they show properties to fix and retain on the surface and in the pores the organic substances from the solutions and the gases with which they come into contact. Carbonic adsorbents are used in large quantities in the pharmaceutical, food, chemical and petrochemical industries, for collective and individual protection equipment in industry and the military, for the purification of waste water and the potability of surface water. Activated carbons are also used in special biological purifications, in medicine for the detoxification of the human body, as well as catalysts in organic synthesis, creating a high vacuum, gas storage, etc.



The chemical reactions that occur in the charring processes of the wood raw material are described, as well as in the synthesis processes of activated carbons through physico-chemical, chemical and mixed processes. The mechanisms of immobilization of textile dyes from aqueous solutions on the surface of activated carbons, of the wastewater treatment phases from fabric dyeing enterprises, are also presented. The results of the research related to the use of carbonic adsorbents in the potable processes of surface and underground water are also highlighted. The work also contains experimental data regarding the processes of modifying the geometric surface of activated carbons and the mechanisms of immobilization of heavy metal ions in aqueous solutions.

The results of the research aimed at the use of activated carbons as enterosorbents and hemosorbents for the detoxification of the human body, as well as the immobilization processes of bacteria and fungi in aqueous environments, are also elucidated.

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CHEMICAL SYNERGISM DEFINED: INSIGHTS INTO COMPLEX INTERACTIONS

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The synergistic effect becomes evident as the combined impact of multiple agents is not simply the sum of their individual effects. Instead, it results in the simultaneous impairment of various human organ systems by different types of limiting factors, leading to more severe consequences within the organism.

In this paper, the researchers aim to elucidate the common feature shared by all synergistic chemical processes. Frequently, this common element remains concealed, leading to diverse interpretations of the synergism phenomenon. These interpretations vary based on the specific chemical processes under investigation, including their unique characteristics such as the chemical structures of the reagents involved, their mechanisms, kinetics, energy considerations, and more. The study encompasses a comprehensive analysis of various chemical processes employed in different physico-chemical research methods across various fields of application. Our research has been established that the unifying aspect of the synergism phenomenon in all these processes is the formation of a *mixed compound/complex*. Recognizing this shared characteristic in advance provides an opportunity for a deeper comprehension of this phenomenon and facilitates the targeted exploration or prediction of necessary or pre-planned synergistic effects. Frequently, this common feature remains concealed, remaining “hidden”, and as a result, the phenomenon of synergism finds various explanations. These explanations vary depending on the specific chemical processes under scrutiny and their unique attributes, including the chemical compositions of the reagents in question, their mechanisms, kinetics, energy considerations, and more.

Hence, when a synergistic effect arises from a chemical process, it is essential to recognize that it entails the formation of a mixed complex, which can exhibit diverse characteristics. These identified relationships can be leveraged in the exploration and development of novel synergistic processes tailored to specific desired properties.

Thanks to these inherent properties, the systems under examination have the potential for extensive applications across various domains of chemical and biochemical research. This versatility extends to fields such as analytical chemistry, pharmacology, pharmaceuticals, the medical industry, and synthetic organic chemistry.

Future research on chemical synergism should focus on isolating and characterizing more mixed compounds prior to their use in further reactions, as well as providing more detailed thermodynamic and kinetic knowledge, supported by theoretical calculations, since understanding is currently based mainly on empirical observations.

Acknowledgements. This work is a part of the Moldovan State Program (2020-2023) “Study and management of pollution sources to develop recommendations for implementing measures to mitigate the negative impact on environment and human health”, Project number: 20.80009.7007.20.

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ADSORPTION CAPACITY OF SILICA SBA-15 AND TITANOSILICATE ETS-10 TOWARD INDIUM IONS

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Indium is an extremely important element for industry that is distributed in the Earth's crust at very low concentrations. The recovery of indium by silica SBA-15 and titanosilicate ETS-10 was investigated at different pH levels, temperatures, times of contact and indium concentrations. A maximum removal of indium by ETS-10 was achieved at pH 3.0, while by SBA-15 it was within the pH range of 5.0–6.0. By studying kinetics, the applicability of the Elovich model for the description of indium adsorption on silica SBA-15 was shown, while its sorption on titanosilicate ETS-10 fitted well with the pseudo-first-order model. Langmuir and Freundlich adsorption isotherms were used to explain the equanimity of the sorption process. The Langmuir model showed its applicability for the explanation of the equilibrium data obtained for both sorbents, the maximum sorption capacity obtained using the model constituted 366 mg/g for titanosilicate ETS-10 at pH 3.0, temperature 22 °C and contact time 60 min, and 2036 mg/g for silica SBA-15 at pH 6.0, temperature 22 °C and contact time 60 min. Indium recovery was not dependent on the temperature and the sorption process was spontaneous in nature. The interactions between the indium sulfate structure and surfaces of adsorbents were investigated theoretically using the ORCA quantum chemistry program package. The spent SBA-15 and ETS-10 could be easily regenerated by using 0.01 M HCl and reused with up to 6 cycles of adsorption/desorption with a decrease in the removal efficiency between 4% and 10% for SBA-15 and 5% and 10% for ETS-10, respectively.

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COMPOSITES – PRECURSORS FOR OBTAINING NEW SORBEMTS AND CATALISTS

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Obtaining new sorbents with selective sorption and catalytic properties is an important field of research. This report discusses the results of studies on obtaining new sorbent-catalysts for the removal of nitrite ions from water, but not only.

A series of composites (7 pieces) was obtained by the hydrothermal method. The composites were obtained from walnut shells by impregnation with compounds of Mn, Co, Cu. The composites were examined using SEM EDX, XRD, FT-IR spectroscopy and thermogravimetry methods. The concentration of nitrite ions in the solution was determined spectrophotometrically [1].

Four types of composites based on Mn compounds have been obtained. Three of them also contain impurities of Fe, C, K and others. The data in Figure 1 serve as an example. Also, 2 composites based on Co and Cu were obtained. All composites contain O and predominantly C.

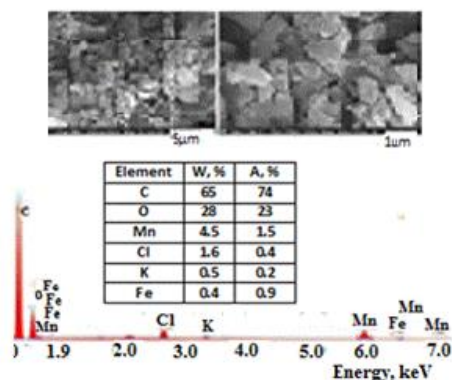


Figure 1. SEM EDX of Mn-containing composite

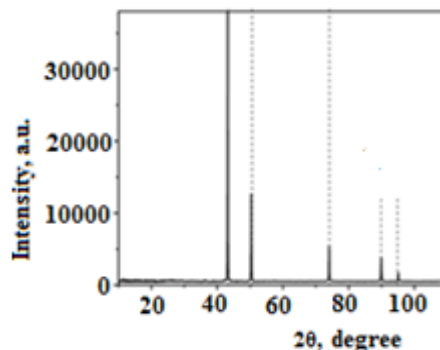


Figure 2. X-ray diffraction pattern of the Cu-containing composite

The EDX data allowed the calculation of the approximate average surface composition of the composites. Studies carried out using IR-Fourier spectroscopy show that, in addition to inorganic compounds, the composition of composites also includes organic compounds. Surprisingly, out of all the composites obtained, only one contains crystalline phases, namely metallic copper (Fig. 2). When heated in air at a temperature of 650°C, crystalline phases appear in all composites. The composites are thermally stable up to 240°C. Nitrogen adsorption isotherms were obtained. Tests have shown that the composites transform (remove) nitrite ions from the solution.

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ADSORPTION OF O-NITROPHENOL ON LOCAL CARBONIC ADSORBENTS

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Ensuring daily life with safe drinking water is an essential issue of human society [1]. Among the pollutants identified in water, toxic substances are of particular concern, even at very high dilutions, showing maximum resistance to biological degradation. Phenolic pollutants, which occupy the 11th position in the list of 126 priority pollutants listed in the United States Environmental Protection Agency refers to this category of contaminants [2].

In the present research, the adsorption parameters of o-nitrophenol were studied on two samples of autochthonous carbonic adsorbents, obtained from apricot stones (AC-C) and from apple wood (AC-MR). The advantages of the new adsorbent materials were evaluated in relation to the results determined for the retention of o-nitrophenol on two samples of commercial activated carbons, AG-5 and BAU. The time required to reach the adsorption equilibrium of o-nitrophenol on the investigated activated carbons was determined from the adsorption kinetic curves, measured at three initial concentrations (50, 100 and 200 mg/l) in the interval of time between 15 -360 minutes.

The obtained experimental results show that, at the initial stage the immobilization of the phenolic pollutant is quite a fast process. Thus, in the first 30 min, the autochthonous activated carbons retain approx. 76.5% (AC-MR) and 57.2% (AC-C) from the total amount of adsorbate and on the commercial activated carbons they immobilize between 51% (BAU) and 20% (AG-5). The nature of the adsorbents also significantly influences the contact/stirring time required to reach the equilibrium of the adsorption process, which oscillates between 120 min - 180 min for local carbonic adsorbents (AC-MR, AC-C) and 240 min - 300 min for commercial samples (BAU, AG-5).

The adsorption isotherms of o-nitrophenol on the investigated activated carbons were determined at different temperatures (25°C, 35°C and 45°C). The results show that, with the increase of the temperature values by 20°C, the retention of o-nitrophenol decreases by approx. 5-8%, which indicates that the adsorption process studied is an exothermic one.

The research carried out indicates the advantage of autochthonous activated carbons over commercial ones in parameters such as the speed and duration of the immobilization process, as well as the retention rate of the investigated adsorbate

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SYNTHESIS OF NANOSTRUCTURED SILICA WITH COMBINED MICRO- AND MESOPOROSITY AS BISMUTH CARRIER

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There is a strong demand for selective capture and storage of radioactive fission products, of which iodine-129 (¹²⁹I) is one of the most problematic radioisotopes due to its long half-life of 1.57×10^7 years. Selective chemical adsorption of radioactive iodine (I₂ or RI) requires nanoporous solid sorbents. Most studies note that iodine adsorption is physical, despite its preference only for reused materials. Since the stability of materials decreases during physical sorption, the regenerability of adsorbents conflicts with their long-term stability. Therefore, for the adsorption of iodine, solid porous bodies with surface functional groups are developed, which can interact with iodine chemically when chemical stability is required, although the sorption capacity is reduced. A reliable option is mesostructured silica materials, which provide both stability and high capture capacity.

Irreversible iodine uptake can be achieved by its chemisorption in the pore space of bismuth-modified mesoporous silica materials. In this case, the absorption of iodine with the formation of a Bi-I chemical bond in the pores filled with the resulting compound simulates the process of physical sorption. The purpose of this work is to study the adsorption and structural properties of ordered mesoporous bismuthosilicate deposited by the alkoxide sol-gel method from tetraethoxysilane in an acidic medium on a block copolymer of polyoxyethylene and polyoxypropylene, Sunperonic F108. Despite reports on the prospects of using Bi-SBA-15 materials in the adsorption of iodine gas, the method for self-assembly of bismuth-substituted silica nanoparticles remains open.

In this work, bismuth-substituted plugged hexagonally templated silica (PHTS) was synthesized at Bi/Si molar ratios of 1/99 and 5/95. It is a composite material, an analogue of SBA-15, consisting of fairly large homogeneous mesopores containing microporous nanoparticles in the form of plugs in mesopore channels.

The measured nitrogen sorption isotherms are Type IV, according to the IUPAC classification, have an H5 Hysteresis loop and demonstrate single-step capillary condensation, indicating the filling of homogeneous mesopores. with two-stage desorption [1]. The resulting material demonstrates a bimodal size distribution of mesopores, a controlled number of open and clogged mesopores, has thickened pore walls (≈ 3 nm), “perforated” by micropores, which leads to large surface areas of micropores (up to 230 m²/g).

The combined micro- and mesoporosity, high stability, and ability to control the texture and morphological characteristics of bismuth-substituted silica may be useful in the selective chemical adsorption of radioactive iodine.

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ADSORPTION OF CAFFEIC ACID ON ACTIVATED CARBONS

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Caffeic acid is a phenolic compound (strong and active antioxidant) synthesized by all plant species and found in foods such as coffee, wine, tea and others. Caffeic acid (3,4-dihydroxycinnamic acid) is a hydroxycinnamic acid, belonging to the family of phenolic acids, with a 3,4-dihydroxylated aromatic ring structure linked to a carboxylic acid by a transethylenic wire [1].

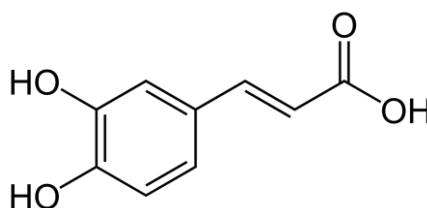


Figure 1. Chemical structure of caffeic acid

The purpose of this work was to perform adsorption experiments of caffeic acid from water solutions on activated carbons of different origin: AC-C obtained from apricot stones (Republic of Moldova) and Granucol FA commercial activated carbon (Germany).

All the adsorption experiments were performed at the temperature of 293K because caffeic acid is not stable at high temperatures. The adsorption kinetics were studied at different initial concentrations (1, 3, 4.5 mM), at a solid/liquid ratio of 1/1000. The equilibrium of adsorption was established in about 150 minutes. The adsorption capacity of caffeic acid on the studied activated carbons was determined from the adsorption isotherms, being of 1.25 mmol/g and 2.0 mmol/g for Granucol FA and AC-C, respectively. The experimental data were described by the following kinetic models: pseudo-first order, pseudo-second order, intraparticle diffusion (Weber-Morris model) and the theoretical isotherm models of Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich. The caffeic acid adsorption on both activated carbons is very well described by the pseudo-second order kinetic model and by the Langmuir theoretical model. The applicability of these models suggests that the adsorption of caffeic acid on the studied activated carbons is based on chemisorption.

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UDC:661.183.4:663.25

THE EFFICIENCY OF EXPERIMENTAL ACTIVATED CHARCOAL OF VEGETABLE ORIGIN IN IMPROVING THE QUALITY OF WINES

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The use of activated charcoals in winemaking is known and widespread, offering oenologists an important tool for correcting the chemical and microbiological composition of wines in the case of damaged raw material, technological deviations in the production, maturation and storage of wines. Western industry offers a wide range of plant-derived activated carbons with various applications in the oenological field - deodorization, disinfection and bleaching. The purpose of our research was to assess the quality of experimental activated carbons (AC-C, AC-C*, AC-2, AC MRF), obtained in the Laboratory of Ecology of the Institute of Chemistry, at USM – Moldova State University (produced in the Laboratory of Ecological Chemistry of the Institute of Chemistry of the Republic of Moldova) from various local vegetable raw materials, including waste from the food industry (kernels, walnut shells, apple wood) for various contaminations and defects of wines. As well, it was studied their influence on wines, obtained experimentally at the Department of Enology and Chemistry of the Technical University of Moldova from a wide range of grapes of international varieties, such as Cabernet Sauvignon, Malbec, Sauvignon Blanc, Chardonnay and others. Various contaminations and defects in wines made the subject of research.



Toxins, which can seriously affect the health of the consumer, pose an increased danger to wines. In this regard, there was determined the ability of experimental activated charcoals to eliminate the danger of mycotoxin production by molds on damaged grapes, by the wine cellar (*Botrytis cinerea*, *Aspergillus niger*, etc.) - the main substrate of these contaminants. In terms of this AC-C parameter, it was comparable to the oenologically activated carbons, used in winemaking in the Republic of Moldova and which also contain another useful co-adjutant - bentonite. At identical concentrations, within the limits of permissible values (1 g/l), the effectiveness of AC-C was 73-98% of the effectiveness of carbons, which significantly reduced the risk of toxin synthesis. At the same time, AC-C also removed the mold shades from the aromatic profile of wines, contributing to organoleptic correction.

In addition to the curative effect for must from damaged grapes, experimental activated charcoals, already in low concentrations, have improved the process of alcoholic fermentation by harmonizing its kinetics over time, which has a positive effect on the quality of the finished product (Malbec variety). Experimental activated carbons have demonstrated effectiveness in eliminating one of the most dangerous side effects of the reducing technologies application in the production of white wines – the pinking phenomenon.

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USING BUFFER THEORY TO ASSESS IONIC POLLUTANT REDUCTION IN SOILS

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The ability of buffer systems to resist changes in their composition (typically changes in pH) when subjected to the influx of chemical substances of natural or anthropogenic origin that shift the equilibrium is referred to as buffering capacity. The effectiveness of this ability is known as buffering action or simply “buffering”. The challenge of determining the buffering capacity of soils, as an indicator that allows us to calculate the dose of a pollutant that does not significantly disrupt the natural functioning of the system, is one of the most critical issues in soil science, ecology, and natural resource management. Under real conditions, the buffering capacity of natural heterogeneous aqueous systems manifests in such a way that when a certain element is consumed from the solution, partial dissolution of solid phases takes place and the solution composition is subsequently restored.

The paper discusses the fundamental quantitative aspects of the buffering theory in multi-component homogeneous and heterogeneous systems. It is demonstrated that buffering properties concerning solid-phase components intensify with increasing solubility due to protolytic reactions or complex formation processes in saturated solutions. It is established that the buffering capacities of components are mutually proportional, with these relationships dependent on the stoichiometric composition of the solid phase for heterogeneous systems. The derived equations are applied to assess the buffering action in “natural mineral - soil solution” systems, encompassing soluble and insoluble phosphate forms. Analysis of the derived equations reveals that buffering capacities increase with the solubility of the precipitate, i.e., with an increase in the residual concentration of the solid-phase components. The buffering capacity of a component in a multi-component system is a complex function of its equilibrium composition and temperature.

The concept of buffering capacity (or buffering intensity) has been applied to predict the stability of aqueous systems concerning various ions or neutral (molecular) compounds. The buffering capacity of heterogeneous systems, such as mineral-solid solution systems, depends on the chemical composition of the aqueous solution and the composition and properties of the mineral phases. It has been demonstrated that the buffering capacities of components are mutually proportional, with these relationships dependent on the stoichiometric composition of the solid phase for heterogeneous systems. The derived equations have been applied to assess the buffering action in “natural mineral - soil solution” systems, encompassing soluble and insoluble phosphate forms. The utilization of the results of this research will enable the prediction of changes in soil composition and reactions as a consequence of increased anthropogenic load. The obtained results are of interest to soil scientists and ecologists.

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UDC: 544.7:544.723+544.23

EUROPIUM(III) ION REMOVAL FROM WATER USING SILICA ADSORBENTS: INFLUENCE OF N-CONTAINING GROUPS AND STRUCTURING AGENTS

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Among the effective ways of obtaining the rare-earth metals is their extraction from water with silica-based adsorbents [1]. We synthesised sorbents via the one-pot modified Stöber method using three different structuring agents and functionalizing silanes. Tetraethyl orthosilicate (TEOS), silanes with ethylene ($\equiv\text{Si}-\text{C}_2\text{H}_4-\text{Si}\equiv$) and phenylene bridges ($\equiv\text{Si}-\text{C}_6\text{H}_4-\text{Si}\equiv$) were used as structuring agents. Meanwhile, functionalizing silanes contained diverse amino groups (aminopropyl, diamino and secondary amino). The characteristics and sorption properties of the samples to Eu(III) rare earth metal ions are given in Table 1.

Table 1. Composition and characteristics of the samples

Structuring silane	Functional silane	S _{BET} , m ² /g	V _p , cm ³ /g	N, % wt	C _{gr} , mmol/g	pI	SSC Eu ³⁺ , mmol/g
Si(OC ₂ H ₅) ₄	-(CH ₂) ₃ NH ₂	88	0.26	2.35	1.6	8.8	0.23
$\equiv\text{Si}-\text{C}_2\text{H}_4-\text{Si}\equiv$		64	0.11	6.10	4.1	9.4	1.04
$\equiv\text{Si}-\text{C}_6\text{H}_4-\text{Si}\equiv$		620	0.43	3.55	2.4	3.7	0.54
Si(OC ₂ H ₅) ₄	-(CH ₂) ₃ NH(CH ₂) ₂ NH ₂	427	0.51	7.54	2.9	10.1	0.55
$\equiv\text{Si}-\text{C}_2\text{H}_4-\text{Si}\equiv$		147	0.12	6.19	2.4	3.3	0.37
$\equiv\text{Si}-\text{C}_6\text{H}_4-\text{Si}\equiv$		190	0.21	7.54	2.9	9.2	0.52
Si(OC ₂ H ₅) ₄	=[(CH ₂) ₃] ₂ NH	607	0.52	4.29	3.2	4.7	0.67
$\equiv\text{Si}-\text{C}_2\text{H}_4-\text{Si}\equiv$		759	0.62	4.28	3.2	4.0	0.66
$\equiv\text{Si}-\text{C}_6\text{H}_4-\text{Si}\equiv$		718	0.58	3.65	2.7	2.9	0.63

Generally, the static sorption capacity (SSC) of adsorbents is affected by porosity (accessibility of groups) and functional groups content (C_{gr}). The structuring agent usually determines the porosity of the materials (e.g. bridging silanes ensures larger specific surface (S_{BET}) values). But the size and charge of the groups also affect the formation of pores (the particles sizes and the spaces between them). For the studied samples, the Eu³⁺ SSC completely correlates with C_{gr}. TEOS-based sample with aminopropyl groups has the lowest SSC value, explained by the poor S_{BET} and C_{gr} in this sample. Comparing the materials with the same C_{gr} (e.g. 2.4 or 2.9 mmol/g), the higher Eu³⁺ SSC is observed for the sample with better S_{BET}. Furthermore, samples with a secondary amine group (with high S_{BET} and C_{gr} ranging from 2.7 to 3.2 mmol/g), demonstrate sufficiently large SSC of 0.63 to 0.67 mmol/g.

Thus, analyzing Eu(III) ions sorption, it can be concluded that C_{gr} is important to achieve high sorption capacity by adsorbents. However, the well-developed porous structure of the samples and the accessibility of the groups also have a great advantage.

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ADSORPTION OF *BACILLUS SUBTILIS* AND *BACILLUS CEREUS* GRAM-POSITIVE BACTERIA ON ENTEROSORBENTS OBTAINED FROM APRICOT HUSKS

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The microorganisms pollution represent a dangerous condition of the water and the removing of these contaminants from it is very important to human and animal health. Adsorption is primarily used at the end of a treatment sequence for pollution control due to a high degree of purification that can be achieved. Activated carbon is considered the most popular adsorbent used for the application of the adsorption technique [1]. Granular carbon filters have been used for several hundred years and are considered one of the oldest means of water purification [2]. Our study presents the ability of activated carbons obtained from apricot husks to adsorb the bacteria from Gram-positive group: *Bacillus subtilis* and *Bacillus cereus*. These bacteria occur naturally in soils, at a concentration of up to one million per gram, and are therefore some of the most common microorganisms that can be grown in the soil. Also, because of the structure similarity with bacteria from other groups these species can be used as test-models for the evaluation of the adsorptive properties of the activated carbon for bacteria from different species.

In the research as enterosorbent was used the activated carbon (AC-A) obtained from apricot kernels in a fluidized layer at a temperature of 1000°C by activation with steam for 30 min. It was determined the kinetics of the adsorption process of bacteria on the mentioned carbon enterosorbents and subsequently established the adsorption isotherms of bacteria at different temperatures. Results of the kinetics allows us to conclude that 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 adsorption isotherms of *B. subtilis* and *B. cereus* bacteria measured after 120 minutes of stirring at a frequency of 150 rpm at different pH values (1.97; 3.71; 4.05) and at different temperatures (26-36°C) showed that 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.

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DEVELOPMENT OF SBA-BASED ADSORBENTS FOR URANIUM REMOVAL FROM NATURAL AND WASTEWATER

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Generally, Uranium(VI) ions are getting into the water from natural deposits or as a result of its contamination with waste from mines or nuclear power plants. Even a few amounts of radionuclides in drinking water are fraught with human health problems. P-derivative compounds exhibit strong affinity for radionuclides and have a promising application for U(VI) removal in environmental protection. Also, the porous structure increases the number of active centres on the surface of the adsorbents, which removal U(VI) ions with increasing efficiency of the water purification [1].

The authors synthesized a series of SBA-15 type mesoporous materials with different structures and assessed their U(VI) removal performance. Phosphor-derivatives modified SBA-15 adsorbents were synthesized by two-rout procedures. In *route I* bare SBA-15 was reacted with Diethylphosphatoethyltriethoxysilane followed by salinization reaction procedure (*post-grafting* procedure, $\text{SBA}(\text{CH}_2)_2\text{PO}_3\text{H}_2$). In *route II* involved preparation of vinyl-functionalized diatomite, which was reacted with the Di-n-Butyl Phosphine Oxide in the presence of AIBN as an initiator (*polymerisation* procedure, $\text{SBA}(\text{CH}_2)_2\text{PhOx}$). The effects of the SBA-15 modification have been studied using powder XRD, SEM/TEM, N_2 isotherms ad/desorption, FTIR spectroscopy, acid-base titrations, etc.

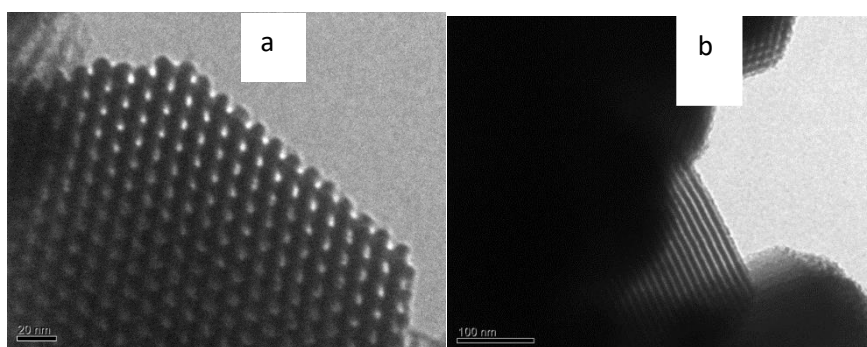


Figure 1. TEM images of $\text{SBA}(\text{CH}_2)_2\text{PhOx}$ (a) and $\text{SBA}(\text{CH}_2)_2\text{PO}_3\text{H}_2$ (b) samples.

The adsorption amount of U(VI) ions using the prepared $\text{SBA}(\text{CH}_2)_2\text{PhOx}$ and $\text{SBA}(\text{CH}_2)_2\text{PO}_3\text{H}_2$ adsorbents were 95.63% and 95.50%, respectively, which are higher compared to other published adsorbents. Thus, the proposed methodology can be used for the production of a high-performance sorbents for U(VI) ion removal in large volumes.

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SILICA-BASED HYBRIDS AS HIGHLY EFFECTIVE ADSORBENTS FOR THE REMOVAL OF Ni(II) AND Mn(II) IONS FROM AQUEOUS SOLUTIONS

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In response to growing concerns over heavy metal contamination of water sources [1], this study presents a comprehensive investigation into the development and application of highly efficient silica-based adsorbents.

Silica materials containing carboxyl groups were synthesized using the sol-gel technique. However, carboxyl groups tend to bind to silanol groups on the silica surface, limiting their effectiveness in ion exchange. To address this issue, our study aimed to introduce phenyl and methyl groups to protect carboxyl groups on the silica surface. This innovative approach aimed to enhance the sorbent's ability to interact with metal ions. Three materials were prepared on the basis of silica with the functional agent of the carboxyethylsilanetriol disodium salt (SiO₂/-COOH) with additional methyl (SiO₂/-COOH/-CH₃) and phenyl (SiO₂/-COOH/-C₆H₅) groups.

The composition and structure of hybrids were probed using physico-chemical methods. Solid-state ¹³C NMR spectroscopy affirmed the presence of carboxyl, methyl, and phenyl groups in the silica hybrid materials, while ²⁹Si NMR spectra revealed the efficient formation of silica networks and surface functionalisation. Elemental analysis results confirmed the integration of the precursor organic component into the hybrids, with carbon content (mass.%) as follows: SiO₂/-COOH – 6.8%, SiO₂/-COOH/-CH₃ – 6.6%, and SiO₂/-COOH/-C₆H₅ – 11.2%. The SEM-EDX spectroscopy confirmed the presence of an inorganic part with Si content (wt.%): SiO₂/-COOH – 46.5%, SiO₂/-COOH/-CH₃ – 42.0%, and SiO₂/-COOH/-C₆H₅ – 29.5%. Additionally, acid-base titration data (C(-COOH) ranging from 3.0 to 6.0 mmol/g) and isoelectric point values (pH ranging from 2.2 to 2.3) verify the existence of acid groups. Based on the data of low-temperature nitrogen adsorption and S_{BET} calculations provided, the specific surface area of the SiO₂/-COOH – 27 m²/g, SiO₂/-COOH/-CH₃ – 10 m²/g and SiO₂/-COOH/-C₆H₅ – 12 m²/g. Consequently, such samples are not porous, because their particle size exceeds 100 nm and they are loosely packed.

Hybrid materials were used as effective adsorbents to removal of Ni(II) and Mn(II) ions from the aqueous solution. The impacts of factors such as pH, contact time, and initial concentration of heavy metal ions were examined in adsorption investigations. Key parameters include pH=6-7 and t=24h (the pseudo-second-order model best fits the kinetics data). The maximum adsorption capacities were determined to be SiO₂/-COOH – 75 mg/g, SiO₂/-COOH/-CH₃ – 83.6 mg/g and SiO₂/-COOH/-C₆H₅ – 122.4 mg/g for Ni(II) ions. Also, SiO₂/-COOH – 72 mg/g, SiO₂/-COOH/-CH₃ – 65 mg/g and SiO₂/-COOH/-C₆H₅ – 95.6 mg/g for Mn(II) ions. The equilibrium data followed the Langmuir model, rather than the Freundlich model, which indicates chemisorption. Furthermore, the materials could be regenerated up to 95% using HCl as the desorbent.

Thus, the materials with carboxyl groups exhibited a high adsorption capacity for the removal of Ni(II) and Mn(II) ions from the aqueous solution. Additionally, the incorporation of organic groups was observed to enhance adsorption, likely attributed to the formation of simplified complexes on the surface.

Acknowledgements. This work was supported by the APVV-19-0302 project.

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PILOT STUDIES OF PHENAZONE ADSORPTION ON CARBONIC ADSORBENT AC-K

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Pharmaceuticals and personal care products, known as emerging contaminants (ECs), receive a special attention for the reason of their potential impact on the environment and human health [1]. The efficiency of ECs removal strongly depends on the technology implemented in the wastewater treatment plants which are usually based on conventional systems: chlorine, biological treatments, activated carbon adsorption, advanced oxidation processes, electrochemical systems [2]. The use of activated carbons (ACs) in these technologies have demonstrated a high adsorption capacity for ECs depending on their porous structure and surface chemistry.

Here we present the research of the adsorption processes of phenazone (C₁₁H₁₂N₂O, MM 188.23) on activated carbon AC-K in order to establish its adsorption capacities against emergent contaminants. The measurements were carried out at two pH values (pH=3 and pH=5.5) at the temperature of 35⁰C. Acetate buffer solution (mixture of CH₃ COOH 0.2 M and CH₃COONa 0.2 M) was used to obtain and maintain the required pH values. The adsorption kinetic curves of phenazone on the active carbon AC-K, determined from solutions with an initial concentration of 100 mg/l, were measured in the time interval between 5-300 minutes. It has been established that the adsorption process of phenazone is rather fast and the establishment of the adsorption equilibrium is reached after approx. 30-60 min of contacting/stirring, depending on the pH value. The degree of immobilization of phenazone on AC-K coal is significant, its value being about 90% (pH 3) - 95% (pH 5) of the total amount of adsorbate. The adsorption experiments were carried out in a thermostatic shaker by contacting a series of samples using constant masses of carbonic adsorbent (50 mg) with aqueous solutions of adsorbate (50 mL) with the initial concentration between 50-500 mg/l. The adsorption isotherms of Phenazone AC-K coal were determined after establishing equilibrium in the adsorbate/adsorbent systems at pH values 3 and 5.5 and temperature 35⁰C. The phases were separated by filtration and the residual Phenazone was determined by UV-Vis spectroscopy. The obtained data shows a major dependence of the immobilization rate of phenazone on the pH value of the contact medium. It was determined that increasing the pH value from 3 to 5.5 increases the maximum adsorption value (a_m) of Phenazone on AC-K charcoal by more than 30%.

Summarizing the preliminary results, it was found that, the rate and degree of immobilization of phenazone on AC-K coal indicates to an encouraging potential for its use for the removal of emergent contaminants from various water sources.

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SYNTHESIS AND CHARACTERISATION OF DIETHYLENTRIAMINE-PHENYLENE-BRIDGED POLYSILSESQUOXANE AS SORPTION MATERIAL

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Heavy metals rank high among the environmental pollutants nowadays. The rare-earth elements (REE) emissions in the environment have also increased due to the growth of high-tech production. Therefore, the development of materials for effective removal of heavy and REE for the purpose of future reuse is relevant. We obtained diethylenetriamine-functionalized polysilsesquioxane with phenylene bridges, thoroughly characterized it and compared its sorption properties towards different heavy and REE metal ions (Fig.1).

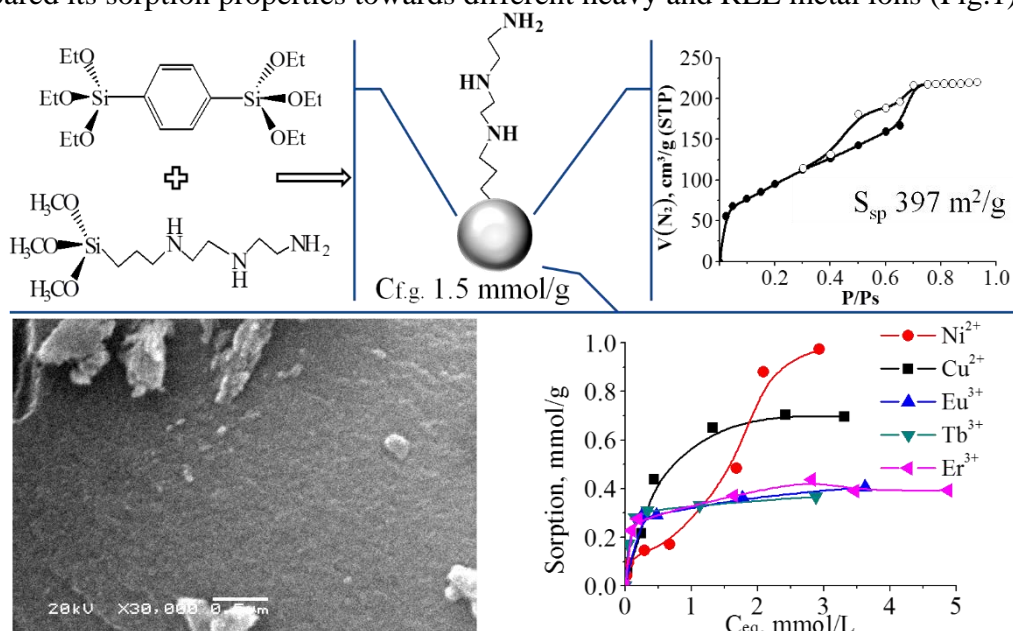


Figure 1. Synthesis, characterisation, and sorption properties of diethylenetriamine-silica

Typically for the phenylene-bridged materials [1], the bulk of the sample is comprised by very small particles (<50 nm in size) forming a well-developed three-dimensional mesoporous structure (as witnessed by N₂ adsorption-desorption isotherms). Qualitatively the incorporation of diethylenetriamine groups was confirmed by characteristic adsorption bands in the infrared spectra, while analysis on CHNS elements indicates the quantitative content of groups at the level of 1.5 mmol/g. Comparing the sorption of different metal ions in mmol/g, the uptake of Ni²⁺ is the highest, while the uptake of the attested REE is similar: 0.97 (Ni²⁺) > 0.65 (Cu²⁺) > 0.4 (Eu³⁺, Er³⁺, or Tb³⁺). Thus, samples of this type have potential for use in sorption to remove metal ions from water.

Acknowledgements. This research is funded by APVV-19-0302 project.

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SYNTHESIS AND CHARACTERIZATION OF POLYMERIC AND CARBON MATERIALS FOR SEPARATION APPLICATIONS

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Polymeric materials, especially those of spherical in shape, have been utilized in numerous applications for decades.

Numerous polymerization techniques are used to obtain polymeric sorbents with different grain sizes. Polymers in the form of porous or non-porous microspheres we can obtain by one of the heterogeneous polymerization: emulsion, suspension dispersion polymerization, membrane emulsification, or swelling and polymerization techniques.

The obtained materials can be used in solid-phase extraction for the isolation of organic compounds from water and air, and as stationary phases in high performance liquid, supercritical fluid, ion-exchange and size-exclusion chromatography [1, 2].

For certain applications, polymer materials are chemically modified. For this purpose, functional groups or unreacted double bonds present in the polymer structure are used.

Carbonization is one method which enables the generation of polymer microspheres with carbonaceous surface. However, polymers often undergo sintering or shrinking during carbonization. This has an unfavourable influence on the porous structure and causes that the material to become microporous and lose its sorption properties. For this reason, to improve sorption properties of carbonized sorbents, various pretreatment methods are employed. Our experience shows that modification with phosphoric acid is an effective method [3,4].

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DFT STUDY OF STRUCTURAL FEATURES OF CAFFEIC ACID AND QUERCETIN RESPONSIBLE FOR REALIZATION OF POSSIBLE SYNERGISTIC EFFECT IN THEIR JOINT REACTION WITH THE CATION-RADICAL ABTS^{*+}

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On the basis of Density Functional Theory (DFT) calculations it was shown in our previous work [1] that namely the 3-OH and 4-OH hydroxyl groups of caffeic acid (CA) are responsible for the synergistic antioxidant effect with glutathione taking place in their joint reaction with the cation-radical of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS^{*+}). At the same time the experimental data (see [2]) indicate on the existence of the synergistic effect between CA and quercetin (Q) in their joint FRAP test. Thus, it seems to us interesting to investigate by means of the DFT method the structural features of CA and Q which could cause the possible antioxidant synergistic effect in their joint reaction with ABTS^{*+}. The data of our DFT calculations show that in the case when neutral molecules of CA and Q form their complexes with ABTS^{*+} (by means of one of the two –SO₃H groups of the cation-radical ABTS^{*+}) the electronic density of the unpaired electron of ABTS^{*+} remains mainly on the ABTS^{*+}'s structural fragments of these complexes. However, in their turn, these complexes: [CA & ABTS^{*+}] and [Q & ABTS^{*+}] can easily interact respectively with the anions Q⁻ and CA⁻ arising due to deprotonation of the 4-OH group of Q and 4-OH group of CA. The given interactions lead to the situation, when the ABTS^{*+}'s structural fragments of both the above complexes do not contain any unpaired electrons. Here it is to be noted, that 3-OH' and 3-OH groups of Q and CA also take part in their co-ordination with –SO₃H groups in the corresponding complexes [CA & ABTS^{*+}] and [Q & ABTS^{*+}] (Figure1).

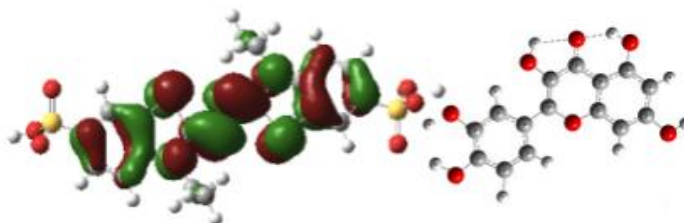


Figure 1. The interaction of the 3-OH' and 4-OH' hydroxyl groups of quercetin with the SO₃H group of ABTS^{+}.*

Thus, basing on the DFT calculations, one can conclude that in the case under study the antioxidant synergistic effect in the joint reaction of CA and Q with ABTS^{*+} will take place. Moreover, namely 3-OH and 4-OH hydroxyl groups of CA along with 3-OH' and 4-OH' hydroxyl groups of Q will be responsible for the arising of the given effect.

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PHOTODEGRADATION OF DOXYCYCLINE BY ADVANCED OXIDATION PROCESSES (AOP) IN WATER SOLUTIONS

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The SARS-CoV-2 outbreak, which caused countless deaths and infections in 216 countries, has become the biggest pandemic of last 100 years [1]. Moreover, the absence of any permanent medicine protocol caused medical, social and economic problems worldwide. The rapid spread of the virus has required doctors to urgently develop treatment using all known drugs.

Doxycycline (DOX), a tetracycline antibiotic originally used only in veterinary medicine, was found to be effective against COVID-19 [2]. Due to the high consumption of DOX and other anti-covid drugs, they have penetrated surface waters with human and animal excreta, from industrial wastewater, from human waste, due to improper disposal of expired drugs in the garbage chute or sewerage, from pharmaceutical industries producing antibiotics.

This is why it is very important to solve the problem of deep DOX oxidation by applying advanced oxidation processes (AOPs). Among the AOPs, there are used UV, UV/H₂O₂ systems and the last one represents a cyclic process with OH• radicals generation. The application of these systems is promising for solving the problem of wastewater treatment in the pharmaceutical industry [3-4].

In this work there was studied the kinetics of DOX oxidation under UV irradiation and by the UV-H₂O₂ system using the spectrophotometric method. Antibiotic concentrations varied between (1,69 -5,625) ·10⁻⁵ mol/L. For the DOX degradation in the UV-DOX system the mercury-deuterium high-pressure lamp “DRT-100” was used. The degree of degradation at different concentrations of the drug was only 9.1 -11.4%.

The conditions of DOX decomposition in the UV/H₂O₂ system were studied and optimal degradation conditions were identified: [H₂O₂] = 0.005-0.02 mol/L; [DOX] = (1.69-7.75)·10⁻⁵ mol/L; pH = 4,8; T = 298 K; t = 30 - 40 min; λ = 275 nm. The degree of DOX degradation in UV/H₂O₂ system is 85.58%, which is 74.18% more than in the previous system. It was found that in both systems the decomposition kinetics corresponded to the pseudo-first model with rate constants varying in the range 0.0289-0.0685 min⁻¹. By the method of competing acceptors, the rate constant of the interaction between OH• radicals with the drug used was determined: k_{OH+DOX} = 7.2·10⁹ L/mol·s.

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THE INFLUENCE OF ISONIAZID ON THE SELF-PURIFICATION CAPACITY OF AQUATIC SYSTEMS

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The Republic of Moldova ranks among the countries with relatively poor water resources. This is the reason why their protection and adequate utilization continue to be a problem at the national level. One of the factors causing the deterioration of their quality is the increase in the volume of untreated wastewater. Pharmaceutical compounds released into the aquatic environment are famed for their persistence in the environment. That is why studies of their influence on aquatic ecosystems have prevailed recently. One of the drugs often used in the treatment of tuberculosis, which is a fairly common disease in the Republic of Moldova, is isoniazid (INH) [1,2]. The presence of INH in aquatic systems is inevitable, so the goal of this research was to find out how this drug mixture affects the natural waters' self-purification capacity. For this purpose, the following systems were modeled: *INH-H₂O-H₂O₂-PNDMA-hv*; *INH-H₂O-H₂O₂-Cu(II)-PNDMA-hv*. All model systems were irradiated with the polychromatic lamp *DRT-400*. In this way, the inhibition capacity and stationary concentration of OH radicals in the modeled systems were determined, using the radical trap PNDMA (p-nitroso-N,N-dimethylaniline) [3].

From the obtained results, it was found that increasing the concentration of INH in the system leads to an increase in the inhibition capacity and a decrease in the OH radical concentration. The values for the inhibition capacity when INH was added at concentrations ranging from $3.8 \cdot 10^{-5}$ M to $3.2 \cdot 10^{-4}$ M were found to be on the order of 10^6 to 10^7 s⁻¹. According to the inhibition capacity parameter, the systems are classified as highly polluted waters. Self-purification processes decrease considerably in water systems with an increase in INH concentration. It was discovered that when the concentration of hydrogen peroxide in the system increased, the concentration of OH radicals increased and the inhibition capacity decreased. This proves that isoniazid effectively scavenges OH radicals, which are generated during hydrogen peroxide photodissociation.

It was found that when Cu(II) ions are added to the system, the concentration of OH radicals rises 3–6 times and the inhibition capacity falls. This is explained by the fact that Cu(II) ions catalyze the photodissociation of hydrogen peroxide, producing a much greater quantity of OH radicals. So, in the presence of Cu(II) ions, according to the inhibition capacity parameter, the systems are classified as polluted waters. Based on this, it was shown that INH, which has a reducing character, consumes the oxidative equivalents in aquatic systems. Thus, INH leads to a reduction in the self-purification capacity of aquatic systems.

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EVALUATING THE IMPACT OF AQUATIC POLLUTANTS THROUGH LABORATORY SIMULATIONS WITH AMMONIUM INITIATION: A METHODOLOGICAL APPROACH

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The toxicity of different forms of mineral nitrogen, particularly the reduced ones, is a significant factor driving the attention to water quality in rivers within the Republic of Moldova. Ammonium, in particular, is of great concern due to its similarity to an amino acid, where a hydrogen atom is substituted with an organic radical containing a carboxylic group. Amino acids are the building blocks of proteins, the essential molecules supporting life processes. As a result, ammonium in aquatic environments can play a dual role: it can serve as a building block for the creation of living organisms and also provide energy support for the activities of aquatic organisms. Ammonium serves also as a universal catalyst for the emergence of a new state within the aquatic environment.

Laboratory modeling involving by ammonium initiation is highly responsive to the presence of anthropogenic pollutants, such as surfactants, heavy metals, and the existence of antibacterial agents, among others. It can even detect variations in the different states of these pollutants within the aquatic (polluted) environment. Consequently, the discharged water into the natural water bodies often fails to meet these two crucial (trophic and environmental) water quality indicators for a river. Starting from the pollution source (the city of Soroca, Republic of Moldova) along the water course, laboratory simulations easily highlight the degree of self-purification. For instance, comparing the ammonium (NH_4^+) oxidation process in water samples from the Nistru River, Vărăncău section, with those from the Bursuc section, reveals a difference in the time required for ammonium oxidation in samples subjected to the same modeling approach. This difference becomes even more pronounced when fine particles of calcium carbonate are added to the river water samples. The decomposition of the complex compounds of anionic and cationic surfactants ($\text{SAS An} \cdot \text{SAS Ct}$), in which the cationic component constitutes a bacteriotoxic pollutant, leads to the stagnation of self-purification process. This phenomenon is commonly observed in technologized biological treatment systems. In wastewater treatment plants (WWTPs), the phenomenon of inhibiting ammonium oxidation occurs, especially when oxidation did not occur at the initial stage of treatment, where both aerobic and anaerobic processes take place, involving the oxidation of ammonium ions, as well as the reduction of nitrates and nitrites returning from the final stage of the treatment process. Typically, in wastewater treatment plants (e.g., WWTP Chisinau), the emergence phenomenon is combined in the final stage with an inhibition of the oxidation and assimilation of both organic carbon and ammonia nitrogen. Therefore, the discharged water into the natural water bodies often fails to meet these two crucial water quality indicators for a river. Laboratory simulations conducted with river water samples exhibit sensitivity to the presence of various substrates, including different fractions of granite and spongy clay. These simulations reveal an acceleration in the oxidation of both ammonium and nitrite ions, underscoring the clear and beneficial effects of self-purification processes.

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CARBONACEOUS ADSORBENTS FROM SOLID INDUSTRIAL WASTE

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Solid carbon residue, also known as carbon black, is the carbonaceous material left after rubber degradation during the pyrolysis process. It is a potential human carcinogen, and short-term exposure to high concentrations can cause discomfort in the upper respiratory tract, leading to mechanical irritation. Industrial waste poses a significant environmental challenge, and finding effective methods to utilize and mitigate its impact is of paramount importance.

Activation is one of the methods used to modify carbonaceous materials and involves the partial oxidation of carbonized layers in its structure, using water vapor, carbon dioxide, hydroxides, or carbonates of alkali metals as activation agents.

The aim of this study was to develop and characterize adsorbent materials derived from solid industrial waste. A series of carbonaceous adsorbents were obtained from the pyrolysis residue of tires. Various techniques such as physical, chemical, and thermal treatments were employed to modify the waste materials and enhance their adsorption properties. Activation was carried out in a horizontal reactor, using water vapor as the activation agent, as well as pre-treatment with KOH, H₃PO₄, and HNO₃. The obtained adsorbents were characterized using gas adsorption, IR spectroscopy, and thermal analysis.

The pyrolysis residue of the tires presents a homogeneous substance with a black color, finely dispersed, immiscible in water. In order to assess the thermal stability of the residue, thermal analysis was performed in a dynamic air atmosphere with an airflow rate of 100 cm³/min and a heating rate of 10°C/min. The analysis results indicate that the residue remains stable up to 320°C, and the total thermal degradation occurs at 750°C. From the adsorption isotherm data, the pore volume distribution curve was constructed as a function of radius. The obtained results allow us to characterize the morphology of the char: the specific surface area is 20 m²/g, and the reversibility of the isotherm indicates the presence of open pores with cylindrical shape, formed as a result of agglomeration of char particles, with an effective pore radius of 11 nm. The activation of the carbonized material allowed the production of activated carbons with a specific surface area of up to 700 m²/g.

The obtained results indicate the possibility of obtaining carbonaceous adsorbents with economic potential from solid waste generated during tire pyrolysis. This study highlights the feasibility of obtaining and characterizing adsorbent materials from solid industrial waste. The utilization of such materials not only offers a sustainable solution for waste management but also presents an opportunity to address environmental concerns and promote cleaner industrial practices.

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THE EFFECT OF LONG-TERM ORAL ADMINISTRATION OF ACTIVATED CHARCOAL ON THE OCCURRENCE OF TUMORS AND THE MORPHOLOGY OF INTERNAL ORGANS IN RATS

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Activated carbon or charcoal (AC) with a high adsorptive surface & pore volume for oral administration is a good candidate for treating different pathological states accompanied by inflammation. The biocompatibility of such ACs in vivo is evaluated by studying the total body weight dynamic, occurrence of tumors, and morphology of organs in rats fed with this AC.

HSGD granulated (derived from N-containing synthetic polymers, Ukraine), and CA-M (derived from apple wood, handy milled, Moldova). Both ACs were obtained by the method of steam activation in the fluidized bed of the laboratory furnace. AC samples were evaluated using low-temperature nitrogen adsorption and the adsorption of albumin-bound toxins (unconjugated bilirubin) [1]. 45 Wistar female rats 2 months old were allocated into 3 groups: HSGD, CA-M, and Control. The daily dose of ACs was 1.2 g per 1 kg of the rat's body weight over the course of 10 days every 2 months, mixed in a small amount of food [2] during 14 months (in 9 rats-histology) and till death in other 36 rats. Animals were weighed, and visually examined for tumor occurrence, and 3 animals from each group 14 months after the start of the experiment were sacrificed and organ tissues were carefully isolated for histological examination [2].

Table 1 presents the results of nitrogen adsorption by ACs (BET surface and total pore volume) as well as the quantity of unconjugated bilirubin adsorbed by AC from the albumin solution. These results indicate the high adsorptive capacity of both ACs in comparison with existing commercial analog eg. (Kremezin, AST—120- 1600 m²/g).

Table 1.

Activated carbon (AC)	BET surface, m ² /g	V mesopores, (cm ³ /g)	Adsorbed albumin-bound bilirubin (mg/per 1 g of AC)
HSGD	2667	3.15	36.4
CA-M	1857	0.84	30.4

No statistical difference in total body weight dynamic, in the percentage of visually detected spontaneous tumors and the average age of tumor, was found in both AC groups in comparison with the Control (Table 2).

Table 2.

Groups of rats	Total duration of AC administration (days)	Total body weight (g)			% of detected tumors	The average age of tumor (months)
		Before Experiment	9 months after	18 months after		
HSGD (n=15)	~115	155±11	296±31	356±38	29	22
CA-M (n=15)	~115-120	159±7	292±23	330±46	40	27
Control (n=15)	0	160±5	295±19	333±38	43	25

Histological examination of kidneys, liver, thymus, heart, spleen, stomach, lunge, small intestine, and colon reveals after 70 days of AC administration any difference with those of Control. These preliminary results indicate the signs of good biocompatibility of both highly-activated ACs long-time administered orally in relatively high doses.

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ADSORPTION OF TANNIC ACID ON ACTIVATED CARBONS WITH DIFFERENT SURFACE CHEMISTRY

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Activated carbons are materials of major importance for industrial applications. This is due to their remarkably high surface area which gives them specific adsorption properties for the removal of pollutants in the liquid phase. Tannic acid (1,2,3,4,6-penta-O-galloyl-D-glucose) is a pentagalloylglucoside; the central part of the molecule esterified to the hydroxyl groups with gallic acid and is a hydrolyzable tannin [1], and this compound generally gives colour. One of the most promising ways to remove this compound from a liquid medium is adsorption on the activated carbons.

The purpose of this work was to perform adsorption experiments of tannic acid from water solutions on activated carbons with different surface chemistry (AC-C obtained from apricot stones (Republic of Moldova) has a slightly basic surface - pH 8.8 and Granucol FA commercial activated carbon (Germany) has an acidic surface - pH 4.3).

To evaluate the adsorption process of tannic acid on activated carbons the adsorption kinetics at three temperatures (20, 35, 45°C) were determined. According to experimental data, the adsorption equilibrium is established after 8 hours and about 12 hours for activated carbons FA and AC-C, respectively. During the first 2 hours of contact, the adsorption speed of tannic acid on the activated carbon Granucol FA is higher by about 30% compared to the activated carbon AC-C. The adsorption capacity of the studied activated carbons for tannic acid was determined from the adsorption isotherms, being about 0.4 and 0.32 mmol/g for FA and AC-C, respectively.

The experimental data were described using mathematical models, such as the pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models, and Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich theoretical isotherms. The adsorption of tannic acid on the studied activated carbons is based on chemisorption because the experimental data are best described by the pseudo-second order kinetic and the Langmuir models.

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THE IMPACT OF EXPERIMENTAL ACTIVATED CHARCOAL ON THE ANTIOXIDANT POTENTIAL AND ANTIOXIDANT STABILITY OF FETEASCA NEAGRA WINE

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The treatment of wines with activated charcoal is accompanied by partial removal of certain groups of substances, which, in addition to having a negative impact on quality or the risk of transformation into undesirable factors, can determine important antioxidant properties. These are beneficial both for the stability of wine itself over time and for the health of consumer. In this aspect, it is advisable to determine the impact of the developed experimental carbons on the antioxidant stability of wines in order to optimize the effectiveness of sorbents

Activated charcoal AC-2 and AC MRF were used in the study, which have been obtained in the Laboratory of Ecology of the Institute of Chemistry at USM – Moldova State University, from walnut shells and apple wood and Feteasca Neagră wines from Purcari vineyard grapes, respectively (2022). In the study it was highlighted the varied adsorption capacity of the targeted carbons in relation to various groups of phenolic substances, including anthocyanins. The FRAP (Ferric ion Reducing Antioxidant Power) method was used to determine the antioxidant capacity of the treated wines, using Trolox as a reference. In the range of administered sorbent concentrations of 0.1-0.75 g/l, minor decreases in FRAP antioxidant potential have been observed (<3% in the case of AC-2 and <6% for MRF). Relevant negative correlations are valid for both sorbents ($R^2=0.9654$ for AC-2 and 0.9970 for MRF). Thus, the use of activated charcoal AC-2 and MRF does not significantly affect the antioxidant potential with respect to the Fe^{2+} - Fe^{3+} redox couple.

AC-2 and MRF negatively influence the antioxidant stability of wine in a more pronounced way. Compared to untreated wine, AC-2 (0.75 g/l) causes a decrease by 7.3 %, while MRF- by 15.8 %. The decrease in antioxidant stability of both sorbents negatively correlates with the administered concentrations. Therefore, in the production of Feteasca Neagra wines the application of the mentioned activated carbons for the removal of unwanted compounds should be carried out carefully and selectively in order to reduce the negative impact on the antioxidant potential and antioxidant stability of the finished product.

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THE REDOX PROPERTIES OF ACTIVATED CARBONS EVALUATED BY THE ABTS CATION-RADICAL METHOD

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The purpose of this work was the determination of redox properties of activated carbons by the ABTS^{•+} method. The ABTS^{•+} method is based on the ability of antioxidant compounds to annihilate the ABTS^{•+} and reduce the radical to the colourless neutral form. In this method, trolox is used as a reference substance [1]. In this work, in order to adjust the ABTS^{•+} method for heterogeneous systems, some experimental details were taken into consideration, such as: the activated carbon grain size, solid/liquid ratio, agitation time, total contact time and separation of phases. All measurements were performed on UV-Vis Spectrophotometer (Model 6505, Jenway, UK), using quartz cuvettes, $l = 10$ mm.

The UV-Vis spectrum of the ABTS solution was recorded in order to identify the absorption maxima. The calibration curves, which practically coincide, have had a correlation coefficient of 0.998, demonstrating that the trolox solution exhibits stability for 10 min. It was found that stable and reproducible results are obtained in about 5 minutes of contacting the phases. The comparison results of the antiradical activity of the different fractions of activated carbons reveal the series for: (1) activated carbon obtained from apple wood (CA-MT) $90 \div 125 \mu\text{m} > 630 \div 800 \mu\text{m} > 125 \div 630 \mu\text{m}$; (2) activated carbon obtained from walnut shells (CANF) $90 \div 125 \mu\text{m} > 125 \div 630 \mu\text{m} > 630 \div 800 \mu\text{m}$.

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THE CATALYTIC ACTIVITY OF CARBON CATALYSTS IMPREGNATED WITH MANGANESE, COPPER, AND COBALT IONS

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The catalytic activity of different samples of catalysts known in the specialized literature, but also obtained by us, in the laboratory, in an autoclave at different temperatures and pressures, was studied. The kinetics of the decomposition process of hydrogen peroxide in the presence of the catalysts under study was studied at the installation set up in the laboratory. The hydrogen peroxide used was diluted 50 times and was 0.5412 N. 5 ml H₂O₂ (1:50) and 5 ml H₂SO₄ (1:4) were taken and titrated with 0.1 N KMnO₄. Manganese ions, which are formed in the first titrant portions, catalyze the redox process and further discoloration of the solution occurs very quickly. The results of the study indicate that the Centaur catalyst, obtained in the USA at 300 revolutions per minute of the mixer, has the greatest activity in order to decompose hydrogen peroxide. AC-Co1 and AC-Cu1 catalyst samples were found to decompose hydrogen peroxide better than AC-Mn2 catalyst sample, all these kinetic curves being measured at 200 rpm of the mixer. If we compare the kinetics of the hydrogen peroxide decomposition process on the AC-Mn1+KMnO₄ samples with AC-Mn1+KMnO₄, held for 2 hours in the oven at 95 °C, with demineralized water added, we find a significant decrease in the catalytic activity of the sample kept for 2 hours in the oven, at 95 C, with demineralized water added. Probably, when heating the manganese, in the form in which it is, simply a part of it is washed away. The other 2 samples have a rather low catalytic activity, especially on AC-Mn2+KMnO₄.

With the increase in the speed of the mixer, the granulometric composition of the Sorbent AC catalyst undergoes transformations (it breaks down) and the catalytic activity decreases significantly.

The best catalyst obtained by us AC-Mn1+KMnO₄ does not remove ammonium ions (ammonia) from deep waters. We are going to test another pollutant from these water categories.

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MONONUCLEAR NICKEL(II) AND COPPER(II) COMPLEXES WITH SCHIFF BASE LIGANDS DERIVED FROM QUINOLINE-8-ALDEHYDE AND S-METHYLISOTHIOSEMICARBAZONES

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Complexes of Schiff bases with some transition metals show significant biological notification including antimicrobial, antibacterial, antifungal and anticancer activities. Azocompounds have been studied widely because of their excellent thermal, antibacterial activity and optical properties in applications such as optical recording medium, toner, ink-jet printing and oil-soluble lightfast dyes.

Metal complexes of thiosemicarbazone are well known for their pharmacological applications, while quinoline derivatives (in particular, quinoline carbaldehydes) display bactericidal, insecticidal and fungicidal properties. The combination of both active moieties in one molecular entity appears promising for the preparation of biologically active compounds.

In this paper, we report new four mononuclear Ni(II) and Cu(II) complexes: NiL¹]I (1), [CuL¹]I (2), [NiL²]I (3) and [CuL²]I (4) with N₃O binding system obtained by metal-directed condensation of quinoline-8-aldehyde with acetyl or benzoylacetone mono-S-methylisothiosemicarbazone (H₂L¹ and H₂L²). The compounds were characterized by elemental analysis, ESI MS and IR-spectroscopy. The molecular structures of 1 and 2 were established by X-ray diffraction method (Fig. 1).

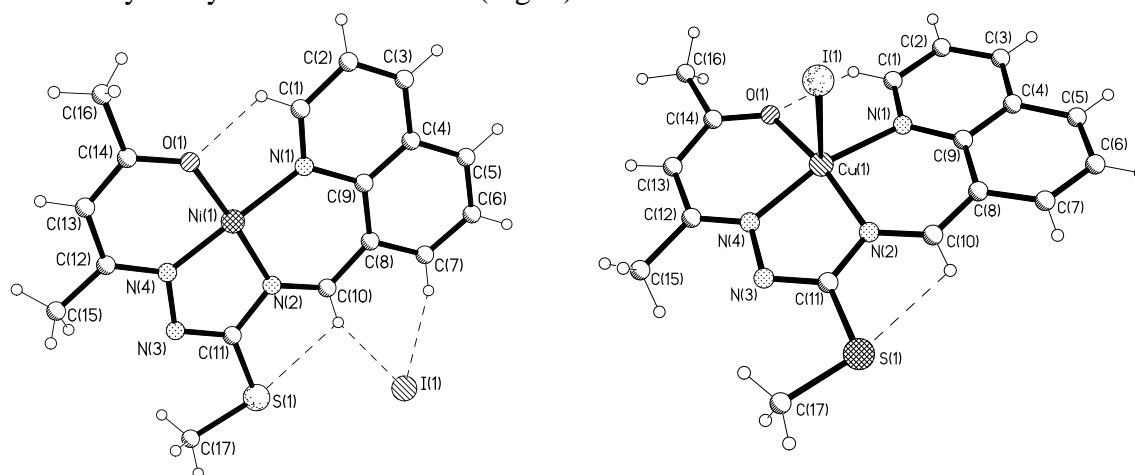


Figure 1. Molecular structure of complexes 1 and 2

The investigations confirmed that the Ni(II) compounds are ionic with an iodide anion in the external sphere and the Cu(II) complexes are molecular, the iodide anion being coordinated to the metal atom. The X-ray diffraction studies revealed a square-planar structure of the Ni(II) ionic complex and a square-pyramidal structure of the Cu(II) molecular complex.

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ENVIRONMENTAL CONDITIONS IN THE SYNTHESIS OF MONASTROL

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The synthesis of eutectic mixtures based on 3- (carboxymethyl) -1-vinyl-1H-imidazole-3-ium (chloride, bromide, hexofluorophosphate) and thiourea in various ratios (from 2: 1 to 1: 3) was realized, the aggregate state and established catalytic activity for the synthesis of Monastrol, which showed a wide range of pharmacological activity.

The most effective method currently used for the synthesis of dihydropyrimidines remains the well-studied multicomponent Biginelli reaction [1]. The Biginelli reaction, which is commonly used for the direct preparation of Monastrol and its derivatives, has many advantages over traditional synthetic methods [2]. Three-component and one-pot synthesis under Biginelli reaction conditions makes it possible to obtain monastrol based on the result of the interaction of acetoacetic ester, thiourea, and 3-hydroxybenzaldehyde in the presence of various eutectic catalysts and various solvents and without them [3]. From the point of view of environmentally friendly conditions, they have the advantage of many reagents collected in one vessel, which avoids waste from multi-stage purification and the formation of residues.

The biological role of Monastrol has led to significant interest in its synthesis and is a 3-component one-pot synthesis based on the interaction of acetoacetic ester, thiourea and 3-hydroxybenzaldehyde, which avoids waste from multi-stage purification and the formation of residues. The synthesis is catalyzed by inorganic acids, ionic liquids, eutectic solvents, or under microwave irradiation. As a result of compounds as catalysts, a yellowish-gray crystalline substance was obtained as a result, the physicochemical constants of which, including $T_m = 182-184^{\circ}\text{C}$, indicated the formation of monastrol, the yield of which was 40%. The maximum yield of the product was 79%.

In the synthesis of Monastrol, the goal is to select reagents and test various catalysts that are environmentally friendly, least toxic and financially attractive in order to maximize product yield, reduce reaction time, selectivity and minimize reagent surpluses, formation of by-products, high temperatures, environmental pollution. environment, waste and costs. Catalysis plays a fundamental role in Biginelli synthesis, especially in developing strategies to approach eco-friendly catalytic conditions for further use in the renewable chemical industry [4].



Acknowledgements. This work is a part of the Moldovan State Program (2020-2023), Project number: 20.80009.5007.17.

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ASSESSING THE THERMODYNAMIC EQUILIBRIA IN SOILS

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Soil is a complex, multi-component, and polydisperse system with multiple phases. It consists of a solid component and pores (comprising the solid phase), which are filled with soil solution (forming the liquid phase), as well as soil air (representing the gaseous phase), and living organisms. Most soils are primarily composed of minerals. The solid phase, mainly consisting of mineral substances, makes up 40-65% of the soil volume (or 90-99% or more of its mass). In soil solutions, numerous chemical reactions take place, including competitive reactions such as complex formation and protonation, among others. Under these conditions, a single element can exist in multiple ionic forms, either as a free ion or as part of various complex ions. Consequently, the concentration of any ionic form the variations in the composition and concentration of soil solutions can be substantial. However, despite the inherent heterogeneity of soil cover, these variations generally fall within the bounds characteristic of soils of a given type.

This study explores the application of chemical thermodynamics and computer-based equilibrium composition calculations in describing chemical reactions in “mineral-soil solution” systems. A limitation of instrumental physicochemical methods for analyzing solutions is that they either characterize the overall composition or ion activity or do not provide insights into the equilibrium distribution of various chemical forms of elements. It is known that most metal ions in soil solutions exist in ionic forms, complexes with mineral acid anions, and organic compounds. Furthermore, the bioavailability and toxicity of chemical elements, especially metals, depend on the chemical form in which they are present in the soil solution. Therefore, to assess the equilibrium distribution of chemical forms of elements in soil solutions, a combination of analytical, thermodynamic and computational methods is necessary. Consequently, thermodynamic calculations reveal that the state of several elements, especially metal ions prone to forming complexes, varies significantly in solutions with different pH levels.

Chemical equilibrium processes in the “mineral-water solution” system have been described by a generalized equation of reactions, where water-soluble species are assumed to be formed in quantities proportional to their partial molar fractions. Mathematical expressions have been derived to calculate the change in Gibbs energy for overall processes, taking into account side reactions such as hydrolysis and complex formation under real, non-standard conditions. The developed approach for calculating Gibbs energy has been successfully applied to chemical processes in soil involving kaolinite and montmorillonite. This method is versatile and can be applied to any heterogeneous processes in aqueous systems involving the formation of a solid phase.

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EVALUATION OF WATER QUALITY IN WATER SOURCES IN THE SOUTH OF THE REPUBLIC OF MOLDOVA

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Water from twenty-five sources from seventeen villages located in the south of the Republic of Moldova was studied. Thirteen of these villages are situated in the south-west in the regions of Hâncești and Leova, and four are in the south-east, in the region of Căușeni. All the analyzed sources are actively used by local population as drinking water sources. Water quality assessment for use as a drinking water was done according the criteria set by the national regulation – Law 182/ 19/12/2019. The research was performed in the water quality accredited laboratory (ISO 17025/2018) according to the standardized methods.

Figure 1 shows the percentage of samples (%) not meeting the requirements for drinking water by at least one parameter. The values of the incompliance of each parameter with the corresponding allowable concentration vary greatly. The lowest hardness content – 0.84°Germany (min. allowable concentrations 5°Germany) was found in the v. Ciuciuleni, the highest sodium ion content- 531.5 mg/L (maximum allowable concentrations, mac 200 mg/L) and nitrite content – 2.0 mg/L (mac 0.5 mg/L) were found in Cupciu. The highest ammonia and ammonium ion content -7.11 mg/L (mac 0.5 mg/L) was found in v. Minjir. The highest contents of hydrogen sulfide and dissolved sulfides – 22.0 mg/L (mac 0.1 mg/L), fluorides 8.96 mg/L (mac 0.1 mg/L) and permanganate index 29.6 mg O₂/L (mac 5 mg O₂/L) were detected in Sarata Galbenei. The highest content of iron ions -1.28 mg/L with mac of 0.2 mg/l was found in v. Lapușna. The highest content of nitrates – 1522.6 mg/L with mac of 50 mg/L, total dissolved solids (TDS) – 4289.2 mg/L (mac 1500 mg/L), chlorides 406.3 mg/L (mac 150 mg/L) were detected in v. Tomai.

The research has shown that none of the analyzed sources had water complying with the requirements to the Law 182/ 19/12/2019 by one or more parameters, which means that the population of the south of Moldova do not have access to quality drinking water. Thus, development and implementation of the modern water treatment is essential for this region.

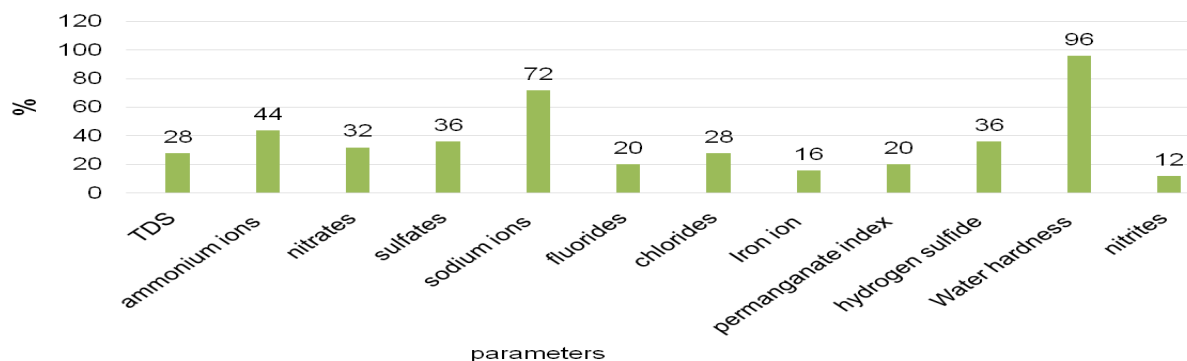


Figure 1. Percentage of samples not meeting the requirements for drinking water by at least one parameter.

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UDC: 556.114

CORRELATION BETWEEN RAINWATER CHEMICAL COMPOSITION AND ITS EROSION PROPERTIES

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The pollution of the atmosphere through the release of significant quantities of gaseous industrial pollutants leads to rainwater contamination, rendering it corrosive to terrestrial rocks and soils. Furthermore, the trend of aridification in the Republic of Moldova is altering the dynamics of rainfall patterns. This trend is characterized by a reduction in the duration of rainfall events and an escalation in their intensity, resulting in a higher rate of rainwater flow per unit of time. In such circumstances, despite a roughly similar volume of rainwater, the consequences are markedly different, as the potential for soil erosion is on the rise. The objective of this research was to assess the influence of rainwater chemical composition and specific conditions on the process of soil particle washing.

The action of rainwater washing soil not only depletes the soil itself but also results in the sedimentation of lakes and ponds, leading to the clogging of surrounding areas. Consequently, this phenomenon can cause natural lakes and, particularly, man-made reservoirs (such as dam lakes) to become murky and silt-laden. Following the analysis of the results of a series of rainwater samples collected on the territory of the Republic of Moldova and other regions presented in scientific publications, three types of rainwater were modeled: “Moderate” in which HCO_3^- ions predominate along with $\text{CO}_2\cdot\text{H}_2\text{O}$, $\text{NH}_3\cdot\text{H}_2\text{O}$; “Acid” (in which strong acid anions Cl^- , NO_3^- , SO_4^{2-} predominate along with HCO_3^- , $\text{CO}_2\cdot\text{H}_2\text{O}$, $\text{NH}_3\cdot\text{H}_2\text{O}$, etc.); and “Ammoniacal” (in which the ammonium ion predominates along with HCO_3^- , $\text{CO}_2\cdot\text{H}_2\text{O}$ and the anions of strong acids). Diluted versions (by 2, 4, 8 times) of these three rainwater types were as well modeled. In all types of rainwater CO_2 was obtained supersaturated. To get the pH titration curves, the automatic titrator 848 Titrio plus was used. COD, Ca^{2+} , Mg^{2+} et al. were carried out according to the accepted methodology. For the soil washing research, three types of soils, well known in the Republic of Moldova (*Typical Chernozium*, *Clay Carbonate Chernozium* and *Argiloiluvial Chernozium*) and the most aggressive types of rainwater (*Acid* and *Ammoniacal*) were used in models. The multiple freeze/thaw cycle was practiced in order to understand the effect of the winter period. The following important conclusions were obtained: 1) strong *Acid* rainwater solubilizes calcareous rock most strongly; 2) CO_2 and NH_3 are the main components that retain the washing/hydrating properties of limestone particles; 3) by the dilution of the mineral component of rainwater, the limestone washing activity is best preserved in *Ammoniacal* rainwater; 4) *Typical Chernozium* soil is the most resistant to the aggressiveness of the rains; 5) the vulnerability of the soils gradually increases in the *Typical Chernozium*, *Clay-Carbonate Chernozium* and *Argiloiluvial Chernozium* consequence; 6) the study of changes in soils at low temperatures demonstrates the strengthening of their stability after multiple freezes.

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SORPTIVE PROPERTIES OF SUBAQUATIC SEDIMENT FRACTIONS IN A EUTROPHICATED LAKE

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The aim of this research was to elucidate the role of physicochemical processes, such as adsorption, ion exchange, and others, conducted on natural substrates/minerals (soil, underwater deposits) and the potential utilization of these materials as a support for microorganisms responsible for self-purification effects in aerobic and anaerobic processes, both in laboratory conditions and in WWTP. The investigations encompassed the study of the sorptive properties of fractions obtained from underwater sediment as well as the adjacent soils of the Ghidighici Lake in the Republic of Moldova, from which a sediment sample was extracted. The hydrologic basin surrounding this lake primarily consists of “*Chernozem*” soil, from which this specific sample was collected. Following selective sedimentation separation, five mineral fractions (*Coarse Calcareous*, *Heavy Sandy*, *Semi-Heavy Sandy*, *Argillo-Sandy*, and *Clay*, also referred to as organo-mineral, and the *Nano-Clay* fraction, highly hydrated, also named as “peptizing”) and two organic fractions (*Coarse Organic* and *Medium Organic*) were obtained. To highlight the composition of the soil and underwater sediment, the samples underwent X-ray analysis using the Dron UM-1 refractometer with a FeK α detector. Each tested fraction was obtained in a dry form. The same amount of 50 mg was taken for each fraction, to which 40 mL of previously tested distilled water was added as a reference sample. Each of the fraction samples was subjected to multiple titrations, resulting in the generation of curves for the seven fractions. The clay fraction contains higher quantities of carbonate minerals and humified organic matter. The medium clay fraction exhibits remarkable buffering capacity compared to the other fractions. In terms of sorptive qualities, the soil and sediment samples are very close in values. In one of the major fractions, medium clay, the organo-mineral complex washed from the soil was accumulated. Different concentrations of dye were also used in the experiment, with the same volume, while fractions separated from underwater sediments from the Ghidighici Lake, obtained through consecutive sedimentation, served as adsorbents over time. After contact, the adsorption systems (dye solution + sediment fraction) were subjected to centrifugation, separating the solution from the solid adsorbent. Equilibrium concentrations of the dye in the solution were measured and then compared with the initial concentrations, prior to adsorption. This revealed a sequence in increasing order of adsorptive properties (Medium Clay, Argillo-Sandy, and then Semi-Heavy Sandy). The most hydrated, finest fraction was chosen from the obtained fractions and named “peptizing”. A solution of cetylpyridinium chloride (CPir) C₂₁H₃₈ClN at a level of 6 - 10 mol/L was used in the model. The experiment demonstrated a very efficient separation of this surface-active substance. Upon fixation of CPir on the hydrated fraction, significant sedimentation properties were acquired, leading to complete separation within five hours. The capture efficiency of this fraction exceeded 2.6 mmol/g of CPir. This process helps to understand the self-purification process in the water-particle (hydrated clay) suspension system. A similar fixation and purification effect is presumed to occur in WWTP.

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UDC: 628.5:614.7

ENVIRONMENTAL FRIENDLY SOLUTIONS FOR THE REMEDIATION OF POPs CONTAMINATED SITES

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The soil contamination by toxic organic substances (POPs, PAHs, BTEX, petroleum hydrocarbons, pesticides etc.) is very important problem worldwide and for Republic of Moldova. The management of contaminated sites includes different remediation approaches. The aim of this work is to test a bioremediation technology for the decontamination of POPs contaminated soil for the analysis of their implementation for the management purposes. The review of existing bioremediation technologies showed their importance for the sustainable management of POPs contaminated sites. One case study of high POPs contaminated site was realized for the risk assessment procedure and the evaluation of the bioremediation technology. The site was studied in detail which included sampling, laboratory analysis, determination of hotspots and contamination area, evaluation of the contaminated soils volume, the conceptual model elaboration for the risk assessment, and recommendation for the selection of the appropriate remediation technology. for the soil and geological condition. POPs concentration and spectrum were analysed using GC/MS method. The bioremediation experiment in the laboratory condition was realised for the demonstration of the capacity of this method.

The fertilizer supplement was prepared from the local materials for the acceleration of the bioremediation process as follows: 40 % of iron powder (0.3 – 0.50 mm); 50 % of small wood shavings; 10 % of composted chicken manure. This fertilizer was used as an additive to the soil in the amount of 5 and 10% of the soil mass. The soil treatment after the fertilizer addition included cycles of anaerobic and aerobic conditions. The anaerobic condition phase included the soil hydration up to 70% of the maximum molecular moisture capacity, heating to 30⁰ C and isolation from the air. This phase lasted for 14 days. The aerobic condition phase included the open-air condition for the temperature 20 – 25⁰ C, soil loosening and drying up to 20% of the humidity. This phase lasted for 7 days. The remediation had 8 cycles.

The obtained results showed that the initial POPs concentration from 500 – 650 mg/kg decreased to up 100 – 120 mg/kg (70 – 85 % of the initial concentrations). The blank experiment showed a reduction up to 60 %. The increase in the total number of microorganisms participating in the bioremediation process in all experimental schemes from 40 to 120 % compared to the blank was indicated. The principal conclusion is that the bioremediation technologies are perspective, cost-effective and simple approach among all methods for the remediation of contaminated soils in the comparison with existing remediation approaches (https://frtr.gov/matrix2/section3/table3_2.pdf). The in-situ soil treatment is a better approach because leaves the soil structure intact, reduces the potential migration of contaminants through soil and water systems.

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UDC: 661.981:621.311

THERE IS AN OPPORTUNITY TO REDUCE EMISSION OF NO_x AND GHG ON ANY THERMAL POWER PLANT IF THEY USE NATURAL GAS AS FUEL

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In process combustion of fuel on thermal power plants, excess air might be from 10% up to 60% by volume of all volume outdoor air, which supply for complete combustion of fuel. Excess air is a part of the total flow of air but the oxygen which is not participated in the chemical reaction of oxidation (combustion) of fuel but it is required for create a desired speed regime of outflow of fuel-air mixture from a burner of a thermal power installation.

Excess air is the variable for the same thermal power installation and it is inversely proportional to the amount combustion of fuel thus the less of fuel is burned, the less oxygen is required for its oxidation (combustion), but must be more excess air for the creation of a desired speed regime expiration of the fuel-air mixture from a burner device thermal power plant. The percentage of excess air in the general flow of air for complete combustion of the fuel is determined by the percentage of oxygen in the flue gases.

The oxygen contained in the excess air, which is not involved in the chemical reaction of fuel combustion in high temperature zone of 1200°C - 1400°C, is oxidized the nitrogen, forming «NO_x» (toxic gases) that are emitted to atmosphere by the flue gases.

If you reduce the percentage of the excess air, then in the flue gases will appear carbon monoxide "CO" (toxic gas), indicating about of the unborn fuel that is his loss, and the use of excess air leads to the loss of thermal energy for heating the excess air, that is increases expenditure of fuel burning and increases emissions «Greenhouse Gases» in the atmosphere.

The air consists of 79% nitrogen (N₂ - inert gas without color, taste and smell), which performs the basic function to create the desired speed outflow fuel-air mixture from a burner of power installation for a full and sustainable fuel combustion and 21% oxygen (O₂), which is an oxidizer fuel. Flue gases at the rated regime complete combustion of natural gas in the boiler units are composed of 71% nitrogen (N₂), 18% water (H₂O), 9% carbon dioxide (CO₂) and 2% of oxygen (O₂). The percentage of oxygen in the flue gas of 2% indicates 10% of the amount of excess air in the total flow of air participating in the creation of the desired speed regime of outflow of fuel-air mixture from a burner of a boiler unit for complete oxidation (combustion) of fuel.

In the process of complete combustion on thermal power plants must be disposed of flue gases which substitute the excess air and thus prevent the formation of «NO_x» and reduce emissions of GHG.

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UDC: 504.064:551.583(478)“2023/2030”

NATIONAL STRATEGY ON EDUCATION FOR THE ENVIRONMENT AND CLIMATE CHANGE 2023-2030

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The world is facing two major crises - climate change and environmental degradation - which generate devastating effects on people's lives and well-being. Therefore, systemic solutions and multi-level action are needed: international cooperation, the involvement of all state institutions, but also the private, academic environment, and citizens.

In this context, the education of young people plays a fundamental role in behavioral and mental adaptation, in the formation of transversal skills, necessary to cultivate sensitivity towards moral-civic values and respect for nature, its resources, and the natural, social and cultural environment.

The adoption at government level of the "National Strategy on Education for the Environment and Climate Change 2023-2030", a programmatic document that will include eco-social skills among the key skills starting from the 2023-2024 school year, represents a moment of utmost importance, being a first for Romania to adopt this national strategy.

The strategy is based on the Report of the Presidential Administration "Education on climate change and the environment in sustainable schools", a continuation of the "Educated Romania" Project, young people being both bearers of a message to their families and communities, as well as directly involved in actions to stop the degradation of the environment and to develop public policies for its protection.

Students will acquire competencies, skills and attitudes: to develop systems thinking and understand “green” energy, responsible exploitation of natural resources, pollution, extractive industry, energy industry, social justice, food waste, natural disasters, etc.; to relate to environmental factors and living environments; to make decisions and start relevant actions, through behavior to protect and improve the quality of the environment and reduce the impact of negative factors; to protect, restore and promote the sustainable use of terrestrial ecosystems, flowing waters, lakes, seas and marine resources and halt the loss of biodiversity; understand environmental legislation and the roles of relevant actors in the area of environmental protection; to participate, in the future, in the development of public environmental policies and of new technologies for combating environmental degradation.

The objectives assumed by our country until 2030 are: improving education, awareness and human and institutional capacity on adaptation, reducing the impact of factors affecting the environment; intensifying Romania's efforts to achieve the transition to a "green" economy, for the integration of measures to combat environmental degradation in vulnerable economic, social and environmental sectors, in accordance with EU policies.

The implementation of the strategy and the action plan assumes that the legal and the strategic framework will evolve in accordance with the proposed objectives, taking into account the European and national legislative context in the field of environmental protection.

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REMOVAL MIXTURE OF DRUGS IN AQUEOUS SOLUTION BY USING TITANIUM DIOXIDE PHOTOCATALYST

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Water is considered one of the most important components of life. In recent years, the problem of pollution of water sources by pharmaceutical compounds of various groups and their metabolites has become an urgent problem all over the world. They can have significant adverse effects on the aquatic environment. At present, to make efforts to remediate and minimize traditional pollutants in the environment, other compounds of “emerging” concern (CECs) are now warranting attention. These compounds, although there are not very persistent, their continuous influx in the environment renders them pseudo-persistent and their “emerging” environmental issue is that they have been proved to be more than sufficient in inducing antibiotic resistance. Thus, advanced oxidation processes (AOPs) are recommended for wastewater pre-treatment or tertiary treatment, when wastewater contaminants have high chemical stability and/or low biodegradability. Among different AOPs, heterogeneous photocatalysis employing nanosize TiO₂ has been an attractive research and development subject in water/wastewater treatment owing to its proven capability in the degradation of bio-recalcitrant organic contaminants.

The main goal of this work was to study the degradation/mineralization of a drugs mixture (amoxicillin, cephalexin and diclofenac) by applying heterogeneous oxidation with titanium dioxide. For each analysed systems, some physicochemical parameters have been optimized and the kinetic regularities of the transformation of pollutant oxidation processes have been studied.

Degradation of drugs mixture (30 mg/L) by photocatalytic oxidation in the TiO₂/H₂O₂/UV system with the aim of splitting benzene rings and turning substrates into simpler compounds depends on several parameters, such as: concentrations of oxidant (hydrogen peroxide) and catalyst dosage (titanium dioxide), temperature, reaction time, and pH value. As a result of laboratory studies, the oxidation conditions are optimized depending on the oxidant and catalyst concentration, wavelength irradiation for heterogeneous photocatalysis. It is presented that increasing the concentration of H₂O₂ to a certain level increases the concentration of OH radicals, which contribute to further degradation and increase efficiency. However, as the H₂O₂ concentration increases further, the oxidation efficiency begins to decrease as excess H₂O₂ can react with the OH radicals present to form water and oxygen. Based on the obtained results, it was found that the studied oxidation processes are very effective for treatment wastewater containing various pharmaceutical pollutants. The oxidation/mineralization in almost all cases reaches over 80% during first 10 min when substrate concentrations was 30 mg/L, H₂O₂ concentration - 1.5 mM/L, and catalyst dosage - 0.05 g/L for irradiation with UV-C rays.

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Scientific seminar

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CHEMICALS ON THE ENVIRONMENT AND HEALTH**

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