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ABSTRACTS

The 5th International Conference on Carpathian Euroregion

ECOLOGY

CERECO - 2014

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FOREWORD

The Carpathian Euroregion Organization was established in February 1993 by an agreement signed in Debrecen (Hungary) by regional government bodies of border regions of Poland, Hungary, Slovakia and Ukraine. In 1997 Romania joined the organization. It includes now 14 neighbouring provinces of these countries, with the territory of almost 150,000 sq.km and population of 15 million. The aim of the Organization is to facilitate cross-border cooperation among its members and to coordinate the activities in economics, sport, protection of environment, science, tourism and education. The aim of the CERECO conferences (the CERECO-94 was held in Uzhgorod, Ukraine, the CERECO-97, CERECO-2000 and CERECO-2003 conferences were held in Miskolc, Hungary) is to facilitate solving the environmental problems of the Carpathian Euroregion, to bring together scientists, professionals, law-makers and politicians from different countries, to establish transborder cooperation in the field of environmental monitoring and protection.

BIOSORPTION OF COPPER BY PEANUT SHELL FROM AQUEOUS SOLUTIONS

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Biosorption of Cu(II) ions from aqueous solutions has been studied and the adsorption capacity of peanut shell has been determined.

The experimental data obtained from batch equilibrium tests have been analysed by two- and three-parameter isotherm models (Freundlich, Langmuir, Redlich-Peterson) and the data obtained from kinetics experiments have been analysed by the model of Urano-Tachikawa.

The peanut shell was cleaned and dried at room temperature. The material was washed and oven dried at 50°C for 72 hours. The shell was ground and sieved under 71 μm of particle size.

The equilibrium experiments were carried out by varying concentrations of initial Cu(II) solution. In all experiments, the flasks were shaken on orbital shaker at 200 rpm and at 25˚C for 6 hours to ensure ion-exchange equilibrium. The suspensions were then filtered through a micro filter of pore size 0.8 μm and filtrates were analysed using flame AAS in order to determine the final Cu(II) concentration in solution.

The kinetics experiments were performed with initial metal concentrations 100 mg/L. The aqueous samples were taken at different time intervals (1-90 min) and then filtered through a micro filter. The concentration of biosorbent was 0.1 g/L.

According to the results of the experiments the adsorption equilibrium of Cu(II) on peanut shell was best described by Freundlich and Redlich-Peterson isotherms (almost identically). The maximum sorption capacity was 100 mg/g. The effective diffusion coefficient was in the order of magnitude 10^{-16} m^2/s estimated by the model of Urano-Tachikawa. The kinetics of adsorption is fast. The Cu(II) concentration decreased markedly during the first minute. The actual concentration decreased from 103 mg/L to 54, 51, and 66 mg/L at 150, 250, and 350 rpm, respectively, after the first minute. Further on the Cu (II) concentration did not change significantly with time.

The experimental results of this study demonstrate that peanut shell is suitable for adsorption of copper from aqueous solutions at low concentrations.

TOXIC ELEMENT CONTENTS IN SURFACE SEDIMENTS IN OXBOWS

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There are many oxbows in the Upper Tisza region. From conservation aspect the study and the assessment of the state of these oxbows is important conservation subject. Many organic and inorganic contaminants can accumulate in the sediment, so the sediment is good indicator to assess the contaminated state of oxbows. In our study the toxic element contents were studied in 8 oxbows. From these oxbows two are protected (Foltos-kerti-, Boroszló-kerti-Holt-Tisza) while the 6 other oxbows are characterized with markedly anthropogenic activites (Gyürei-, Vargaszegi-Holt-Tisza, Lónyai-morotva, Bodony-szögi-, Szabolcsi-Holt-Tisza, tímári Morotva-tó). The following toxic elements: Al, Cd, Cu, Fe, Mn, Pb and Zn were measured with MP-AES in surface sediment. The studied oxbows were separated totally from each other based on the toxic element contents of sediment using canonical discriminant analysis (CDA). The toxic element concentration was compared with the toxicity classes of EPA (Environmental Protection Agency). Based on the Cr concentration the tímári Morotva-tó, Bodony-szögi- and Szabolcsi-Holt-Tisza are moderately contaminated, while other oxbows are strongly contaminated.

The Gyürei-Holt-Tisza is moderately contaminated and others are strongly contaminated for Cu. The Boroszló-kerti-, Foltos-kerti-, Vargaszegi-, Szabolcsi-Holt-Tisza and the tímári Morotva-tó is uncontaminated for Pb, but the Lónyai-morotva, Bodony-szögi and Szabolcsi-Holt-Tisza is strongly contaminated. All oxbows are moderately contaminated for Zn, except the tímári Morotva-tó, Szabolcsi- and Bodony-szögi-Holt-Tisza, which are strongly contaminated. Based on the Mn and Fe concentration all oxbows are strongly contaminated which is caused by geochemical background of Upper Tisza region. Our results demonstrated that the effects of anthropogenic activities are markedly on the toxic elements of surface sediment in oxbows. However, the sediment is a useful indicator to assess the effects of anthropogenic activities on toxic element contents of oxbows.

Keywords: *Upper Tisza region, heavy metals, anthropogenic activities, MP-AES*

NANOPARTICLES OF ALUMINUM SALTS HYDROLYSIS PRODUCTS AND THEIR USE IN WATER TREATMENT

SÁNDOR BÁRÁNY

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Aggregation of dispersed particles plays a key role during phase separation processes in the course of water conditioning and treatment. This process can be initiated or enhanced by adding hydrolyzing salts. The mechanisms of water purification in the presence of aluminum salts are discussed.

We have investigated the effect of major variables (hydrolyzing salt concentration, its dosage, pH, alkalinity and ionic strength of the solution) on the size and surface area, electrokinetic potential, degree of hydration and aggregation of hydrolysis product particles (HPP) formed from aluminum sulfate, aluminum chloride and their basic salts. The kinetics of formation, destruction and re-growth as well as strength of aggregates of HPP formed from aluminum salts has been studied in a flow system in detail. It has been shown that HPP arising in water under conditions that favor formation of small particles with high surface charge density and low hydration (pH 7.5, alkalinity 1 mmol/l), are aggregating in a primary minimum, and under intensive shear (stirring the system at 500 rpm) they undergo weak destruction and are relatively easily reformed. In the case of bigger primary hydrolysis product particles having low surface charge density and higher hydration (pH 9.3, alkalinity 3 mmol/l) it is likely that the aggregation takes place in a secondary minimum, giving weak aggregates, which can be easily broken even at low stirring velocity (50 rpm). These aggregates show very little re-growth after intensive stirring of the system. The efficiency of aluminium salts HPP in removal of dispersed particles/bacterial cells from water is demonstrated. It is established that the degree of removal of mineral particles and E. coli bacteria cells from waters can be regulated by varying the OH/Al ratio in the aluminum salts molecule and the water parameters.

SURFACE AND ELECTROSURFACE CHARACTERIZATION OF MULTIWALL N-DOPED OXIDIZED CARBON NANOTUBES

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In recent years carbon nanotubes (CNTs) have attracted much interest due to their unique structural and transporting properties, such as high tensile strength, modulus, electrical and thermal conductivities alongside with low density. CNTs are also well suitable for preparation of carbon supported catalyst and adsorbents, of metal-carbon and polymer-carbon composites.

The potential of employing CNTs in most of cases is associated with surface/electrosurface properties of nanotubes, i.e. its chemical nature and number of surface functional groups that determine the wetting, surface charge density and electrokinetic potential as well as dispersion/aggregative stability of nanotubes. Despite the numerous papers, the electrosurface properties of multi-wall CNTs with well characterized surface groups are not properly studied with account of modern ideas on the electrical double layer (EDL) structure and electrophoresis. We have studied the relationship between electrokinetic behavior of multiwall N-doped carbon nanotubes and nature/density of functional groups resulted from surface oxidation.

Using Catalytic Vapor Deposition method, N-doped multiwall carbon nanotubes were produced, which was treated with oxidizing agents: H_2O_2, HNO_3, $HClO_4$ and HNO_3/H_2SO_4 mixture. By TEM and FTIR spectroscopy it has been shown that the oxidative treatment produces OH- groups on the CNT surface, the amount of which increases with the above given sequence of oxidizers. Also a small amount of COOH-groups on the surface of all CNT samples has been detected. In line with these results, the maximum value of the zeta-potential of carbon nanotubes (in alkali media, at pH>10) increases from –0.8 mV to –27.2 mV, -40.9 mV and –66.5 mV for the samples treated by H_2O_2, $HClO_4$, HNO_3 and HNO_3/H_2SO_4, correspondingly. Electrokinetic measurements show also that the surface of nanotubes treated with the first three oxidizers in acidic media (pH 2-6) has a positive charge due to the presence of imino-or amino-groups on the surface, and an increase in pH leads to charge reversal of the surface. In contrary to this, the surface of CNT oxidized by HNO_3/H_2SO_4 mixture has a negative charge in a wide range of pH values (2-12) due to appearance of a big number of weak OH- and probably some strong $–SO_3H$-groups. The electrokinetic behavior of CNTs resembles the behavior typical for lyophobic colloids: for negatively charged samples the ζ (C_{KCl}) curves reveal a maximum or plateau region; the addition of Ca^{2+} ions results in a sharp decrease of the zeta-potential of nanotubes, while increasing amount of trivalent Ce^{3+} counterions produces charge reversal of the surface. A good correlation between electrokinetic potential of nanotubes and sedimentation stability of their suspensions has been found.

Also, Using X-Ray Photoelectron Spectroscopy the nitrogen coordination in the graphitic structure of N- doped carbon nanotubes has been determined. The pyridine nitrogen and quaternary nitrogen binding energy in the carbon lattice turned out to be 498.3 -399.8 eV and 401-401.4 eV, respectively.

SOME ASPECTS OF ECOLOGICAL EDUCATION

ISTVÁN BUCZKÓ

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Wildlife from the very moment of appearing must fight for its surviving. Natural background where life itself has originated along with the favorable conditions, also includes antagonists to all alive-gaseous and solid emissions of active volcanoes, short-wave solar radiation, solutions of mineral acids, heavy metal ions etc. In spite of all this, nature has managed to establish some balance. Laws of thermodynamics have worked as well as the Le Chatelier's principle. System where rules self regulation of balance in atmosphere, has been created in the result. To all short - term local actions that are harmful for atmosphere, nature reacted with counteractions, restoring the balance. Over millennia human activity did not violate the balance substantially as far as sometimes results of human's negative activity did not move beyond tolerance of nature. Much to our regret, the intensification of human intervention into the nature processes, connected with increasing of population on Earth, moreover - with appearing of new human activities, led overtime to the system disharmony: surrounding environment - human being. Particularly sensitive strikes to nature from human side have been done over the last one hundred years. During this period of time such activities as extraction and combustion of different forms of fuel has increased in hundreds and thousands times. This respectively evoked incredible growth of harmful emissions into the atmosphere. Annually 1.5 billion tons of coal is burned in thermal power plants all over the world. As a result-emissions into atmosphere of about 5 billion tons of carbon dioxide, 100 million tons of sulfur dioxide, huge amount of solid materials and warm. The amount of emissions of the iron and steel industry annually could be measured in hundreds of millions of tons. Essential contribution into the environmental pollution makes chemical industry, ore mining. In case of ore mining - extraction of heavy metals and radioactive elements are especially harmful. We find it difficult to assess the ecological damage which is caused by the wrong transportation, storage and use of biologically active substances - mineral fertilizers, pesticides, insecticides, surfactants etc. Lack of reliably operating treatment facilities on sewer facilities, wrong storage of household waste create in many cases catastrophic situations. Never before a human being took from nature so much as it is being done nowadays, never before our common home endured such attacks on it as it is being done nowadays. The situation when we have to talk not of comfort but of mankind's surviving has been created in the result. Obviously, the efforts of all countries all over the world should be combined in looking for the way out from this complicated situation. Tasks that mankind faces now are very difficult and they could be solved only by the joint collective efforts of specialists of different professions: biologists and chemists, power engineers and metallurgists, physicists and economists and many others. Educators occupy a special place in this wide palette. They bear extremely responsible task - alteration of human psychology. By the proper organization and implementation of the ecological education they have to form a healthy outlook of people, cultivate love for nature, understanding of human duties towards nature. In our opinion, the ecologization of education appears to be effective in case it touches all disciplines lectured at schools and high schools. The inter discipline connections thus become very important from this point of view. The competent ecological education enriches people with the knowledge of nature, changes their passive attitude to the numerous ecological violations, numerous bans of ministries. One of the most significant consequences of ecologization of education will become the fact that people who occupy leadership positions will not act against nature, contrary to environment, not because of the pain of fines, but following their own conviction and conscience. In case we do not over persuade Ivanko, Olechka or Vasyl'ko, pupils of the secondary schools they have to stand in the ranks of nature conservationists, we could not expect the future leaders of enterprises and companies Ivan Ivanovych, Ol'ha Petrivna or Vasyl Mykhailovych will fight for the clean air, clean water and wonderful woods.

AZ IVÓVIZEK NITRÁT SZENNYEZETTSÉGE A KÁRPÁTALJAI-ALFÖLD TELEPÜLÉSEIN

ZOLTÁN CSOMA

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A felszín alatti vizek nitrát szennyezettségét számos országban kimutatták. Vizsgálatok igazolják a vizek magas nitrát koncentrációját Ukrajna több megyéjében is. A problémának sokkal súlyosabb következményei lehetnek ott, ahol a felszínhez közel található, így viszonylag egyszerűen és alacsony üzemeltetési költségen hozzáférhető készleteket ivóvízként fogyasztják. Kárpátalja falvaiban, de részben városaiban is, a lakosság a felszín közeli vízkészletet termeli ki és rendszerint bármiféle tisztítás, előkészítés nélkül azt ivóvízként (is) használja. Kialakításukat tekintve az ásott vagy fúrt kutak mélysége többnyire 8–12 m között változik, egyes településeken eléri a 18–22 métert. A mélyebben (40–60 m) található készletekből történő víznyerés, valamint az erre kiépített vízellátás ez idáig kevés településen valósult meg és a működőek is csak a lakosság egy részét képesek ellátni a talajvizeknél lényegesen jobb minőségű ivóvízzel.

Munkánkban a nitrát terheltség mértékének feltárását tűztűk ki célul a Kárpátaljai-alföld több településének ivóvizeiben. A méréshez nitrát-ion szelektív elektródát és pX-150.1 típusú mérőkészüléket használtunk. Az ivóvizek maximálisan megengedhető nitrát koncentrációját Ukrajnában egy 2010-ben bevezetett törvényerejű rendelet (ДСанПіН 2.2.4-171-10) 50 $mg{\cdot}l^{-1}$ állapítja meg.

A kutatómunka során 18 településen végeztünk vizsgálatokat, ahol több mint 350 ásott, vert és mélységi kút, továbbá forrás vizeinek nitrát koncentrációját mértük meg. Az összes bevizsgált vízminta nitrát tartalmának átlag értéke 75 $mg{\cdot}l^{-1}$ volt, amely másfélszer haladja meg az elfogadott határértéket. A vízminták 54%-nak minősége a nitrát koncentráció szempontjából elfogadható, 46%-ban a vizek az egészségre káros mennyiségű nitrát-iont tartalmaztak. A vizsgálatba bevont települések mintegy felében az ivóvizek több mint 50%-ában, ezen belül pedig négy településen a vizek 80%-ában haladta meg a nitrát tartalom a határértéket. A nitrát-ion településenkénti maximális koncentrációinak átlag értéke 176 mg·l^{-1}, ami 3,5-szer nagyobb a rendeletig meghatározott megengedhető értéktől. A legnagyobb mért nitrát tartalom 294 mg·l^{-1} volt, ami közel hatszorosa a határértéknek. A minimális értékek átlagát magasnak találtuk, ez számszerűleg az összes vizsgált településre vetítve 24 mg·l^{-1}, tehát közel a megengedett érték fele.

A kutak vizének nitrát koncentrációja több esetben is jelentős évszakos ingadozásokat mutatott. Az egyazon kutakban, különböző időszakokban elvégzett mérések alapján a nitrát tartalom változásának az évszakoktól függő iránya és mértéke között nem sikerült egyértelmű összefüggéseket megállapitani. A jelentősebb mennyiségű felszínre jutó és részben a kutakba beszivárgó csapadék értelemszerűen a vizekben fennálló nitrát-ion koncentráció hígulását eredményezi. Megfigyeléseink szerint a nitrát tartalom csökkenése vagy növekedése viszont már annak a függvénye, hogy a kutakba beszivárgó csapadék a felszínen vagy a talajban milyen mértékben szennyeződik el.

Vizsgáltuk a vizek nitrát koncentrációját a kutak kialakításának és azok mélységének függvényében. A mérések azt mutatták, hogy a vert kutak nitrát tartalma minden esetben lényegesen alacsonyabb volt, mint az ugyanazon földtani és hidrológiai viszonyok között lévő ásott kutaké. A vert kutak vizében a nitrát koncentráció csak kevés esetben haladta meg a rendeletileg előirt határértéket. Az ásott kutak vizében ugyanakkor a nitrát tartalom többnyire 50 mg·l^{-1} felett volt, 10÷100-szorosan meghaladva a közelben található vert kutakban mért értékeket. A mélységi kutak vizeiben számottevő nitrát-ion mennyiséget nem mértünk.

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SYNTHESIS OF INEXPENSIVE MESOPOROUS SILICEOUS SORBENTS FOR REMOVAL OF URANYL IONS FROM AQUEOUS ENVIRONMENT

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Mesoporous silicas with phosphonic acid groups [$\equiv Si(CH_2)_2P(O)(OH)_2$], obtained by block copolymer templating (Pluronic P123), were shown to be effective sorbents for the extraction of uranyl, Th(IV) and Pu(IV) ions from acidic solutions [1]. Uranium sorption capacities (SC)of these sorbents were reported to be 125-132mg/g in the case of sulfuric acid solutions and 276-299 mg/g in the case of nitric acid media (0.5-3.0 mol/L HNO_3). The SC value for sorption of Th(IV) ions from nitric acid solutions was 60-66 mg/g. The reported distribution coefficient for ^{239}Pu(IV) ion sorption is 4500 cm^3/g. However, the phosphorus-containing silica hardly adsorbs ^{241}Am ions from acid solutions, allowing effective separation of a pair of Pu/Am ions with a separation factor of at least 2×10^3. Tetraethoxysilane as a framework-forming agent was used in the synthesis of the aforementioned sorbents. In this report an attempt was made to obtain phosphorus-containing mesoporous silicas by using sodium silicate (NaSil) in order to significantly reduce the cost of the final product.

The aforementioned sorbents were synthesized in the presence of concentrated acetic acid and $(C_2H_5O)_3Si(CH_2)_2P(O)(OC_2H_5)_2$ (DFTS) as a functionalized agent. The surfactant was removed from the resulting mesophase by extraction with acidified ethanol at temperatures close to boiling temperature. The obtained samples contained $\equiv Si(CH_2)_2P(O)(OH)_2$ groups in the surface layer. Their presence was confirmed by IR spectroscopy. It was established by means of XRD and TEM that all the materials showed hexagonal structure like SBA-15 silica. Nitrogen adsorption isotherms recorded for these materials are type IV according to the classification of IUPAC with a distinct hysteresis loop in the 0.45-0.85 range of relative pressures, indicating the presence of a well-developed mesoporous structure that depends on the ratio of NaSil/DPTS (see Table 1). The influence of the parameters of the mesoporous structure of the samples on their sorption properties in relation to uranyl ions was studied.

Table 1. **Parameters of the porous structure for the synthesized sorbents**

Sample	**NaSil/DPTS**	S_{BET}, m^2/g	V_{sp}, cm^3/g	^1d_m, nm
1	10:1	417	0.66	8.9
2	10:2	533	0.55	6.9
3	10:3	515	0.56	6.9
4	10:4	362	0.40	6.4

Note: 1 - pore diameter calculated from adsorption branch of the isotherms by KJS method [2]

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BACTERICIDE ACTIVITY OF STABILIZED SILVER AND COPPER NANOPARTICLES IN COLLOIDS AND ON THE DISPERSED SILICA SURFACES

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Due to the significant increase of resistance of microorganisms to the action of drugs, especially antibiotics, it is extremely important in a medical practice to search for other antibacterial agents, including drugs based primarily on silver. At low concentrations (at the MPC 0.5 mg/l) silver is safe for the human organism, but it shows a destructive action against the most of bacteria and viruses, so for years it has been actively used for disinfecting water and infection control. High catalytic and bactericidal activity have also nanosized copper particles, which play a key role in the metabolism of all living organisms, from simple cells. The use of silver and copper in the form of nanoparticles (NPs) can reduce its concentration in hundreds of times compared to ionic form while retaining all antimicrobial properties. One of the main problems in obtaining of Ag and Cu NPs is their instability due to easy oxidation. The purpose of this work is to obtain stable Ag and Cu NPs and characterize their antimicrobial action with prolonged persistence of bactericidal activity.

Conditions for obtaining stable silver nanoparticles smaller than 10 nm were developed using a binary stabilizerbased on surfactant/polymer in optimal ratio. Optical spectra, morphology and size of the nanoparticles were studied. Solutions and suspensions of nanosilver showed a high bactericidal activity against strains of *Staphylococcus aureus, Escherichia coli* and *Pseudomonas aeruginosa,* and fungicidal activity against *Candida albicans.* CuNPs demonstrate high bactericide effect against *Escherichia coli.* The use of the terms Cu NPs in this case is quite conditional and relative, because Cu NPs, copper oxides and copper ions coexist both in solution and on the surface of $SiO_{2.}$ We use the sign Cu NPs for convenience in discussing, referring to the co-existence of all of the states of copper in this system. High antimicrobial activity of the synthesized NPs is provided by two main parameters: the size and well-defined ratio of components in binary stabilizers that prevent aggregation of particles and thus maintains their stability during two years of observation. It is shown that the first step of destroying of microorganisms is destruction of cell membranes and penetration of NPs into the microbial cell. Data on the antimicrobial activity of colloidal solution of Ag NPs and Cu NPs indicate the possibility of its use as effective antimicrobial agent.

FLOOD EFFECTS OF RIVER TISZA ON THE CLADOCERA TAXONS OF A SMALL LAKE IN SPRING 2013

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In the shallow waters of Hungary Cladoceras form a significant group regarding their high number of species and individuals. Cladocera species have clear preferences towards specific lake habitats. The absence/presence and relative abudance features of key species provide information about the intensity of changes in a habitat. In 2013 a flood from Tisza had obvious impacts on the habitats and organisms of the floodplain. During our research we investigated if the flood had an impact on the occurrence of Cladocera species, and if so, to what extent. In our work we defined Cladocera species from filtered samples collected in the Lake Kis- Zátony in Rakamaz, and compared the results from the years of 2012 and 2013. The evaluation revealed that there were clear differences between the samples of the two years. In the water samples taken after the flood there were gradually more individuals comparing to the samples from 2012. In addition there were differences also in species composition, which is probably resulted by the change in macrovegetation and the increase in accessable habitat.

Key words: *Cladocera, filtered water sample, flood, shallow waters*

AGGREGATION OF PARTICLES IN WATER

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Natural waters contain a wide range of impurities, some of which are insoluble in water and exist as suspended particles of various shapes and sizes. Aquatic particles may be inorganic, such as clays, organic, including macromolecular substances, and living and dead micro-organisms. These can have sizes ranging from macromolecular dimensions (nm) up to several hundred μm. The distribution of particle sizes in natural waters often follows a simple mathematical form, which makes modelling much easier. Larger particles are removed quite rapidly from water by sedimentation, but smaller ones may remain suspended in water for long periods.

Aquatic particles may aggregate, giving clusters (flocs) of larger size, and this has very important consequences. Aggregation is brought about by collisions of particles and the rate of aggregation depends directly on the collision frequency, which, in turn, depends on the particle concentration and on the mode of particle transport. However, it is usually found that only a fraction of collisions lead to aggregation. This *collision efficiency* depends on inter-particle forces, which can vary greatly, depending on the nature and type of dissolved salts and the presence of soluble organic materials in the water.

Fundamental aspects of particle aggregation in natural waters will be briefly discussed, along with some important practical consequences for the transport and ultimate fate of pollutants in the aquatic environment.

TOWARDS THE EUTROPHY, THE ALGOLOGICAL, PHYSICAL AND CHEMICAL CHANGES IN A DRINKING WATER RESERVOIR

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Reservoirs in agricultural dominated watersheds are particularly vulnerable to algal blooms, but few results detail those drinking water reservoirs, which has no agricultural impact however algal blooms often or regularly occur. During May 2007 to September 2008, we studied spatial and temporal patterns of algal abundance and composition with respect to a series of physical and chemical properties in Lázbérci-tározó, located in north-east Hungary. Our results suggest that nutrients (in particular TN, NO3–N concentrations), turbidity, and hydrologic regime all played potentially important roles in regulating algal biomass. The low level of nitrogen coupled with the internal release of phosphorus from the lake sediment under brief periods of anoxia may have helped promote cyanobacterial algal bloom. There was also a strong association between algal biomass increase.

RECOLONIZATION RESEARCH IN OXBOW LAKES OF RIVER TISZA BASED ON CLADOCERA TAXA

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In the shallow waters of Hungary Cladoceras form a major group regarding their number of species and individuals. The microhabitat bondig of Cladocera species in shallow lakes is well-known. This research was born to reveal if the microhabitat bonds are preserved or they form a completely different type of habitat structure after water returns to the parched habitats. The absence/presence and relative abudance of key species provide information about the changes of habitats, the occuring reeding process in the oxbow and the changes in water level. The research was based on five oxbow lakes (Lake Nagy-Mester, Lake Sulymos, Lake Kis-Morotva, Lake Nagy-Nádas and Lake Papp) and a total of 23 sampling sites were investigated. Our aim was to reveal how the Cladocera communities bond to the different habitats, and if the certain macrovegetation types are distinguishable based on Cladocera taxa. Based on the remains the pelagic and benthic habitats are well separated from each other. Our results show that the vegetation coverage is completely different considering the sampling sites.

Key words: *Cladocera, oxbow, open water, habitat, macrovegetation, sediment.*

FUSION OF DIVERSE ELEMENTS: AN ENABLING STRATEGY

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The Carpathian Euro Region is the new name for a cross-border region that has for centuries been a collection of wild remote lands, of diverse peoples, cultures, languages and ancient ways. It is a confluence of mountains, lakes, river-lands, of rich black earth next to unyielding soils, along with deep subterranean water sources and latent energy potentials. It has also been the fulcrum of geo-political power plays and failed attempts to extract its wealth without any sense of maintaining a natural balance.

The aim of CERECO over the past twenty years has been to facilitate cross-border cooperation and to coordinate the undertakings of tourism, sport, science, the protection of environment in harmony with education, economic achievement. In addition, interaction between scientists, professional's, law-makers and politicians from the current five regional nations to establish cross-border agreements in the field of environmental monitoring and protection. To succeed will be to achieve Gold Medals of Olympian proportions. But failure can result if these prime movers forget to bring the people of the region into these game plans. For any enabling strategy to be successful then bottom up thinking is critical with a joint educational programme of a new dimension. For 60 years the author has developed and undertaken specialised enabling strategy audits to achieve these aims.

Our slogan should be: EXPERTS SHOULD BE PUT ON TAP & NOT ON TOP

The creation of the Eastern Carpathian Bio-sphere Reserve should become an important centre-point or 'Fountainhead' with its crux of transportation links. In addition there is the need for the land-locked country of Moldavia between the frontier river's Prut and Dniester to also be a Fountainhead. This land should have a sea link to the Black Sea. In a Club of Six the whole region would then have a cross-

European river-way link between the Black Sea and the North Sea. Natural bio-spheres have no frontiers. The inclusion of Moldavia is critical to ensure that all the peoples of the region can benefit from selective and commonsense development of the geothermal energy resources of this Carpathian region. Of introducing the new and radical concept of a Bio-based agricultural economy where crops are grown for sustainable and low-carbon products such as aviation fuel and materials for new manufacturing products as being developed in the Netherlands. Prof. Suli-Zakar, István, Lajos Kossuth University of Debrecen, has written, *'"....the inevitability of a radical consolidation in a future European context could be politically destabilising if more jobs are not generated in manufacturing in an expanded tertiary sector."* Apart from manufacturing there is also potential in other associated industries and tourism. All must be carefully and sensitively designed and developed.

The subject matter of this conference deals with ecological and I would suggest all the climatic factors of influence that deal with waste, water and soil treatment and other relevant factors, must also address the rush by powerful global forces to extract fossil fuel energy that also destroys our whole environment and ways of living. The critical ingredient to ensure counter these malign forces is to undertake a series of in-depth Green Strategy Audits in the fields of energy (solar, wind, ground source, bio-mass), agriculture, bio-diversity, transportation, urban building and infrastructures. In addition there must be a co-active educational programme with the support of regional centres of excellence.

THE ESSENCE OF NANOSCIENCE AND NANOTECHNOLOGY

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As any subject connected with natural sciences and engineering, CERECO is also partly connected with nanoscience and nanotechnology. This talk will shortly describe the major differences between science vs nanoscience and between technology vs nanotechnology. The emphasis will be on surface related phenomena, such as size dependence of different thermodynamic properties of phases and systems: equilibrium melting point, equilibrium vapour pressure, equilibrium solubility, etc.

Related recent paper of the author

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DEVELOPMENT OF GREEN TECHNOLOGY FOR REMEDIATION OF MUNICIPAL SLUDGE SOLIDS CONTAMINATED BY HEAVY METALS

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Widespread biological municipal wastewater treatment leads to the formation and storage of huge amounts of biosolids – stabilized sewage sludge exposed at sludge fields for a long time. These are significant environmental hazard. There are over 7 million dry tons of biosolids produced per year in the USA, 80 million tons in Russia, 1.8 million tons in Ukraine. The biosolids occupy vast suburban fields. In particular, the need in sludge fields for Ukraine is 120 ha and for Kyiv is 14 ha annually. Therefore, the reducing sewage sludge volume and its utilization is the problem facing many communities. Sewage sludge contents plant-essential nutrients, including nitrogen, phosphorus, potassium, microelements (heavy metals), vitamins, aminoacids and organic matter. All that causes the value of biosolids for soil quality enhancement. Depending on the density of population and industrial activity of regions, the amounts of heavy metals (microelements) in sewage sludge can vary quite considerably and substantially exceeding the maximum permissible concentrations. Thus, the purpose of our study is to explore the possibility of partial heavy metals removal from biosolids for land application.

A green technology for reducing the heavy metals concentrations from sewage sludge to values satisfying EU limits is proposed. It includes the enhancing of the vital ability of heterotrophic sludge biota by adding easily metabolized nutrients and synthesis of metabolites by growing sludge cenoses. As an alternative carbon sources it can be also used easily metabolized carbon sources (sodium acetate, glucose, herbs, food wastes, etc.), namely, protein or carbohydrate containing substrates for providing alkaligenous or acidogenous vector of sludge metabolism, respectively. The metabolites with the properties of heavy metals extractants and sludge flocks flocculants provide sludge suspension sedimentation and flocks concentration. The sludge concentrate is a biomineral fertilizer of prolonged action with immobilized bioelements. It is established that organic matter content increases up to 60 %. heavy metals solubilization activity varies from 83 % (Zn) up to 14 % (Cr) and corresponds to the following series: Zn (83-78%) > Mn (72-50%) > Cu (70-48%) > Ni (55-39%) > Co (52-32%) > Pb (27-19%) > Cr (18-14%). Depending on nutrient substrate, heavy metals are extracted from sludge solid as stable oxycarbonic complexes or slightly soluble hydroxycarbonate nanoparticles. These substances are ecologically friendly. At similar efficiency, the processes of HMs removal with heterotrophic biota have considerable advantages versus the processes with chemoautotrophic biota due to their high speed and exclusion of secondary chemical pollution.

The obtained sludge sediments with 99% humidity were additionally stabilized (secured from pathogens) in such a way: pH adjustment to 10.0 – 11.0 by dry K_2O, exposure during 4 hours, neutralization to pH = 8.0 by phosphoric acid and drying up to humidity value 40 – 60 %. As it is known, fertilizers with alkaline pH are favorable to the formation of waterstable aggregates which are soil fertility indicator. The fertilizer obtained meets heavy metals and pathogens requirements.

There are heavy metals which can occur in slightly soluble or unsoluble forms as phosphates, sulphates, carbonates, hydroxides and so on in sludge solids. Under the influence of organic acids excreted by growing plants, the sludge bioelements can be gradually released from immobilized state into environment and can be absorbed by plants.

The fertilizer efficiency was proved in vegetation experiments. Its application to the soil resulted in faster growth of agricultural plants and harvest increase of 5 – 10 times as compared with control (unfertilized) soil.

SILICATE MINERALS IN ENVIRONMENTAL PROTECTION TECHNOLOGIES

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The report represents data on ecologic situation in Dnipropetrovsk region which has a major importance for national economy as the largest Ukrainian industrial centre where metallic ore mining and enriching are made. The main mechanism of uranium and other heavy metals migration in soils was analysed and the effectiveness of such cleanup techniques as chemical treatment of soils with the use of complexing reagents and electrokinetic soil processing for metal contaminated soils were established. Results for heavy metal and uranium removal from surface, mine and groundwater by coagulation, precipitation, sorption, membrane separation and biological methods were presented. Special attention is devoted to the use of the clay minerals as precursors in synthesis of sorbents and catalysts for water basin protection.

Recent results on modified iron nanoparticles which are widely used in environmental practice are presented. Such modified materials have been synthesized to further enhance the speed and efficiency of remediation of soil and ground water. Matrix-supported iron materials demonstrated good transport properties in water-saturated porous media and at low cost. Clay minerals, which are abundant, environmental-friendly, and much cheaper than others matrixes, are applied as the supporting materials of iron nanoparticles. It is shown that the use of surfactants for mineral surface modification during nanoparticle synthesis greatly increases the reactivity of iron-clay mineral composites and enhances the transport of iron nanoparticles through the contamination plume in the subsurface environment for effective remediation of contaminants.

THE USE OF PERMEABLE REACTIVE BARRIERS FOR GROUNDWATER PROTECTION IN UKRAINE

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There is significant pollution and degradation of the environment, particularly contamination of water resources, soil, and air near towns associated with past and present mining practices. Ukraine has a diverse mining industry that produces a wide variety of metallic and nonmetallic minerals that accounts for a significant part of the county's economic output. The major mining products include iron, manganese, uranium ores, coal, titanium, zirconium, beryllium, sulfur, mercury, non-metallic raw material for metallurgy and potash salt.

The main mining region in Ukraine - the Kryvyi Rig basin in the east central part of Ukraine - is one of the largest uranium mining districts in Europe. Uranium mining has a long history in Ukraine and occurred throughout the Soviet period. Zhovty Vody is one of the largest cities within the uranium mining district and is a center of uranium and iron ore milling and processing.

One of the key objectives of this work was to pilot the use of an innovative remediation technology for groundwater impacted by mining activities – permeable reactive barrier (PRB) technology. In the summer of 2011 the PRB was installed at a hydrogeologically suitable location to treat groundwater contaminated by leachate from a large tailings facility near Zhoty Vody A new design of PRB was constructed – cylinders with reactive materials installed in rows - instead of a conventional continuous barrier or a funnel-and gate setup. The PRB contains three different treatment media, and 8 monitoring wells. The three different treatment media include: inorganic reactive material (zero-valent-iron) and two biologically active materials based on zero-valent iron, calcium phosphate, sawdust and sewage sludge. Water level and water chemistry data are currently being collected under an approved long term monitoring program. These data are being analyzed to evaluate the effectiveness of the PRB over time.

Obtained results indicate that during the last six month period, the concentration of uranium in the groundwater being treated by the biologically active materials was practically unchanged – perhaps due to the low content of microorganisms in clayey and sandy soil near uranium tailings storage facility. At the same time, the uranium concentration in groundwater treated by zero-valent iron decreased to 0.1mg/liter which may demonstrate the effectiveness of zero-valent-iron as active material for use at contaminated sites in Zhovty Vody region.

THE STUDY OF THE SELECTED PHYSICO-CHEMICAL PROPERTIES OF THE ENVIRONMENTAL LOAD SLOVINKY MATERIAL

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Mining and mineral processing of raw materials has a long tradition in Slovakia. Consequences in the form of old environmental loads were remained after these activities. The issue of such loads is currently in the spotlight of public authorities, institutions and the media and is focused on regular monitoring. Sludge bed Slovinky (Eastern Slovakia) is one of these loads and contains flotation waste from mineral processing of sulphide ores and industrial slag from metallurgical processing in fine-grained form.

Our research was focused on the study of the selected physico-chemical properties of Slovinky material. Particle size was determined by sieve analysis, XRF method was used to obtain chemical composition of sludge bed material. Electrical conductivity, pH, total dissolved solids and concentration of heavy metals were determined in an aqueous extract. Assessment of neutralization potential was performed as a static extraction test using US EPA method. Concentrations of heavy metals in an aqueous extracts were measured by AAS.

It was found that the grain class 0.080 to 0.180mm has the largest percentage of a particle size. Chemical composition of the sludge bed material indicated high concentration of potentially toxic elements. The concentrations of Cu (8 803 mg.kg^{-1}), Zn (33 200 mg.kg^{-1}), As (488.8 mg.kg^{-1}), Pb (4 535 mg.kg^{-1}), Cd (98. 9 mg.kg^{-1}), Cr (4 748 mg.kg^{-1}), Ni (439.7 mg.kg^{-1}) and Hg (16.7 mg.kg^{-1}) far exceed limit values in comparison with the law of National Council of Slovak Republic No. 203/2009.

The sludge bed has alkaline character, the pH range from 8.57 to 8.9. Specific electrical conductivity and total dissolved solids could not be measured due to the detection limits of the used apparature. Values of neutralization potential demonstrate impossibility of active acidity production.

Results of AAS showed overload of limits Ni, Cu and Zn (law of National Council of Slovak Republic No. 263/2010).

MERCURY SORPTION BY COAL

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The improving demand of the protection of the environment urge the scientists to find efficient and environmentally friendly methods for both stop the dispersion of contaminates and for remediation of the contaminated areas. To solve the problems, the research activity covers many fields: besides the application of newly fabricated artificial substances it has focused on the use of natural materials and the biological systems.

The phenomenon of sorption one of the applicable principles for retarding the contaminants in soils and underground aquatic environments. In the soil the clay minerals and humic materials are those components which able to bound the toxic metal ions. Well compatible to these are the coals and biomass which also exhibit quite high ion sorption ability. Further, an advantage particularly with these materials is that, after loading with the toxic metals, their energy value can be recovered and the metals to be rendered in a safe form for disposal or recovery. The removal of ions by coals and biomass can be the result of different types of interactions. Depending upon the type of ion and the surface functionalities, the uptake can involve ion sorption, ion exchange, chelation and redox mechanisms with the surface functionalities being considered as partners in a simple ion-ion, ion- dipole interaction or electron transfer processes. This wide variety of loading provides an advantageous application for coals for different ion removal from contaminated water streams. It is promising to use coals and biomass as natural, soil compatible material as active component in permeable reactive barrier (PRB) constructions.

The low rank coals and oxidised bituminous coals provide a high sorption capacity for mercury. This capacity approaches the sorption capacity of resins, Fig. 1.

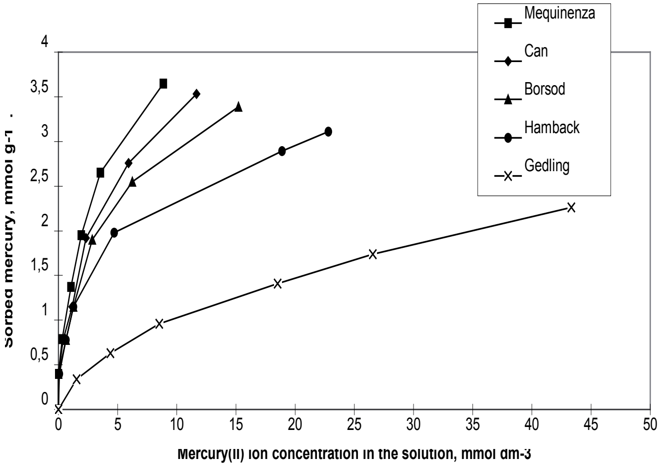

Fig. 1. **Mercury sorption isotherms of lignites come from different origins and Gedling bituminous coal.**

The study covers the effect of coal rank, the coal pre-treatment in mercury removal. The effect of pH and the composition of the aquatic media are demonstrated in dynamic mercury removal tests using model barrier set up.

THE CATALYTIC ACTIVITY OF SUPPORTED PALLADIUM NANOPARTICLES IN PROCESS OF CO-OXIDATION

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The supported on active carbons catalysts on base of noble metals (Pt, Pd, Ru, Rh) are widely used in various processes of environmental catalysis [1]. The reaction of catalytic CO-oxidation is one of these processes. It serves as testing reaction for quality of preparation catalytic materials also. The forming of nanodispersion phases of catalytic active metals on carbon supports is an important method of raising activity and selectivity of catalysts.

We developed the method of synthesis Pd-nanoparticles on active carbons supported by modification of their surface. It consist of oxidation carbons surface with forming of oxygen-containing functional groups and modification of their by covalent bonding chlorine atoms also. The forming of palladium-nanoparticles was realized by sorption of metal ions from its hydroxocomplexes solutions when pH 4,0 – 4,2 with following reduction by reductive reagents.

The oxygen-containing surface groups of active carbons and chlorine atoms also create spatial hindrances to extension of palladium particles in the process of ions reduction. It was established by method of scanning electron microscopy (SEM), that in this process polydispersion system of palladium particles in formed and nanoparticles with sizes of 20 – 30 nm are predominant.

It was studied the temperature dependence of degree conversion of CO to CO_2 for investigation of catalytic activity obtained materials in reaction to CO-oxidation. The catalytic process of CO-oxidation on palladium-nanoparticles passes with less energetic expenditures (with low temperature) than on large-dispersion phase of Pd on active carbons surface. Thus, degree of conversion CO to CO_2 with using of nanodispersion catalyst constitutes 22 % already when room temperature, it increases and with raise of temperature when 60 ^{0}C it reaches 80 %. Degree of conversion CO to CO_2 reduces with further raise of temperature and after that increases when temperature 180 – 200 ^{o}C only and reaches 100 %.

Evidently, it is caused by extension (by sintering) of palladium-nanoparticles and transition of them to large-dispersion phase of metal with increasing of temperature. It is known, that large-dispersion metal carry out catalysis of this reaction when temperature reaches 180 – 200 ^{0}C only [2].

Thus, the optimum condition of using synthesized catalytic material in process of CO-oxidation is temperature interval 50 – 60 ^{o}C.

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КАТАЛИТИЧЕСКАЯ АКТИВНОСТЬ НАНЕСЕННЫХ НАНОЧАСТИЦ ПАЛЛАДИЯ В РЕАКЦИИ ОКИСЛЕНИЯ CO

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Нанесенные на активные угли катализаторы на основе благородных металлов (Pt, Pd, Ru, Rh) широко применяются в различных процессах экологического катализа [1]. Одним из таких процессов является реакция каталитического окисления CO. Она служит также тестовой для испытания качества приготовления каталитических материалов. Важным способом повышения активности и селективности катализаторов является формирование нанодисперсных фаз каталитически-активных металлов на углеродных носителях.

Нами разработан метод синтеза наночастиц Pd на активных углях модифицированием их поверхности. Он заключается в окислении поверхности углей с формированием кислородсодержащих функциональных групп, а также ее модифицировании ковалентно связанными атомами хлора. Формирование наночастиц Pd осуществляли сорбцией ионов металла из растворов его гидроксокомплексов при pH 4,0 – 4,2 с последующим восстановлением реагентами-восстановителями. Поверхностные кислородсодержащие группы активных углей, а также атомы хлора создают пространственные препятствия укрупнению частиц палладия при восстановлении его ионов. Методом сканирующей электронной микроскопии (СЭМ) установлено, что при этом формируется полидисперсная система частиц палладия, где преобладающими являются наночастицы с размерами 20 – 30 нм.

Для исследования каталитической активности полученных материалов в реакции окисления CO изучена зависимость степени конверсии CO в CO_2 от температуры. Каталитический процесс окисления CO на наночастицах палладия протекает с меньшими энергетическими затратами (при более низкой температуре) чем на крупнодисперсной фазе Pd на поверхности активных углей. Так, уже при комнатной температуре с использованием нанодисперсного катализатора степень превращения CO в CO_2 составляет 22 %, с повышением температуры она растет и при 60^0C достигает 80 %. При дальнейшем повышении температуры степень конверсии CO в CO_2 снижается и затем возрастает только при температурах 180 – 200 ^{0}C. Это обусловлено, очевидно, укрупнением (спеканием) наночастиц палладия и переходом их в крупнодисперсную фазу металла при повышении температуры. Известно, что крупнодисперсный металл катализирует указанную реакцию лишь при температурах 180 – 200 ^{0}C [2].

Таким образом, оптимальным условием эксплуатации синтезированного нами каталитического материала в процессе окисления CO является температурный интервал 50 – 60 ^{0}C.

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PHOTOCATALYTIC PURIFICATION OF WASTEWATERS FROM ANTIBIOTIC TETRACYCLINE HYDROCHLORIDE (TC)

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Antibiotics are now recognized as a new class of pollutants and their purification is the subject of growing concern and scientific interest. Urban wastewaters and effluents from sewage treatment plants are continuously contaminated by inappropriate disposal of the drugs, which results in their introduction to a wide range of environmental matrixes, including surface, ground, and drinking water, as well as soils. The use of antibiotics in food animals selects for bacteria resistant to antibiotics used in humans, and these might spread via the food to humans and cause human infection, hence the banning of growth-promoters.

The application of efficient water and wastewater treatments, especially photocatalysis, has attracted the foremost attention. It is known that tetracycline is a class of the compound that is sensitive to light and classified as a phototoxic drug. TC residues in wastewaters, culture pond and on the surface of soil follow through the formation of the TC derivatives that could be even more dangerous for public health. Therefore, the way of TC and its derivated removal have to be followed through the degradation rather than oxidation.

The photocatalytic degradation of TC in the presence of mesoporous nitrogen-doped TiO_2 and nitrogen-metal ions-doped TiO_2 films was performed under UV and visible light irradiation. The films were synthesized by sol-gel method using urea as a nitrogen source and corresponding metal organic species (zinc acetate and zirconoum propoxide). Mesoporous structure of the coating was created by association of partially hydrolyzed polar titanium oxopolymeric fragments with hydrophilic polyethylene oxide (the organic template P123) in acidic medium. The films obtained by dip-coating technique were treated at 300 and 450 °C. The enhanced absorption in the visible region is observed for the nitrogen-metal ions-doped titania comparing to the metal free films. The formation of crystalline structure of TiO_2 confirmed by Raman investigation is started for the nitrogen-metal ions-doped titania at 300 °C while the metal free films were completely amorphous at this temperature. Raman spectra and XRD analysis confirmed the titania crystallization to anatase after thermal treatment at 450 °C.

The influence of nitrogen and metal ions doping as well as the treatment temperatures on the efficiency of tetracycline photodegradation is shown. The significant increase of photocatalytic activity in the process of tetracycline photodegradation under both UV and visible light was fixed for nitrogen-doped titania film in comparison with bare titania. The enhanced activity is explained by an interstitial nitrogen bond formation in titania matrix. The presence of the metal ions resulted in activity decrease under visible light while the high percentage of degradated TC was obtained under UV light as a result of the formation of new acidic centers on the surface. It must be noted that the photocatalyst contained the zirconium ions treated at 300 °C is able to degradate the TC molecule in greater extent.

MODIFICATION OF SYNTHETIC LAYERED MAGNESIUM SILICATE BY ALKIL AMMONIUM SALTS

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For the first time organically modified clays (organoclays) were obtained on the basis of montmorillonite at the beginning of the 20th century. Organically modified clays have a complex of unique properties. At present time they are perspective for application in various areas such as the environmental protection and industry. Organically modified clays may be used as high-efficiency fillers in production of polymeric nanocomposite materials, thickening and gelling agents in paints, lubricants, ointments, varnishes, and rheological control agents in drilling fluids. The recent interest in nanotechnology has given an additional boost to organically modified layered silicates.

Important and promising areas of use of layered silicates and organoclays are pharmacology (vehicles of drug delivery), catalysis (precursors for mesoporous materials) and environmental protection. Organically modified layered silicates are effective sorbents for removing organic contaminants (phenols), toxic heavy metals (e.g. Hg^{2+}) and metalloids (e.g. CrO_4^{2-}) from soils and water. Therefore these materials are applicable for the waste water treatment processes, and adsorption of contaminants from the environment.

The intercalation of an organic component into the interlayer space of a natural or synthetic silicate is the conventional way to obtain organoclays. The most frequently used organic modifiers are quaternary ammonium compounds with hydrocarbon radicals of varied structure and length. The advantages of synthetic layered structures over their natural analogs are in their purity, reproducible characteristics, and possibility of controlling the composition in the course of synthesis. Template syntheses of organically modified montmorillonites and hectorites have been described in the literature, but there are no reports of template synthesis of organically modified talc.

The results of the synthesis by thermal treatment with refluxed liquid phase («reflux») of layered magnesium silicate with the composition and structure of talc and organically modified by alkyl ammonium salts layered magnesium silicate are presented.

In all syntheses fresh magnesium hydroxide and silica sol were used as parent substances. The amounts of the reagents were calculated on the basis of the empirical formula of talc, $Mg_3Si_4O_{10}(OH)_2$. Molar ratios of the starting components: 1 MgO : 1.33 SiO_2 (synthesis of magnesium silicate); 1.0MgO : 1.33SiO_2 : xR, where R is hexadecyltrimethylammonium bromide $C_{16}H_{33}(CH_3)_3NBr$ (HDTMAB), x = 0.01–0.10 (synthesis of organically modified magnesium silicate).

It was shown that synthesis of layered magnesium silicate in the presence of hexadecyltrimethylammonium bromide yields a hydrophobic organically modified product. As the amount of hexadecyltrimethylammonium bromide introduced into a sample is raised, the hydrophobic properties of the organically modified layered magnesium silicate are enhanced.

It was found that hexadecyltrimethylammonium cations have a horizontal bilayer orientation in the interlayer space of organically modified layered magnesium silicates synthesized at the following molar ratios between the components: 1.0MgO : 1.33SiO2 : xR (where: R is hexadecytrimethylammonium bromide, x = 0.01–0.10).

A scheme by which the structure of layered magnesium silicate is formed in the presence of hexadecyltrimethylammonium serving as a template was suggested.

ELECTROKINETIC REMEDIATION OF FINE CLAY SOILS CONTAMINATED BY CHLOROBENZENE

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In recent years the remediation of industrial contaminated soils from hydrophobic organic compounds becomes a very important and complicated problem because of active accumulation of these contaminations in the environment leading to the problems with human health.

The most problematic objects for decontamination are fine clay soils. On the one hand, due to peculiar surface and volume properties and large specific surface area of this type of soils, they are the most inclined to retain pollution. On the other hand, due to the high values of hydrodynamic and aerodynamic resistance, the choice of effective remediation method is extremely limited. Electrokinetic treatment is the method for which the fine clay soil specific properties ensure its effectiveness in removing of uncharged organic compounds.

Application of an electric field causes several transfer mechanisms, such as electromigration, electrophoresis, electroosmosis. The greatest contribution to the decontamination from uncharged organic compounds is caused by electroosmotic transport, the rate of which depends on the zeta potential of soil particles.

However, the ability of electrical treatment of soils is substantially limited by accompanying chemical and electrochemical processes, the features of which depend both on the nature of treated dispersions and on the conditions of developed processes.

One of the most important factors, which affects the electroosmotic flow and hence the effectiveness of treatment is initial pH of a soil. However, even if the initial value of pH is favorable for electroosmosis, it can be changed by water electrolysis on electrodes, i.e. the electroosmotic mobility of liquid can go down. Traditionally acidic or alkaline reagents are used for control pH. From another side, the electrolysis can pay the positive role, since the electrodes as sources of H and OH ions can be used for directed pH regulation of materials under treatment.

Electrohydrodynamic method of regulation of pH and intensification of electroosmotic permeability for enhancing the stability of the removal of hydrophobic organic compounds is proposed and theoretically and experimentally substantiated. The experimental verification of the developed method for clay soils and the theoretical analysis of the obtained data are conducted.

As a model system we used kaolinite contaminated with chlorobenzene, which is representative of the organochlorine compounds that constitute one of the major groups of uncharged hydrophobic organic substances subjected to detoxification. To convert the hydrophobic chlorobenzene into water-soluble state, available for the transfer by electroosmotic flow, the system was wetted with a solution of surfactants.

The influence of surfactants on the electroosmotic mobility of noncharged contaminants was analyzed. It was shown that the efficiency and the regulation rate of pH and electroosmotic permeability strongly depend not only on different characteristics of disperse or porous systems (total exchange and buffer capacities of materials, its porosity, initial surface potentials and pH), but also on the treatment mode.

It is shown that the electrohydrodynamic regulation of pH of pore solution improves the rate and degree of chlorobenzene removal. The influence of an electric field strength on the efficiency of soil detoxification is investigated and the feasibility of using of its low values is shown.

The obtained experimental data corroborate to the performed theoretical calculations.

THE STABILITY AND PROPERTIES OF AQUEOUS SILICA DISPERSIONS IN THE PRESENCE OF POLYMERS

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Recycling of waste depends on their stability and rheological properties. These properties can be regulated by polymers. Effect of polymer adsorption on the stability and rheological properties of silica dispersions were studied.

The stabilizing effect of polymers in colloidal systems is directly related to their adsorption on the particles surface and structure of adsorbed layers formed.

Adsorption of polyvinyl alcohol (PVA), polyethylene oxide (PEO), polyvinyl pyrrolidone (PVP) and its effect on structural-mechanical properties and aggregative stability of concentrated suspensions of silica were studied in this work. The isotherms of PVA, PEO, PVP adsorption are assigned to an L-type. An increase of molecular masses causes the increase of polymer adsorption.

Adsorption of polymers courses changes in particle interaction and has an influence on the formation of structure. The rheological behaviour of the silica suspensions was investigated with a rotational viscometer. The dependence of viscosity of silica suspensions on the quantity of polymers (PVA, PEO, PVP) was found to have a well expressed maximum. The increase of viscosity at a low content of polymer is connected with the formation of polymer bridges between silica particles. At a high content of polymer the amounts of polymer are enough for coverage of particles; adsorbed polymer layers prevent particles from aggregation and the viscosity decreases. The ability to form bridges depends on the nature of polymer and increases with the increase of its molecular weight. Such bonds between particles could be destroyed by longtime keeping at1312 s^{-1}. Subsequent decrease of speed leads to the restore of bonds between particles and to the increase of viscosity.

To study the influence of dispersed phase concentration the aggregative stability of silica dispersions with different concentration of particles (1%, 3%, 5%) was estimated by light transmission and light backscattering using Turbiscan. It was shown that at the same amounts of polymer (80 mg/g) the increase of particle concentration leads to the increase of stability with reaching maximum value at the 5% content of disperse phase. The 1% and 3% contents of disperse phase are not enough for the formation of structure. That confirms the bonding of particles by polymer bridges. At the larger amounts of polymer (130 mg/g) particles are covered with polymer layers and the formation of structure is not observed.

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DECORATED CARBON NANOTUBES AS EFFECTIVE TOOL FOR EXTRACTION OF DYE (METHYLENE BLUE) FROM WATER

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Methylene blue (MB) is commonly used as a model basic dye for study of extraction of hazardous substances from wastewaters. Recently, the carbon nanotubes (CNTs) and their hybrids with other nanoparticles (decorated CNTs) were shown to be effective for removal of such substances from water. The extraction is mainly controlled by adsorption of organics on the surface of nanoparticles. However, the main mechanisms of dye adsorption by these systems are still unknown in details. This work is devoted to study of adsorption and electro-surface phenomena in aqueous suspensions of multiwall CNTs decorated by nanoplatelets of Laponite.

The multiwall CNTs, which were synthesized by CVD method using Fe-Mo-Al as a catalyst (Specmash, Kyiv, Ukraine), and the synthetic clay Laponite with composition of $Na_{+0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]_{-0.7}$ (Rockwood Additives Ltd., UK), were used in this work. The batch adsorption experiments were done with 0.01% wt concentration of CNTs and Laponite/CNT ratio of x=0-0.3. Earlier experiments have shown that Laponite nanoplatelets were effective as a dispersing substance for hydrophobic carbon nanoparticles, and it was explained by strong binding between Laponite and CNTs. For purposes of optimization of the MB extraction from an aqueous solution, the effects of the adsorbent/adsorbate contact time, initial dye concentration, mass ratio of CNTs-Laponite x and electrokinetic properties of the system were investigated in detail. The zeta-potential versus pH and concentrations of the different types of electrolytes was also studied. It was shown that CNTs, decorated by Laponite platelets at x=0.3, have higher adsorption capacity than CNTs without Laponite platelets. Recommendations regarding optimal parameters for effective removal of MB from an aqueous solution were formulated.

POORLY CRYSTALLINE TITANOSILICATES SORBENTS FOR STRONTIUM

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Titanosilicates are well-known powder sorption materials. They are applied for the purification processes of liquid radioactive wastes from long-lived radionuclides, namely cesium and strontium. However, the mentioned powder form of those materials causes some problems for their practical application

Sol-gel synthesis has a number of advantages which allow to adjust the texture and properties by a variation of gelation parameters. We have developed the original approach for sol-gel synthesis of titanosilicates. It allows to prepare the proper stable sol-gel granules using titanium inorganic salts as raw materials (solutions of chemically pure $TiCl_4$ and titanyl sulfate or technical solution of $TiOSO_4$), sodium silicate, alkalines and acids. The gels with molar ratio of Ti:Si = 0.5-2.5:1 have been synthesized at room temperature.

The dependences of gelation rate versus concentration of initial reagents, pH of medium, time of aging gel before hydrothermal treatment (HT), conditions of HT and washing of liquid were investigated. The introduction of some polyatomic alcohols and oxyacids as ligands gave a possibility to decrease the gelation time of titanosilicates towards some seconds. This fact opens the perspectives to obtain spherically granulated products. Ligands were selected to realize the gelation process at mild conditions. Such ligands allowed to obtain homogeneous hydrogels from concentrated initial solutions, which result in increasing the yield of sorption material. It was found that proper gels are formed in the pH range 8.5-11. The fastest gelation (5-10 s.) occurs at pH 10-10.4. Investigation of aging effects before HT showed that the most developed porous structure is formed after 2-4 days. Hydrothermal treatment impact on the textural parameters titanosilicates was studied in the temperature range of 120-200 ^{o}C within 6-48 hours.

It was shown that the most beneficial effect on the texture titanosilicates occurs in the temperature range of 140-175°C during 6-12 hours. It was established that the most effective and gentle washing liquid is water-alcohol mixture, acidified by 0.05 N acetic acid.

IR spectra of the samples do not contain any absorption bands of organic compounds. This indicates that proposed method of synthesis allows to obtain organic-free sorption materials.

X-ray studies of materials demonstrated that proposed method of sol-gel synthesis allows to prepare titanosilicate materials with pure crystalline phase of sodium titanosilicate or mixed phase of sodium titanosilicate and Engelhard titanosilicate (ETS-4) after HT conditions (200 C/12 hours).

The low-temperature nitrogen adsorption on titanosilicates was studied using high-speed NOVA 2200 analyzer. Nitrogen adsorption isotherms with hysteresis loops H1 and H2 are related to the IV type. Synthesized samples have following texture characteristics: BET surface area is 113-270 m^2/g, total pore volume - 0.2-0.7 cm^3/g, Dubinin-Radushkevich`s micropore volume – 0.03-0.1 cm^3/g. The pore size distribution curve has a maximum in the range of 30-90 Å.

It was shown that sorption capacity of synthesized titanosilicates towards Sr-90 radionuclides is highly competitive with famous powder analogues.

ENDOCRINE DISRUPTING COMPOUNDS IN WATERS AND THE OPPORTUNITIES OF TREATMENT

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It is known from the 30's, that some of the artificial and natural compounds have similar properties to natural hormones. These materials, which have the same properties as human hormones have a great affect on human beings by the molecules specific hormone like influence and the impairment of the immune system. Nowadays these compounds occur with great amount in the environment mainly because of the use of cosmetics and medicines. The qualitative and quantitative determination of Endocrine Disrupting Compounds, *Pharmaceuticals and Personal Care Products* (EDCs and PPCPs) is a serious analytical challenge due to the large number of compounds. Since the chemical, physico-chemical and physical properties of these compounds may differ considerably, therefore their determination can not be achieved using only a single method. The EDC and PPCP contaminants can be removed from waste waters to some extent with conventional water purification methods, however. Fully, 100% effective method is currently not known. Operating data of water purification plants indicates that each of these impurities can be removed with diffrent effection. Therefore, it is important to make further steps in conventional water treatment processes, or inserting additional actions in the secondary water treatment operations to improve the EDCs removal efficiency.

In our experiments we used 0,8 g/l bentonite suspension as model system and 0,07 g/l coffeine as EDC and 0,07 g/l oxybenzone solution as PPCP material. To remove the pollutants we used anionic and

cationic polyelectrolytes and the mixtures of them from SNF. The pollutants were determined before and after the treatment with HPLC.

Keywords: *EDC, detection, water treatment, polyelectrolytes, HPLC*

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FUNDAMENTAL PROBLEMS OF SOIL REMEDIATION BY ELECTROKINETIC METHODS

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Remediation of soils contaminated with radionuclides, heavy metals, hydrophobic organic matters and other pollutants is a very important and complicated problem. Special attention deserves the process of soil recovering by application of an electric field. The method is based on the mass transfer of polluting substances under the action of an external electrical field, together with their subsequent extraction from the cathode chamber. The removal of soil contaminations can be achieved by electrophoresis, electroosmosis and diffusion, hydrodynamic flow of liquid, and depends on many factors: soil chemistry and structure, sorption/desorption processes, ion exchange, polarization of soil particles and electrodes, electrokinetic mobility of pollutants etc., which affect the efficacy of the remediation processes.

The electrokinetic methods of soil decontamination are rather expensive and therefore can be used for relatively small areas (around enterprises, at local industrial accidents etc.). However, in every case the process of decontamination needs careful optimization with account of the properties of soils and type of pollutants. Thus, a comprehensive approach to the detailed analysis of all proceeding processes and the development of new technological ideas is a matter of paramount importance.

It is interesting that the strongest negative factor of soil remediation at application of an electric field is an electric field itself. An electrical current is always accompanied by the electrolysis of water on electrodes, which leads to the change of soil pH, creation of inhomogeneous local electric potential and conductivity of soil, inhomogeneous local solubility, as well as desorption and mobility of pollutants, that complicate the soil decontamination.

Since very often soil alkalinity or acidity pays negative role, the very important stage of soil decontamination is also pH regulation, which can be achieved in a few ways: wetting of the soil by solutions with necessary pH, conditioning of the catholyte or anolyte pH, using electrohydrodynamic method of pH regulation or using of ion-exchange membranes, etc. The efficiency of contaminant removal also can be increased due to the use of complexing agents for removal of ionic contaminants and surfactants for removal of hydrophobic organic pollutants. Therefore, the development of new ways of regulation of pH, solubility and mobility of pollutants and the careful optimization of the electrokinetic methods for given soil or sludge are the most important problems of soil remediation worthy of special attention.

The conducted theoretical analysis of all processes during soil remediation allowed to find the best conditions for soil and sludge decontaminations. The special scheme of pH regulation in entire interelectrode space, which includes regulation of both hydrodynamic and electric movement of hydroxyl and hydrogen ions through the electrode chambers and soil, was proposed. It is shown, that new technology makes possible to achieve a very high degree of model clay system and real soil decontamination (in some cases almost 100%) from a number of impurities, including nickel, cadmium, cesium, strontium, copper, lead, chlorobenzene, orthochlortoluene, cyclohexilbenzene etc. It is necessary also to note, that although the removal of admixtures occurs deeper and faster, than under the earlier developed technological processes, the achievement of a high degree of soil remediation very often is also accompanied with decrease of the electric power consumption.

ELECTROOSMOTIC DEWATERING OF FINE CLAY SLUDGE

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Dewatering of disperse systems is an important task for mining, food, paper and pharmaceutical industries, production of fertilizers, pigments and dyes, as well as for consolidation of sludge occurring in treatment of waste and drinking water. The most used methods include mechanical dewatering methods (pressure and vacuum filtration, centrifugation) and thermal drying. However, mechanical methods are ineffective when handling fine materials characterized by small particle sizes and low hydrodynamic permeability, and thermal methods need high power consumption. For treatment of such materials (gel sewage sludge, different food or arfillaceous waste, etc.) an alternative to the above-mentioned methods is electroosmotic dewatering, for which the hydrodynamic permeability of the material is not a critical parameter, and the power consumption is much smaller comparing with the thermal methods.

Efficiency of electroosmotic dewatering is determined by combination of two opposite factors. On the one hand, it is necessary to enhance the speed of liquid flow through the sludge, i.e. to enlarge the surface potential of disperse particles. On the other hand, to promote the compaction of sludge the electrostatic repulsion between the particles must be decreased, that is possible at the reduction of the surface potential. Taking into account that the surface potential of particles depends on the pH of the equilibrium porous solution, obtaining the optimal conditions is possible, but each type of sludge requires a careful control of the characteristics of particles and liquids, and details of the sludge treatment. Analysis of the conditions necessary for electroosmotic dewatering of fine material is the subject of this presentation.

The investigations were conducted using a model system comprising the dispersion of kaolinite at different initial pH and moisture. In order to optimize the process of sludge dewatering the studies of the dispersion particles properties at different pH values of aqueous media were performed.

First of all, the regularities of achieving of equilibrium pH of the pore solution depending on the concentration of the sludge solid fraction and the concentration of introduced acid or alkali were analyzed. Then, the magnitude and sign of the zeta potential of disperse particles and the velocity of electroosmotic flow at different values of pH were studied. It was shown that there is a sufficiently wide range of high pH of pore solution, wherein the electrokinetic potential of the particles and the electroosmotic velocity of liquid through dispersion remain almost constant, creating optimal conditions for the sludge dewatering.

To intensify the dewatering the kinetics of liquid removal from the model sludge the simultaneous use of an electric field and of pressure was studied. It was shown that the applied pressure leads both to the compression of dispersion and to improvement of the contact of a treated sludge with electrodes, that accelerates dewatering in comparison with the application of an electric field only.

The established behavior of model dispersions at a wide range of pH, voltage and pressure is important for the development of electrokinetic technology because the obtained results allow predicting at which characteristics of sludge one can obtain the stable and effective dewatering.

The obtained data may be also used for regulation of disperse systems properties.

THE ROLE OF FE(II)-FE(III) LDH STRUCTURES IN THE FORMATION OF IRON-OXYGEN STRUCTURES, THE KINETICS OF THEIR FORMATION

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Layered double hydroxides of iron (Fe(II-Fe(III) LDH, Green Rust), their natural analogue fougerite in particular, are the most important natural source of ferrous cations, and thus, being potent reducing agents, are able to provide purification and reclaiming of contaminated water and soil. They are also characterized by having significant adsorption properties [1].

Fe(II)-Fe(III) LDH, as a rule, are considered to be the main product of corrosion at its first stage, the product of pitting corrosion and the processes of iron compounds bioreduction. Hence, one of the main points of the purification and environmental protection methods development is the role of Fe(II)-Fe(III) LDH in PRB-technologies implementation.

We have researched the role of Fe(II)-Fe(III) LDH in the formation of iron-oxygen structures (IOS) in the system Fe^0(St3)-H_2O-O_2 during an alternately contact of steel disk with the air and distilled water or $CoCl_2$, $FeSO_4$ and $Fe_2(SO_4)_3$ dispersion medium [2, 3]. We have also researched the kinetics of these processes using the method of X-ray diffraction *in situ* [4]. The obtained results allowed us to propose and explain the role of Fe(II)-Fe(III) LDH in the development of sewage treatment methods and methods of natural systems purification. Also due to these results our knowledge about the mechanism of corrosion processes has broadened. One more aspect of our research is the obtaining of IOS by the method of oxidation of Fe(II)-Fe(III) LDH.

As a result of our research the scheme of IOS formation in the system Fe^0(St3)-H_2O-O_2 has been proposed (Fig. 1). The role of

Fe(II)-Fe(III) LDH as intermediate structures has been ascertained. It is obvious now that the oxidation of these intermediate structures leads to the formation of IOS and determines, depending on physicochemical conditions, the final products of this process, indicated on the scheme (full line). It is also shown that the growth of IOS in the system reaches the size of about tens nanometers and the accumulation process of monodisperse particles is observed. As we can see on fig. 1 there is a possibility of IOS formation by the way of aquohydroxy complexes of iron or ferrous hydroxide formation (a suppositive denotement $Fe(OH)_2$ is used in the scheme, dotted lines). But it is not the main process, which is proved during our experiments.

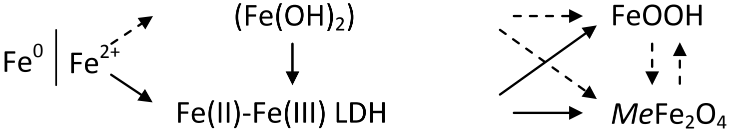

Figure 1. **The scheme of iron-oxygen structures formation in the system Fe^0(St3)-H_2O-O_2**

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ACRYLIC HYDROGEL SORBENTS OF HEAVY METALS FOR WATER TREATMENT AND ARTIFICIAL SOIL FORMATION

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Anthropogenous pressing, ecological and technological accidents lead to comprehensive environment contamination by heavy metals and other toxicants which enter the tap and ground water, as well as soil and plants. So, the urgent and actual problem is to improve sorption methods of water treatment and to exclude plants contamination by these substances. Thus, information about new perspective polymer hydrogels, which has appeared several years ago, is rather interesting.

Due to the unique properties of smart hydrogels, such as reversible swelling/deswelling behavior, sorption capacity, permeability, surface properties, and high sensitivity to external stimuli, the hydrogels provide platform for creating novel smart materials and systems for wide range of applications. Besides, they are biologically safe and that is very important. When swelling they absorb substances of outer solution and give them out at collapse/constriction. However, there is a lack of information about polymer hydrogels application for water treatment and artificial soil formation. These problems are of great importance because of the increasing pollution of environment by heavy metals and other contaminants.

So, the test-objects of our investigation were heavy metals ions Cu^{2+}, MnO_4^-, Mn^{2+}, Fe^{3+}, complexes (Cu-humate, Fe-humate), organic substances (basic dyes methylene blue R_{mb}^+ and basic fuchsin, as well as acid dye fuchsin R_f^-). The polymer hydrogels on the base of polyacrylamide (PA), copolymers of acrylamide-acrilyc acid (AA) and acrylamide-acrylonitrile (AN) as the particles of 1-2 mm in diameter were taken as sorbents. We compared the efficiency of sorption of heavy metals (HMs) in cation and anion form, acidic and basic dyes. This corresponds to row: basic fuchsin › methylene blue › Fe^{3+}› Cu^{2+} › acid fuchsin › Mn^{2+} › Cu-humate › Fe-humate › H_2PO_4. It should be stressed that desorption of investigated substances has opposite directions, besides the organic dyes desorption was very poor. At the initial concentration of the contaminants 1 mM, maximum HMs absorption appeared in the case of AA-gel (up to 99%). At the same time, PA- and AN-gels sorbed only 60-85 % of HMs. The tested acrylic hydrogels are weak cationites containing acidic (mainly carboxylic) active groups in relation AA : AN : PA = 20 : 3 : 2. It explains HMs sorption by AA-gel. Its static exchange capacity (4 mg-eq./g by Cu) is near the best HMs sorbents. The process of swelling and substance absorption occurs synchronically. The equilibrium state is achieved after two hours with maximum sorption and swelling at $pH \geq 6$. In acidic solutions hydrogels collapse and substances desorption occurs. The efficiency of HMs removal from individual and mixed solutions, as well as from natural water, are rather close, depends on HMs types and can reach 95 % from the initial concentration. At the weak acidic conditions, almost full HMs desorption from acrylic hydrogels occurs. At the same time, the sorption capacity of acrylic hydrogels for HMs is retained. That allows reuse of the sorbents under study for HMs removal from contaminated water.

At the next set of experiments we used the hydrogels described earlier, loaded by HMs (bioelements) according to agrochemical tables. They were used for artificial soil formation. That allows obtaining ecologically clean plant crops under controlled conditions. When growing, plants excrete organic acids into rhizosphere continuously and they bind the bioelements immobilized in hydrogels matrix in water soluble complexes absorbed by plant roots. Prolonged desorption of HMs (macro- and microelements) is very important for soil fertility providing. In this connection the AN-gel showed the slowest bioelement desorption. In vegetation experiments it was demonstrated that artificial soil on the base of this gel with immobilized bioelements provides the best plant yield.

Moreover, structure-mechanical properties of tested objects and different soils were investigated. Strength properties of these materials were characterized by interparticle connection parameter (ICP) calculated by Hershel-Bulkley equation. ICP of acrylic gels (native and loaded with HMs) are almost similar. But ICP of acrylic gels is 10-100 times higher of natural soils ICP.

So, the conclusion from the investigation is that the acrylic gels are firm and effective sorbents for HMs removal from water and artificial soil formation.

BIOCOLLOID-CHEMICAL INFLUENCE OF CALCIUM CARBONATE NANOPARTICLES ON MEDICAL-ENDOECOLOGICAL PROPERTIES OF PELOIDS

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Peloids (medical muds) (including peloids of Carpathian region) mainly consist of polydisperse polymineral clay minerals and organic matter transformed due to complex biocolloid and nanochemical transformation in saline disperse media with microorganisms' involvement [1, 2]. Such transformations give unique properties to peloids and create abilities for their active influence on endoecologic processes in organism. One of such processes is nanochemical transformation of calcium carbonate [2]. Their influence on medical and endoecological characteristics of peloids were investigated with physico-chemical and medical-endoecological methods.

Obtained microphotographs of peloids denote the presence of carbonate structures, microfauna and superdispersed silicate particles in them (Fig.1). Also these microphotographs denote additional presence of carbonate nanoparticles (Fig.2) in artificially prepared peloid compositions.

Investigation of influence of calcium carbonate nanoparticles addition onto peloid composition was made using Wistar rats. Thus, the testing results showed that antitoxic ability of liver (diagnosed by durability of animal sleep) increases 2-3 times (Fig.3). Functional state of kidneys significantly improves too. It confirms by 1.5 times increase of filtration speed of urina and diurnal diuresis. And there is intensification of kidney efferent function: removal of creatinine increases 1.5 times and removal of urea increases 1.2 times.

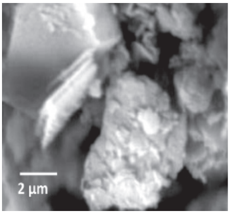


Fig.1

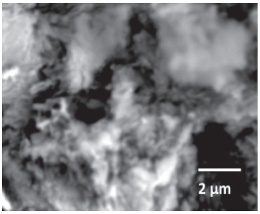


Fig.2

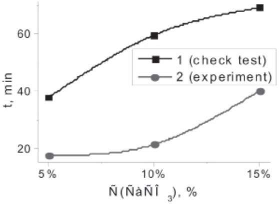
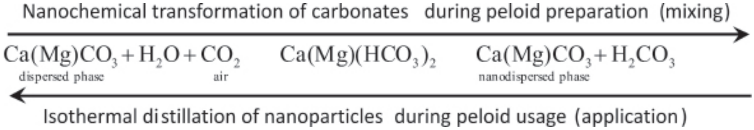


Fig.3

Analysis of obtained results showed that calcium carbonate nanoparticles in structure of peloid compositions considerably improve medical-endoecological characteristics of peloids. And that is the result of colloid-chemical and nanochemical transformations in correspondence with scheme [2]:



$$\underset{\text{dispersed phase}}{Ca(Mg)CO_3} + H_2O + \underset{\text{air}}{CO_2} \quad Ca(Mg)(HCO_3)_2 \quad \underset{\text{nanodispersed phase}}{Ca(Mg)CO_3} + H_2CO_3$$

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STRUCTURE AND OPTICAL PROPERTIES OF NANOSIZED Cu - TiO_2 FILMS AND POWDERS ACTIVE IN ECOLOGICAL PHOTOCATALYSIS

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Among the semiconductors used in environmental photocatalysis, titanium dioxide is very perspective as photoactive, non-toxic, cheap, chemically and biologically inert and photostable material. The doping of TiO_2 with noble metal, 3d-metal ions, organic dyes promotes its activity in photoredox processes and increase the sensitivity of the photocatalysts in the visible. This work is devoted to the synthesis and properties of titania thin transparent films and powders doped with copper ions.

TiO_2 and TiO_2/Cu^{n+} films and powders were obtained by sol-gel method using $Ti(OiPr)_4$, $CuSO_4 \cdot 5H_2O$, C_2H_5OH, H_2O and HCl. Nonionic amphiphilic triblock copolymer Pluronic P123 was used as a template agent and acetylacetone as a complexing agent. The films were calcined at 130 °C, 300 °C, 400 °C subsequently and showed anatase structure. To get corresponding powders, the precursors have been treated at 500 °C or 650 °C.

Obtained films and powders have been characterized by UV-, Vis-, Raman spectroscopy, TEM, SEM and XRD. Pure nanocrystalline TiO_2 films have pore size radius around 5 nm and size of the crystals about 10-15 nm. Cu/TiO_2 films have size of the crystals 8 nm. Copper-doped titania powders with 5% of Cu after 650 °C treatment demonstrate the formation of crystalline phases of Cu_2TiO_3 and Cu_3TiO_4. XPS analysis showed presence of Ti^{3+}, Ti^{4+}, Cu^{2+}, Cu^{+} ions as well as

Cu^0 particles in the structure of the samples Cu/TiO_2. The presence of oxygen vacancies and copper ions, which may act as electron traps and/or electron donor, increased photocatalytic activity. Cu/TiO_2 films contained various amount (from 1% to 30% mass) of copper, exhibit three times higher photocatalytic activity in the reduction of toxic Cr(VI) to non-toxic Cr(III) ions in comparison with the one of pure TiO_2.

ОЧИСТКА ПРОМЫШЛЕННЫХ СТОКОВ ОТ ТОНКОДИСПЕРСНЫХ НЕФТЕПРОДУКТОВ УЛЬТРАФЛОКУЛЯЦИЕЙ И ТУРБУЛЕНТНОЙ МИКРОФЛОТАЦИЕЙ

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Промышленные стоки, содержащие нефтепродукты в тонкодисперсном и/или растворенном состоянии, представляют собой один из наиболее трудно утилизируемых видов отходов промышленных предприятий. Миллионы тонн таких отходов ежедневно образуются и подлежат и утилизации. От того, насколько эффективно будет осуществляться этот процесс, зависит степень риска загрязнения, которому подвергаются прилегающие к этим предприятиям территории. В качестве практического решения этой проблемы все более широкое распространение в последние два десятилетия получают ультрафлокуляция [1, 2], турбулентная микрофлотация [3] а также их комбинация с применением тонкодисперсных сорбентов [4-5]. Основное отличие “ультрафлокуляции” от обычной флокуляции состоит в том, что в ней используется специальная гидродинамическая обработка суспензии после введения в неё флокулянта, при который осреднённый градиент среды изменяется в процессе обработки суспензии от некоторого максимального значения до нуля по определенному закону 2]. Что же касается “турбулентной микро-флотации”, то её основное отличие от обычной микрофлотации состоит в том, что после введения в пульпу микропузырьков последняя подвергается турбулизации путем пропускания её по трубчатому статическому миксеру. В результате такой обработки происходит не только налипание частиц и их агрегатов на поверхность микропузырьков, но и агрегирование и/или коалесценция последних в крупные флотокомплексы, которые затем легко можно отделить от воды седиментацией. Использование упомянутых методов позволяет уменьшить время обработки жидких отходов, содержащих нефтепродукты, до 1-2 минут и снизить остаточное содержание органических загрязнений до 5-15 мг/л.

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SORPTION OF COPPER AND ZINC BY ZEOLITE FROM AQUEOUS SOLUTIONS

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Sorption of Cu(II) and Zn(II) ions from aqueous solutions has been studied and theadsorption capacityofzeolite has beendetermined.

The experimental data obtained from batch equilibrium tests have been analysed by two- and three-parameter isotherm models (Freundlich, Langmuir,Redlich-Peterson).

The zeolite was obtained from Zeocem OJSC. The material was oven dried at 90°C for 72 hours.

The equilibrium experiments were carried out by varying concentrations of initial Cu(II) and Zn(II) solution. In all experiments, the flasks were shaken on orbital shaker at 200 rpm and at 25˚C for 6 hours to ensure ion-exchange equilibrium. The suspensions were then filtered through a micro filter of pore size 0.8 μm and filtrates were analysed using flame AAS in order to determine the final Cu(II) and Zn(II) concentrations in solution.

According to the results of the experiments the adsorption equilibrium of Cu(II) and Zn(II) on zeolite was best described by Freundlich isotherm. The maximum sorption capacity was 3 and 2.5 mg/g for Cu(II) and Zn(II), respectively.

The experimental results of this study demonstrate that zeolite is suitable for adsorption of copper and zinc from aqueous solutions at low concentrations.

TOXIC ELEMENT CONTENTS IN GROUND BEETLES

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The urbanization and anthropogenic activities cause environmental pollution which may cause damage in terrestrial ecosystem and its organisms. The aim of our study was to study the effects of urbanization on toxic element contents in *Carabus violaceus* (N=72) and *Pterostichus oblongopunctatus* (N=51) specimens along an urbanization gradient. Ground beetles were collected from three forested study area: urban parks, suburban forest and rural forest. The following toxic element contents were analysed in all samples: Al, Ba, Cd, Cu, Fe, Mn, Pb, Sr and Zn. Significantly higher concentration was found in *P. oblongopunctatus* specimens than in *C. violaceus* in the case of all toxic elements, except Sr. The Pb and Zn concentration was differed significantly along the urbanization gradient. We also found significant differences between sexes. Significantly higher Cu and Pb concentration was found in males beetles than in females. In spite of this the Sr concentration was higher in the female ground beetles, than in males. Our study demonstrated that the different breeding strategy and sex cause differences in the accumulation of toxic elements. In summary, we demonstrated that ground beetles are suitable bioindicator organisms to monitoring the effects of urbanization and anthropogenic activities on terrestrial ecosystem.

Keywords: *urbanization, monitoring, MP-AES*

INVESTIGATION OF THE EFFICIENCY OF VARIOUS ADVANCED OXIDATION PROCESSES IN THE TRANSFORMATION OF THE PHENYLUREA HERBICIDES

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Environmental contamination by pesticides is an issue of general concern since these compounds can adversely affect human and ecosystem health. A significant fraction of applied pesticides enters the soil, sediments and water where it can undergo various transformation processes which can lead to significant concentrations of stable transformation products in the aquatic environment. The different transformation processes may significantly change the toxicity in comparison to the parent compound.

Advanced oxidation processes (AOPs) are technologies with significant importance in environmental restoration applications. The AOPs are defined as processes involving the generation of highly reactive oxidizing species able to attack and degrade organic substances. Nowadays AOPs are considered high efficiency physical-chemical processes due to their capability to produce deep changes in the chemical structure of the contaminants via the participation of free radicals.

In this work, the efficiency of the various advanced oxidation processes (UV-induced photolysis, heterogeneous photocatalysis, ozonation) and their combinations were investigated and compared in several aspects (initial rate of transformation, rate of mineralization, dehalgenization, and toxicocogy aspects) in the decomposition of diuron, monuron and phenuron, using a very similar experimental apparatuses, with the same energy consumption.

Diuron (N-(3,4-dichlorophenyl)-N,N-dimethyl-urea), monuron (N-(4-chlorophenyl)-N,N-dimethyl-urea) and phenuron (N-carbamoyl-2-phenylacetamide) are widely used herbicides, which are employed to control a wide variety of annual and perennial broadleaf and grassy weeds. Nowadays, diuron, considered a Priority Hazardous Substance by the European Comission, can be detected not only in the agricultural and natural waters but also in drinking waters. On the other hand, diuron is one of the endocrin disrupting chemicals.

Diuron and monuron are only slightly toxic to mammals, but several publications presented that, the transformation results in intermediates with rather high toxicity. In our work toxicology measurements were carried out by different ways. The toxicity tests were done on Selenastrum capricornutum microalgae culture, Daphnia magna zooplankton and bioluminescence inhibition assay using the marine bacterium Vihrio fischeri as the test organism to determine the toxicity of the samples after the 0, 25, 50, 75 and 100% decomposition of parent compounds.

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HYBRID ADSORBENTS FOR PROPHYLAXIS AND REMOVAL OF RADIONUCLIDES FROM HUMAN ORGANISM AND ANIMALS

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In recent years, in connection with growing importance of long-living radionuclides (RN) of cesium, strontium and some transuranic elements vital for both people and animals' life, development and creation of hybrid adsorbents has been executed on the basis of modified active carbons of various texture and dispersion, modified clay minerals of Ukraine – palygorskite ("Ultrasorb"), some food additives – pectin ("Pectopal") and alginate-containing concentrates ("Carboxykam") in the Institute for Sorption and Problems of Endoecology [1,2].

The researchers of these substances have shown their essential advantages on pre-clinical and clinical stage over traditional adsorptive preparations. In particular, their therapeutic action is based on:

- Quite high selectivity of radiocesium extraction from biological liquids (factor of selectivity K_d exceeds 20000) and essential selectivity on radiostronsium (K_d about 600);
- Quite high selectivity of adsorption of heavy metals ions (HM), especially to Pb, Co, Cd, Cu, and Ni (K_d achieves 2000-3500);
- Quite high detoxication ability on harmful organic methabolites and poisons (test on Methylene Blue) – more than 300 mg/g).

Some physicochemical aspects of advantages of using combined enterosorbents are considered in this paper. Data on activity of the combined adsorbents Ultrasorb, Pectopal and Carboxykam for adsorption of the cations Fe, Co, Cd, Pb, Zn, Cu, Ni and radioactive isotope Cs^{137} from a modeling Ringer salt solution are reported. From the obtained data on distribution factors for various ions it is possible to order the selectivity of adsorption of HM ions by Ultrasorb in an interval of concentration 10^{-2} – 1 $mM.L^{-1}$ as:

$Pb^{2+} > Fe^{2+} > Co^{2+} \sim Cu^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+}$.

The analysis of obtained data on influence of hybrid preparations on the human and animal organism shows their efficiency on removing HM and RN from the organism, and also their harmlessness, expressed detoxification and corrective properties. They can be recommended for use in complex therapy of intoxications of various genesis, especially ecology dependent diseases.

Taking into account the effective ability of the hybrid preparations to remove heavy metals and radiocesium and to provide general detoxification and sometimes corrective action on the organism, they should be recommended in medical practice of extreme situations (medicine of accidents), for example, at carrying out the scheduled and emergency works on object “Shelter” in Chernobyl.

In this way the study has allowed to reveal positive and negative effects of the new hybrid adsorbents in animals under conditions of chronic internal and external irradiation. These drug properties should be taken into account at the working out of radioprotective complex therapy.

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CARBON AND INORGANIC SORBENTS AND ION EXCHANGERS IN THE THERAPY OF SEVERE DISEASES AND ECOLOGICAL CONTROL OF MEDIA INTERNAL OF THE ORGANISM

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Now sorption methods for body detoxification in many serious diseases and poisonings are formed into a separate, rapidly developing area of modern medicine. Thus, in the development of medical sorbents there are two basic approaches: creating broad-spectrum hemo- and enterosorbents, and synthesis of selective sorbents with marked selectivity only towards one or several toxicants or harmful metabolic products.

In the current report are presented data that elucidate the main trends of the development of sorption medical technologies in the advanced countries are presented. Particularly, it has been shown that activated carbons are mainly used as a hemosorbents for removing toxic substances from the blood stream and metabolites with molecular nature (primarily carbons, granules of which are covered with porous polymer films), and also spherically granulated porous copolymers of styrene and divinylbenzene. Also there were created selective sorbents on the basis of the same copolymers, but with chemically bounded (immobilized) substances (antigens and oligopeptides, etc.) onto the surface, that display the increased affinity towards pathogenic compounds which should be removed from the blood and plasma in the treatment of one or other diseases. If we talk about enterosorbents, the clinical use of the several varieties is mastered only in CIS countries as well as Japan, South Korea and Taiwan.

In recent years the Institute for Sorption and Problems of Endoecology National Academy of Sciences of Ukraine in recent years has developed granular carbons and hemo-enterosorbents, based on the coconut shells - traditional raw materials available in the world market. It was shown that the parameters of their porous structure corresponds to the synthetic carbon adsorbents with trademarks SCN, SCS and SCF, previously developed by us. Also there are presented data that indicate the necessity in the evaluating of mechanisms of therapeutic action of medical sorbents, based on active carbons, in addition to the sorptive properties, also consider their catalytic activities in the oxidation reactions of harmful and toxic substances, as well as the decomposition of lipid peroxides. The antioxidant properties of carbons are also important here, namely, their ability to neutralize the aggressive free radicals.

To control the electrolytes (NH_4^+, K^+, HPO_4^{2-}, etc.) in body biological environments, we have developed the new inorganic ion exchangers based on amorphous titanium and zirconium silicates. A new concept has been introduced: the combined use of the carbon hemo- and enterosorbents in the comhjsition with the inorganic ion exchangers enables to solve the problem with sorption therapy for most diseases and pathological conditions, including the problems of age-related pathologies.

Also in the report are given examples of medical sorbent use as a preventive measures for accumulation and rapid excretion a number of exotoxicants - pesticides, radionuclides and heavy metals are presented in the report.

РЕКУЛЬТИВАЦІЯ ГРУНТІВ ШЛЯХОМ ЗАЛУЧЕННЯ СОРБЦІЙНИХ ТЕХНОЛОГІЙ

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Забруднення навколишнього середовища та надмірне використання стійких отрутохімікатів призвели до зниження продуктивності та погіршення якості аграрної продукції. Накопичення пестицидів після їх функціонального застосування призводить до загибелі грунтових організмів, негативно впливає на грунтоутворювальні процеси та погіршує родючість грунту. Тому в останні роки науковцями піднімається питання покращення екологічного стану та продуктивності земельних угідь шляхом використання сорбентів різного типу, в тому числі і композиційних матеріалів з мікробіологічними та мікроелементними добавками.

Інститут сорбції та проблем ендоекології НАН України має значні здобутки в розробці біотехнологічних методів, що стосуються біосорбційного очищення ґрунтових та водних середовищ від отрутохімікатів (пестицидів) та рекультивації забруднених пестицидами грунтів, точніше до технології детоксикації пестицидів з використанням мікроорганізмів-деструкторів, іммобілізованих на поверхні спеціалізованих комбінованих сорбентів. Перспективними сорбентами для використання їх в якості носія мікробних клітин є вуглецеві матеріали та їх композити з певними рослинними та мінеральними матеріалами. Матричний сорбційний матеріал повинен бути активним поглиначем забруднення тобто мати сорбційну ємність відносно пестицидів та адсорбувати на поверхні мікроорганізми-деструктори забруднювача. Такі сорбенти-носії мають високу хімічну стійкість, механічну міцність, іонообмінні властивості, достатню проникність для води та інших субстратів, біосумісність та технологічність. Головною відмінність сорбентів-носіїв є те, що за їх основу були взяті дешеві та доступні продукти піролізу рослинних відходів агропромислового комплексу та лісопереробного виробництва, а також збагачені мікроелементами (Zn, Cu і Mn) цеоліти Закарпаття та деякі інші зразки природних алюмосилікатів та оксидів.

Результати багаторічних досліджень дозволили запропонувати біосорбційний препарат на основі вуглецевого, мінерального та рослинного сорбційних матеріалів з іммобілізованою природною асоціацією мікроорганізмів деструкторів з широким діапазоном деструктивної дії відносно пестицидів різного хімічного складу, що дає можливість досягнення кінцевого результату очищення природних середовищ від пестицидів до норм ГДК. Крім того, природна мікобіота в комплексі з сорбційним композитом забезпечує в грунтах засвоєння азоту (азотфіксуючі бактерії) та підвищувати доступність та засвоюваність мікроелементів.

Сорбційні технології перспективні для виділення та використання природної мікрофлори, що складається з асоціації мікроорганізмів-деструкторів певної спрямованості, а використання композиційного сорбенту активного до пестициду в якості носія для іммобілізації цих мікроорганізмів дає можливість створення ефективних сорбційно-біологічних систем детоксикації пестицидів. Такий сорбційний біокомплекс конкурентно здатний в природних умовах. Іммобілізація мікроорганізмів-деструкторів на поверхні сорбційної матриці підсилює деструктивну дію мікроорганізмів та стійкість їх властивостей.

Проведені польові випробування біосорбційного матеріалу (орієнтовна назва Агродетокс) на експериментальному полі показали, що використання комбінованого сорбенту з іммобілізованими на його поверхні мікроорганізмами-деструкторами дозволяють досягти ступеня деструкції пестицидів до 90% протягом вегетаційного періоду. У вирощених рослинах якісні параметри вищі в 1,5-2 рази, що підтверджує можливість одержувати екологічно чисті продукти харчування, які в розвинутих країнах кваліфікуються як “органік”.

ИСПОЛЬЗОВАНИЕ СПЕЦИАЛИЗИРОВАННЫХ СОРБЕНТОВ ДЛЯ ПОВЫШЕНИЯ СОДЕРЖАНИЯ МИКРОЭЛЕМЕНТОВ В ПРОДУКЦИИ ЗЕМЛЕДЕЛИЯ

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В последние годы в обществе все чаще поднимается вопрос об улучшении экологического состояния и продуктивности сельскохозяйственных угодий путем использования новых технологических приемов и материалов. Одним из путей детоксикации грунтов и улучшения их микроэлементного состава является использование сорбентов различного типа, в том числе, и композиционных материалов с микроэлементными добавками.

Основными требованиями к таким сорбентам являються: ценовая доступность, простота технологии изготовления и применения, екологичность и эффективность. Этим требованиям в полной мере отвечают специализированные углеродно-минеральные сорбенты с выраженной способностью к очищению грунтов, а также возможностью регулирования микроэлементного состава растительной продукции аграрного комплекса.

В Институте сорбции и проблем эндоэкологии НАН Украины разработаны и проходять испытания сорбционные материалы для длительного снабжения микронутриентов в органическом земледелии. Важным требованием для органического земледелия является снижение растворимости введенных в грунт микроэлементов. Именно поэтому наше исследование ориентировано на разработке микроудобрений пролонгированного действия. Главным компонентом получаемых нами сорбентов является природный материал – цеолит Сокирницкого месторождения (Закарпатская обл.). Количество микроэлементов, используемых для пропитки цеолита, было оценено на основе его сорбционных свойств. Кинетические характеристики сорбции аммиакатов цинка, меди цеолитом свительствуют о том, что для максимального насыщения минеральной матрицы ионами микроэлементов, длительность пропитки должна составлять примерно 10 часов.

Исследованы структурно-пористые свойства экспериментальных образцов. Показано, что середняя удельная площадь поверхности материала - 18,5 м^2/г, средний удельный объем пор (V) - 0,1 см^3/г, средний радиус пор (R) составляет 5,3 нм.

Разработанные экспериментальные образцы специализированных сорбентов были испытаны в полевых условиях на делянках Института агроэкологии и природопользования НААНУ. Эти испытания показали, что в течении первого года после внесения модифицированных сорбентов имело место статистически достоверное увеличение содержания цинка (в моркови на 17-19%, в свекле на 28-30%) и меди (в моркови на 13-23%, в свекле на 17-19%). Урожайность корнеплодов при это увеличилась на 13-15% (моркови) и на 17-20% (столовой свеклы) по сравнению с контрольною делянкой.

На следующий год посева овса и ячменя на делянках, где предварительно выращивали коренеплоды (без дополнительного внесения сорбента), имело место увеличение содержания цинка и меди на 13-42% для ячменя и на 4-9% для овса по сравнению с контрольною делянкой.

Таким образом, использование специализированных сорбентов на основе цеолитов, модифицированных микроэлементами, может быть рекомендовано для улучшения качества почвы и увеличения содержания микроэлементов в производстве продукции земледелия.

ROLE AND IMPACT OF THE THE FLAPP PROJECT IN THE CROSS-BORDER WATER MANAGEMENT OF THE UPPER TISZA VALLEY

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Cross-border relations, as well as Euroregions may be able to help in the current, rather chaotic international situation in the catchment area of the Tisza River. A significant part of the catchment area of the Tisza belongs to the Carpathian Euroregion, and this interregional and international organisation also dealt with the ecological problems of the Tisza in the recent period. They intend to examine and manage the catchment area of the Tisza as a unified ecological system, rather than as belonging to a set of isolated territorial sovereignties.

The Hungarian part of the Carpathian Euroregion held a meeting in 2001 in Baia Mare, the Romanian city near which the cyanide pollution originated. During this Regional Council meeting, I proposed a new project called the 'Living Tisza'. Mr. Alfred Evers of the Euroregion Meuse-Rhine also participated in the meeting, since the Meuse-Rhine and the Carpathian Euroregions have a cooperation as 'twin-euroregions'. When Mr. Evers heard about the project proposal, he offered support via a training and exchange programme between water and environmental experts from the Meuse and the Tisza areas.

As a first step, the leaders of the Euroregion Meuse-Rhine invited the parties concerned with a programming seminar held in Maastricht. Perhaps it is not too immodest to believe that this was a very important step along the road, as a result of which our big international cooperation, the FLAPP project unfolded.

From January 2005 until August 2007 water managers and researchers from 35 organizations in 12 countries exchange knowledge and experiences on how to apply sustainable flood management solutions in practice. This is done in the framework of an EU-funded (INTERREG III C) network on Flood Awareness and Prevention Policy in border areas (FLAPP).

MODERN WATER PURIFICATION FROM HEAVY METALS BY ACTIVE CARBONS OBTAINED WITH CHEMICAL ACTIVATION OF CORNELIAN CHERRY STONE

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Active carbons with high porous characteristics (S_{BET} = 980-2100 m^2/g, V_Σ = 0,45-1,0 sm^3/g) from cornelian cherry stone have been obtained by chemical activation with phosphoric acid. Optimal impregnation coefficients (Xp= 1,0-1,25) have been established. Sorption activity of ACs obtained against heavy metals (Cd^{2+}, Cr^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) has been investigated.

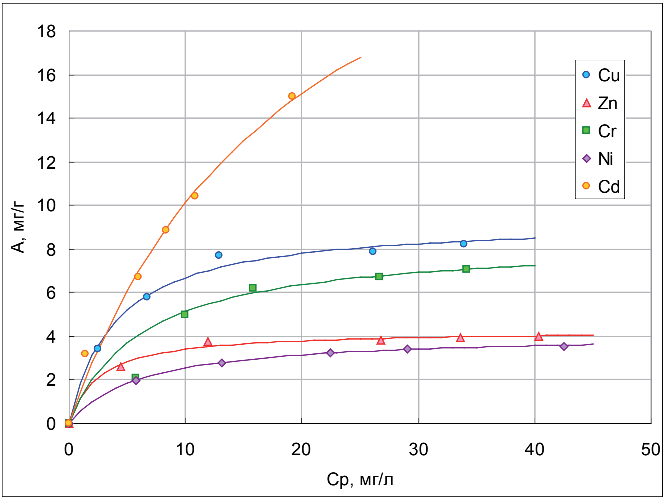

Fig. 1 **Adsorption isotherms of Ni^{2+}, Cr^{3+}, Cu^{2+}, Zn^{2+} and Cd^{2+} ions with active carbon, derived by phosphoric acid activation of cornelian cherry stone with a coefficient of impregnation XP = 1,25.**

By adsorption of ions the activity rank has been defined. It was observed that maximum adsorption becomes apparent concerning to Cd^{2+}, Cu $^{2+}$ и Zn^{2} ions. As may be seen, under increasing of the equilibrium concentration upto 14 or 15 mg/g adsorption capacity of Ni^{2+}, Cr^{3+}, Cu^{2+}, Zn^{2+}ions increases. At higher concentrations adsorption is practically not changed, that testifies to the saturation of the adsorbent and the limit values of sorption. At the same time for the Cd^{2+} ions there is observed a constant sorption capacity in the investigated range of concentrations (up to 20 mg/l). Full saturation of the adsorbent ions Cd^{2+}, should be expect when they reach a higher equilibrium concentrations. Excellent character of Cd^{2+} sorption of ions from sorption of other ions allows to conclude about the prospect of the use of carbons from cornelian cherry stone for the separation of cadmium from other ions at high concentrations (> 20mg/l).

Acknowledgments
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ПОЛИФУНКЦИОНАЛЬНЫЕ СОРБЕНТЫ БЫСТРОГО РЕАГИРОВАНИЯ

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Проведен обзор состояния вопросов синтеза, исследования свойств и практического применения полифункциональных сорбентов (ПС) на основе растительного сырья, углеродных материалов и природных минералов.

Теоретически обоснованы и экспериментально проработаны способы получения полифункциональных сорбентов. Показано, что существенным фактором, определяющим высокие эксплуатационные характеристики, прежде всего селективность и сорбционную емкость, является обеспечение необходимой пропорциональности составляющих.

С использованием методов ЭПР-, ИК-, ЯГР-, ЯМР- спектроскопии, дериватографии, электронной микроскопии, рентгеновской и рентгено-флуоресцентной спектроскопии, физико-химических и микробиологических методов анализа и данных адсорбции из растворов исследована пористая структура ПС, природа функциональных поверхностных групп, наличие дефектов структуры, а также центров сорбции и катализа различного типа.

Изучены сорбционные, ионообменные и каталитические свойства ПС, включая иммобилизованные разновидности сорбентов, в процессах сорбции, десорбции, фитосорбции, биодеструкции, катализа и др. Выявлена повышенная сорбционная способность у ПС, характеризующихся высокими значениями СОЕ и содержащих в поверхностном слое функциональные группы различной природы.

Найдено, что ПС способны проявлять свойства буферного типа, благодаря чему в сочетании с высокой сорбционной способностью к ионам железа-П, могут быть рекомендованы в качестве его эффективных поглотителей из биологических жидкостей.

Разработаны способы модификации ПС путем введения ионов биометаллов, кластерных структур различного типа, иммобилизации микроорганизмами и др.

Экспериментально показано, что ПС проявляют высокую (более 95%) сорбционную способность по отношению к широкому спектру ионов тяжелых металлов и органических соединений, что открывает перспективы их применения для очистки сточных вод полигонов бытовых и промышленных отходов мегаполисов - степень очистки достигает 99 %.

Теоретически обоснована и подтверждена экспериментально возможность получения ПС с управляемыми свойствами с использованием регулируемых параметров в системе хаос-порядок при условии варьирования степени пропорциональности компонентов и переходе системы из состояния детерминириванного хаоса в состояние устойчивого равновесия.

Рассмотрены практические примеры очистки экосистем от радионуклидов, ионов тяжелых металлов, нефтепродуктов, пестицидов, особо опасных вирусов и патогенной микрофлоры, а также перспективы использования ПС при ликвидации последствий экологического терроризма и получения чистых продуктов органического земледелия.

ФИТОСОРБЦИЯ-ЭФФЕКТИВНЫЙ МЕТОД ОЧИСТКИ ПОЧВ ОТ ЭКОТОКСИКАНТОВ

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Обобщены результаты исследований особенностей очистки природных и технологических вод, а также земель, загрязненных радионуклидами и ионами тяжелых металлов (Чернобыльская зона) с использованием разработанного в ИСПЭ НАН Украины фитосорбционного способа. Показано, что внесение углерод - минеральных сорбентов в прикорневую область растений обеспечивает повышенный переход радионуклидов (в 6-8 раз в сравнении с контролем) в зеленую массу с одновременным приростом самой биомассы в 2–3 раза.

Установлено, что степень очистки почвы за один вегетативный период возрастает с 4 до 26 %. Экспериментально обнаружено неизвестное ранее явление влияния внесения в грунт биоактивных сорбентов, ответственных за сорбционно-биологическую деструкцию экотоксикантов, на эффективность процесса накопления биомассы энергетических растений.

Таблица 1

Тип растений	**Степень накопления радионуклидов, кБк/кг**	**Суммарный коэффициент очистки**
рапс в присутствии сорбционного материала	7,65	10,5
рапс без сорбента	1,7	1,0

Новым является уникальное сочетание свойств комбинированных сорбентов, которое состоит, во-первых, в стимулировании перехода радионуклидов в растения благодаря отсутствию в почве и сорбентах ионов калия и кальция, а также наличия в сорбентах повышенного количества азота, амония и фосфора, во-вторых – инициированию процессов перехода радионуклидов в зеленую массу и ускорению процессов накопления зеленой биомасы благодаря синергическому действию микроэлементов комбинированных сорбентов и микробных культур природного происхождения.

Установлено, что природные минералы и композиционные сорбенты на их основе регулируют процессы поступления ионов тяжелых металлов в зеленую массу растений и проявляют высокую (болем 90 %) эффективность в процесах очистки экосистем от них, а также от радионуклидов.

Таблица 2

Вид сорбционного материала	**Участок №1 – природный влажный грунт**		**Участок №2 - повышенная влажность грунта***	
	Содержание радиоцезия в рапсе, кБк/кг	Коэффициент выноса	Содержание радиоцезия в рапсе, кБк/кг	Коефициєнт выноса
контроль **	1.30	0.80	1.30	0.90
уголь	1.03	0.50	1.30	1.60
цеолит	1.19	1.50	1.40	1.70
уголь+цеолит	2.90	1.60	3.40	2.10
комбинированный	3.50	2.15	5.10	3.20

*за счет использования водонакопительных сорбентов

**(дернисто -подзолистые грунты)

КОМПОЗИТНЫЕ СОРБЕНТЫ ДЛЯ ОЧИСТКИ ВОДНЫХ ЭКОСИСТЕМ ОТ ИОНОВ ТЯЖЕЛЫХ МЕТАЛЛОВ

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На сегодняшний день с учетом ухудшения и непредсказуемости экологической ситуации в мире применение природных сорбентов для решения задач очистки экосистем от загрязнений представляет как научный, так и практический интерес. Среди широкого разнообразия сорбционных материалов сорбенты на основе биомассы Мирового океана и прибрежных зон являются наиболее перспективными и эффективными, как постоянно возобновляемые сырьевые источники.

В работе представлены результаты исследования сорбционных свойств сорбционных материалов на основе водорослей по отношению к ионам тяжелых металлов (свинец, кадмий, цинк, медь, железо). Были использованы водоросли Атлантического океана (Великобритания) и Черного моря (Украина), а именно - водоросли типа Laminariales. Анализ концентрации тяжелых металлов производили на атомно-адсорбционном спектрометре типа С-115 М1.

Результаты изучения кинетики поглощения ионов тяжелых металлов сорбентами на основе водорослей из водных растворов показали, что сорбция протекает наиболее эффективно в течение первых 5-ти минут (извлечение >90 %).

***Таблица 1*. Эффективность сорбции ионов тяжелых металлов из водных растворов сорбентами на основе водорослей**

Тип сорбента	**Адсорбция,%**			
сорбент на основе водорослей типа Laminariales	Cd^{2+}	Pb^{2+}	Cu^{2+}	Zn^{2+}
	98,0	95,6	96,6	97,0

Таблица 2. **Сорбция ионов Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} сорбентами на основе водорослей из смеси модельных растворов**

Тип сорбента на основе водорослей	Zn^{2+}		Cu^{2+}		Pb^{2+}		Cd^{2+}	
	а, мг/г	а, %	а, мг/г	а, %	а, мг/г	а, %	а, мг/г	а, %
водоросли-1	5,4	40	15,7	94,0	12,1	94,7	10	84
водоросли- 2	3,7	27	14,6	87,0	12,2	96,0	8,0	67
водоросли- 3	5,9	44	14,8	88,0	12,6	98,4	11,9	90
водоросли- 4	4,7	35	15,7	93,7	12,6	99,1	8,6	32

(Т:Ж =1:100, pH $_{исх}$5,8, $C_{исх\ Cd}$ = 120,3 мг/г, $C_{исх\ Zn}$ = 135 мг/г, $C_{исх\ Cu}$ = 167,5 мг/г, $C_{исх\ Pb}$ = 127,5 мг/г, время контакта - 4,5 час.)

Таким образом, показано, что сорбенты на основе водорослей могут быть успешно использованы для глубокой очистки водных экосистем от ионов тяжелых металлов (Pb, Cu, Zn, Cd).

О ВЛИЯНИИ СИДЕРАТОВ НА ПРОЦЕССЫ ВЫРАЩИВАНИЯ ОВОЩНЫХ КУЛЬТУР НА ПОЧВАХ, ЗАГРЯЗНЕННЫХ ИОНАМИ ТЯЖЕЛЫХ МЕТАЛЛОВ

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Сорбционная терапия грунтов, как направление в развитии европейской и мировой агротехнологии, на сегодняшний день находится в стадии зарождения, хотя первые работы в этом направлении появились в средине 90-х годов XX века. Метод сорбционной терапии грунтов (СТГ) предметно исследуется сейчас во многих странах мира с учетом специфики каждого региона в отдельности.

В рамках общей теории сорбентов метод СТГ применительно к аграрному комплексу рассматривается как разновидность регулирующей, сорбционной, иммобилизационной, каталитической, биоактивирующей, биодеструктирующей, синергической роли природных сорбционных средств, целью которого является, с одной стороны, восстановление плодородности грунтов, с другой – повышение их продуктивности, в третьих - выращивание на восстановленных грунтах экологически чистой сельскохозяйственной продукции.

Новым направлением технологии СТГ является сорбционная нормализация питательных характеристик сельхозпродукции, обеспечивающих нормальный уровень жизни человека в условиях усиливающего загрязнения окружающей среды.

В работе проведено исследование влияния сидератов и природных силикатов на процессы поведения растений на почвах, загрязненных ионами тяжелых металлов.

Выявлено неадекватное поведение растений в условиях экологического загрязнения почв ионами тяжелых металлов, заключающееся в перестройке работы живой клетки растений (ранних овощных культур) под воздействием этих ионов, приводящей к изменению размеров канала клетки, формированию динамически устойчивого равновесия. *Регулирование состояния клетки живых растений* под воздействием углерод-минеральных сорбентов, вносимых в прикорневую систему растений и микробной культуры, сопровождается изменением электрохимических, физических и биохимических показателей водных растворов прикорневой системы и ведет к регуляторному изменению проницаемости клетки. Это позволяет обеспечивать как поступление ионов «элементов жизни», так и блокировать поступление ионов тяжелых металлов в клетки живых растений, находящихся в условиях неустойчивого равновесия непродолжительное время. В течение этого времени происходит неадекватное изменение поведения живой клетки, в результате чего в каналах клетки регулируются процессы миграции ионов тяжелых металлов и «элементов жизни» в структуру растений и обеспечивается жизнедеятельность растения в целом.

Таким образом, установлено, что с применением технологии СТГ в условиях постоянно изменяющегося экологического стресса почв под воздействием неблагоприятных факторов можно получать экологически чистую продукцию, необходимую для нормальной жизнедеятельности человеческого организма.

О ВЛИЯНИИ БИОГУМУСА НА ПРОЦЕССЫ ВЫРАЩИВАНИЯ ОВОЩНЫХ КУЛЬТУР НА ПОЧВАХ, ЗАГРЯЗНЕННЫХ ИОНАМИ ТЯЖЕЛЫХ МЕТАЛЛОВ

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Загрязнение окружающей среды, вызванное техногенными и экологическими катастрофами, требует разработки специфических сорбционных материалов, способных эффективно извлекать из экосистем сложного состава ионы тяжелых металлов, обуславливающих возможность получения экологически чистой продукции.

В последние годы особенно возрос интерес к сорбентам природного происхождения на основе отходов растительного сырья, переработанного с использованием калифорнийского червя и бактерий - биогумуса. Это связано с тем, что такие материалы являются постоянно возобновляемым источником дешевого сырья и их производство не вызывает загрязнения окружающей среды. При этом биогумус улучшает структуру почвы и ее водно-физические свойства, в нем повышенное содержание водорастворимых форм азота, фосфора, калия и др.

В работе проведено исследование поведения ранних овощных культур на почвах, загрязненных ионами тяжелых металлов в присутствии биогумуса.

Изучена специфика сорбции ионов тяжелых металлов из водных растворов сложного состава почвами, содержащими биогумус. В качестве водных растворов использовали растворы, содержащие свинец, кадмий, цинк и медь. Концентрацию ионов тяжелых металлов варьировали в интервале 1-200 мг/л. Сорбцию проводили в динамических условиях в течение от 3 минут до 3 часов. pH растворов варьировали в интервале 5,5 –7,0.

На фото приведены результаты поведения растений в присутствии биогумуса на загрязненных грунтах.

Показано, что применение биогумуса растительного происхождения приводит к повышению поглотительной способности грунтов по отношению к ионам тяжелых металлов. Найдено, что десорбционная способность грунтов по отношению к ионам тяжелых металлов составляет не более 10-15 %, что дает возможность выращивать овощные культуры на загрязненных почвах с регулируемым содержанием ионов меди и цинка, необходимых для обеспечения жизнедеятельности организма человека.

NATURA 2000-ES JELZŐFAJOK MONITOROZÁSA A BEREGI-SÍK KÁRPÁTALJAI RÉSZÉN

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Az Európai Unió felismerte a természeti környezetben bekövetkező nagyléptékű változásokat. Ezért a tagországok biológiai sokféleségének megőrzése érdekében létrehozta az európai vadon élő növény- és állatvilág, valamint élőhelyek védelméről szóló irányelvét (*Habitats Directive*) és ennek eszközeként a *különleges természetmegőrzési területek* rendszerét, NATURA 2000 néven. Az európai uniós csatlakozás részeként Magyarországon is megtörtént a NATURA 2000 hálózat kialakítása (Fülöp, 2005). 2004-ben az EU jogszabályoknak megfelelően lezajlott a NATURA 2000-es területek kijelölése Magyarország egész területén. Ennek megfelelően egyedül a Kárpátaljával szomszédos Szabolcs-Szatmár-Bereg megyében 50 természetmegőrzési területet alakítottak ki, összesen 54 802 hektáron. Ezek közül számos olyan, nagykiterjedésű terület van a Beregi-síkon, amelyet kettészel a magyar-ukrán államhatár, így a kijelölt területek ma még megszakadnak az országhatárnál. Viszont a védendő növény- és állatfajok többségének elterjedési területe átnyúlik az országhatáron, azonban a kárpátaljai részen még semmilyen állománybecslés nem történt, és a védelmi intézkedések sem érvényesek. Ahhoz azonban, hogy egy adott régióban hatékony fajmegőrzési tervet alakíthassunk ki, ismernünk kell az adott faj régión belüli populációinak helyzetét és méretét. Így a Beregi-sík magyar oldalán előforduló, az Élőhelyvédelmi Irányelv hatálya alá tartozó rovarfajok monitorozása a sík ukrajnai oldalán is elengedhetetlen. Eddigi alapozó jellegű kutatások során kiderült (Szanyi 2012 a, b), hogy több NATURA 2000-es jelzőfaj előfordul a sík kárpátaljai részén (nappali lepkék: *Lycaena dispar rutilus;* egyenesszárnyúak: *Isophya stysi, Odontopodisma rubripes*), további fajokról vannak korábbi irodalmi adatok (nappali lepkék: *Zerynthia polyxena, Euphydryas maturna*), valamint a meglévő élőhelyeik alapján valószínűsíthető további fajok (nappali lepkék: *Parnassius mnemosyne, Leptidea morsei, Lopinga achine*; egyenesszárnyúak: *Pholidoptera transsylvanica*) jelenléte is. Ezek az eredmények megalapozzák a kutatások folytatását. A jövőben a már beazonosított fajok populációméretének felmérése mellett el kell végezni a korábban közölt adatok felülvizsgálatát, valamint az alkalmas élőhelyeken a még meg nem talált fajok keresését. Ezzel olyan hiánypótló munka születhet, amely felhasználható határon átnyúló védett területek kijelölésére.

NEW AND NATURE CONSERVATION SIGNIFICANT SPIDER SPECIES ON MOWED MEADOWS OF CARPATIAN BASIN

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The main objective of this article is to report the composition of the spider assemblages of valuable lawns standing under a treatment on the Mátra Mountain of Hungary and fragmented natural habitats of loess valleys of North Serbia. The spiders are distinguished indicator organisations, they respond sensitively to the structural change of the environmental factors and the habitat. The various treatments - than the mowing - have an effect on the communities somposition.

The study areas included nine Hungarian and seven Serbian grassy habitats. The common feautre of the meadows that standing under a nature conservation treatments. Between 2007 and 2012 double glass pitfall traps were established on the sampling sites. Besides the plastic glass traps method we engaged grass netting, as well.

In total we collected 137 species of 27 families, 79 of these species are on Red List of European countries. 5 of these species are critically endangered and other 5 are extinct. The *Nemesia pannonica* is the most valuable spider in Hungary (10 000 HUF). First time was proved its occurrences of North Hungary and North Serbia. Six species, *Alopecosa schmidti, Antistea elegans, Liocranoeca striata, Drassodes villosus, Thanatus striatus, Singa lucina* were first recorded in the fauna of Serbia. From Hungary we did not identify the 6 new speicies of Serbia, but their occurence proved in Hungary earlier. The *D. villosus* has few data from incidence in Hungary, as well. *A. smithi* and *A. elegans* are threatened species in more countries of Europe. From 725 species of Hungary 15 are vulnerable. In Serbia the

recent past 17 spider species got to the list of the protected species. These numbers compared with other European countries are low. E. g. 64 of collected species are on Red List of Germany. Opposite this in Hungary only 5, in Serbia only 2 species are vulnerable.

The grassy habitats have weak fertility but they contain many nature conservation significant species such as endemic and aboriginal species. These semi-natural grassy habitats need the mowing to the survival. The loess valleys of North Serbia are less investigated where many threatened species live and probably so species were found there which unknowns for the science. Therefore the conservation and examinations of these habitats are indispensable.

Key words: *threatened spider species, grassy habitats, Mátra Mountain of Hungary, loess valley of Serbia*

GLOBÁLIS ÉS LOKÁLIS ÖKOLÓGIAI ÉS GAZDASÁGI PROBLÉMÁK AZ IDEGEN NÖVÉNY- ÉS ÁLLATFAJOK KAPCSÁN (ÖKOLÓGIAI ÉS GAZDASÁGI BIZTONSÁG) / GLOBAL AND LOCAL PROBLEM OF ALIEN PLANTS AND ANIMALS IN GENERAL ECOLOGY AND ECONOMICS (ENVIRONMENTAL AND ECONOMIC SECURITY)

Szikura József, Hadnagy István, Kolozsvári István,
Kopor Zoltán, Ljubka Tibor, Zselicki István

II. Rákóczi Ferenc Kárpátaljai Magyar Főiskola, id. Fodor István TTKI

Jelen munka témájának keretében fontos megemlíteni a biológiai szennyezőként értelmezhető invazív – özönnövény és állatfajok elterjedésének globális jelentőségét. Ezek a fajok bizonyos esetekben olyan mennyiségben jelenhetnek meg egy-egy területen, amely környezetünk ökológiai stabilitásának, valamint társadalmunk gazdasági és szociális biztonságának tekintetében komoly veszélyforrásként értékelhető. Példaként említhetjük a filoxérát, a kaliforniai pajzstetvet, a burgonyabogarat (Leptinotarsa decemlineata), a fehér szövőlepkét (Hyphantria cunea), a kukoricabogarat (Tribolium castaneum), a parlagfüvet (Ambrosia artemisiifolia), a Sosnowsky-medvetalpat (Heracleum sosnowskyi), a süntököt (Echinocystis lobata), a kanadai aranyvesszőt (Solidago canadensis), a selyemkórót (Asclepias syriaca), az Amaranthus és sok más nemzetség fajait.

Az erdőirtás korunkra éghajlatformáló tényezővé lépett elő, számtalan újabb környezeti problémát vonva maga után. A genetikailag előállított növény- és állatfajták szintén szennyezik a természetes környezetet. Megjelenésük kiszámíthatatlan és megjósolhatatlan katasztrófák eredőivé léphetnek elő. Ahhoz, hogy megakadályozzuk a lehetséges negatív következményeket, szakképzett, becsületes és megbízható kutatókra van szükség, akik képesek megakadályozni az invazív fajok és az ökológiai degradációs folyamatok továbbterjedését.

Korunk tudósainak kiemelt feladata, hogy elősegítsék az elődeink által, akarva vagy akaratlanul, de évszázadokon keresztül elkövetett, a természetes környezetet átalakító és kifosztó folyamatok megállítását. A mi nemzedékünk és a jövő nemzedékek faladata, hogy visszafordítsuk környezetünk pusztítását, mivel csak így lehet esélyünk megóvni bolygónk ökológiai egyensúlyát.

ELECTROKINETIC POTENTIAL AND FLOCCULATION OF CLAY MINERAL PARTICLES BY POLYELECTROLYTE AND SURFACTANT MIXTURES

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Polymers are widely used as flocculants for suspensions in many industrial applications, such as mineral processing, papermaking, water treatment and biotechnology. In recent years there has been considerable interest in the use of multi-component flocculants, especially dual-polymer and polymer-surfactant systems. In the latter case, there can be significant advantages over the use of single polymers.

The objective of our study was to elucidate the laws and mechanisms of flocculation of kaolin and bentonite particles by anionic and cationic surfactants, polyelectrolytes (PE) as well as their binary mixtures. The effect of the surfactant/polyelectrolyte dose, charge density (CD) of the polyelectrolyte, mixture composition, ratio between positive and negative charges in the mixture, sequence of the components addition on the electrokinetic potential, kinetics of aggregation, size and strength of flocs formed has been determined. Flocculation experiments were performed in a flow system using a Photometric Dispersion Analyzer PDA-2000. Electrokinetic potential of particles was measured by Zeta NS (Malvern) instrument.

It has been shown that addition of cationic polyelectrolytes/surfactants to the suspension leads to a significant decrease in the negative ζ-potential and to a change in the sign of the charge of particles. Changes in the ζ-potential are more pronounced for samples with higher charge density. Addition of anionic polyelectrolytes/surfactant gives a more than twofold increase in the $|\zeta|$-potential of both bentonite and kaolin particles. In mixtures of cationic and anionic polyelectrolytes, whatever the sequence of addition, the particles acquire ζ-potential that is typical for particles bearing only anionic polyelectrolyte.

A synergism in flocculation capacity in mixtures of moderate and weakly charged polyelectrolytes was observed. Mixtures of medium/low charged anionic polyelectrolytes and medium or low charged cationic flocculants gave optimum flocculation at mass ratios, corresponding to many-fold excess of negative charges over positive ones in the adsorbed layer. Deviation from the optimum composition gave slower flocculation and significantly smaller floc sizes. In mixtures of cationic PE+ cationic surfactant the best effect/maximum flocs size was achieved in the event of addition of pre-prepared mixture to the suspension. An initial intensive short stirring the suspension accelerates the aggregation process and increases the size of flocs independently of the sequence of polymers addition. The laws observed were explained by features of polyelectrolytes conformation in adsorbed mixed polymer layers.

Examples on the application of dual polymers and surfactant/polymer mixtures in purification of municipal wastewaters, recycled and wastewaters of mineral processing, in papermaking and wastewater sludge treatment are given.

SYNTHESIS AND MODIFICATION OF HIGH NITROGEN CONTENT CARBON NANOTUBES USED FOR PREPARATION OF CNT BUCKYPAPER MEMBRANES

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Carbon nanotubes (CNTs) are new special sorbents which hold interesting position in carbon-based adsorbents. The carbon nanotubes are highly porous materials and of hollow structure, with large specific surface area, and they are characterised by strong interaction to pollutant molecules. The application of CNTs for removal of hazardous gas components, such as nitrogen-oxides or organic vapour, as adsorbents for heavy metal ions (Ni^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} etc.) or organic pollutants is well known. Adsorption properties of CNTs are strongly affected by their surface functional groups like -OH, -COOH that change the wettability of the CNT surfaces. In membrane technology the self-supported carbon nanotube film, the so called as buckypaper can be used, which is a macroscopic paper-like layer of CNTs; it forms continous and porous network structures. These structures can be produced from stable suspension of carbon nanotubes, and the CNT film is formed by filtration. Doping with metal or nonmetal heteroatoms can change the nanotubes adsorption properties. Also carbon nanotubes doped with heteroatoms, can be used to manipulate the CNT oxidation resistance; for example, the oxidation resistance of the nanotubes doped by nitrogen is decreased.

In our experiments, N-doped multiwall carbon nanotubes (CNTs) were produced by catalytic vapor deposition (CVD) method using buthylamine and cyclohexilamine as the C/N precursors and Ni (5 wt%) and Fe (5 wt%) as catalyst materials . The CNT morphology was investigated with TEM (Transmission Electron Microscopy) technique. Measurements with elemental analyzer (Vario Macro) showed that the synthesis temperature changes the nitrogen content: higher reaction temperature causes lower nitrogen content of CNT. The structural defects of samples were characterized by Raman spectroscopy. The type of the nitrogen that is incorporated into the structure of tubes has been determined by XPS (X-ray photoelectron spectroscopy) technique. The obtained bamboo structure carbon nanotubes were treated with oxidizing acid, H_2SO_4/HNO_3 mixture. Formation and relative content of oxygen-containing functional groups on the CNT surface was measured using FTIR (Fourier transformed Infrared Spectroscopy). It has been shown that due to the presence of functional groups (-COOH, -OH), the hydrophilic character of the carbon nanotubes considerably increased. This enhances the ability of CNTs to form stable dispersions in aqueous medium. The electrokinetic potential of functionalized nanotubes has been determined; negative values of zeta-potential that reach several tens of mV were measured. A correlation between sedimentation stability and zeta-potential of nanotubes has been found. The data obtained will be used for the development of efficient CNT based adsorbents and membranes suitable for solving environmental protection/water treatment problems.

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CONDITION STUDIES OF THE TISZA OXBOWS NEAR RAKAMAZ

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In this study the Nagy-Morotva-backwater system were investigated, in Hungary. The aim of our study was to test the effects of three years on the water chemistry parameters on two studied oxbows (Nagy-Mester and Kis-Zátony) to assess the water quality of Nagy-Morotva-backwater system. Water samples were collected from different vegetation type. The physical parameters were measured on site, and after sampling the chemical parameters were measured in laboratory measurements. The 13 sampling points are chosen in order to correlate with the various macrovegetation. Based on our results, we have established that there are significant differences between Nagy-Mester and Kis-Zátony oxbow based on physical and chemical parameters of water. Seasonal differences were also observed.

Keywords: *physical parameters, chemical parameters, aquatic vegetation, water quality*

OUTDOOR OCCURRENCE OF GREENHOUSE ARMADILLIDIUM NASATUM BUDDE-LUND 1885 (CRUSTACEA: ISOPODA: ONISCIDEA) ON HUNGARIAN HIGHWAY MARGINS

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The composition of terrestrial isopod assemblages was investigated on highway margins in Hungary. The aim of the study was to answer what native species tolerate the conditions of highway margins, collecting faunal data, stating the combination of the species specific of each habitat and examining of its spread and prior natural habitats.

198 pitfall traps were established on 33 collecting sites along 4 Hungarian motorways (M1, M3, M5, and M7) and the ringroad (M0) that is treated like a highway for 3 times (spring, summer, autumn) 3 weeks periods in 2011and 2012. The sampling points are in the side habitats and next to the lay-bys.

In the project 11 individuals of a greenhouse (*Armadillidium nasatum*) species were found incidentally, indicating the role of the human activity in the spreading. 4 individuals were females, while 7 were males. The individuals occurred only in spring and summer but we did not find *A. nasatum* in autumn. The species was described by a Danish zoologist, Gustav Henrik Andreas Budde-Lund in 1885. In Hungary Sándor Farkas found it in Pécs (unpublished data). In Hungary the mediterranean *A. nasatum* is only from greenhouses and big cities, such as Botanical garden of ELTE, Island of Old Buda, Yard of SZIE ÁOTK and Pécs. According to all probabilities it may be from one of Budapest's botanical gardens or parks possibly. The species occured only on one site, Csepel lay-by on M0 highway side region, where the vegetation is grass that is mowed continuously. The surrounding places are plough-land, industrial area and the Danube.

Due to the fact that the species was found in both study years, we suppose that they survived and adapted to the outdoor conditions probably. The increasing outdoor occurrence of greenhouse species these are known in Hungary (*Trichorina tomentosa Buddelundiella cataractae* and *A. nasatum*) is notable, and it is necessary to expect repetitive appearance and adaptation of invasive alien species in changed habitats primarily. Motorway margins may function as connecting ecological passages among natural habitats for several arthropod species. Accordingly, species being able to live in the grass level of motorways may expand further their area along motorways.

Keywords: *Isopods, Armadillidium nasatum, highway margins, Hungary.*

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TRANSPORT MODELLING OF DNAPL POLLUTANTS AND THE INCREASE OF RELIABILITY

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The study of the effects of chlorinated hydrocarbons has been given due care for 30-40 years in the world, and for 20 years in Hungary. Nowadays, a lot of modern in situ remediation technologies are known connected with these contaminants.

In any case forward laboratory tests and technological investigations are essential. The concentration of the contaminants, the relation of the flow, and geological morphology of the location are absolutely necessary to know. In order to plan the ground and groundwater treatment technology it is important to obtain the aforementioned information, because the underground layers are heterogeneous and the hydrogeological relations are complex.

The main point of our research is to find and select appropriate transport-modelling programs, which can handle the underground transport processes of chlorinated hydrocarbons. In our research the Groundwater Modelling System (GMS) was used to handle case-study problems connected to DNAPLs. For modelling objectives the UTCHEM code was applied which is suitable for modelling continuous aqua-phase. Relative permeability curves from laboratory measurements were used to make more accurate calculations. A new method applying immiscible displacement was proposed at the University of Miskolc to provide these petrophysical properties. The SEAM3D module can be used for transporting modelling solute DNAPL contaminants. The result of modelling the Hungarian TCE compound has been shown.

Keywords: *DNAPL, transport modeling, GMS, groundwater.*

POROUS STRUCTURE AND SORPTION PROPERTIES OF THE SOL-GEL SYNTHESIZED ZIRCONIUM PHOSPHATES AND SILICATES

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Zirconium phosphates and silicates have recently found wide use in the chemistry, technology and medicine as ion exchangers, adsorbents, catalysts, carriers for active reagents, fillers. This is mainly due to their high thermal and hydrolytic stability in various media, and the possibility of the targeted synthesis of materials with a high selectivity to specific ions, for example, towards certain ions in the case of solution or gas purifications. Among the large variety of phosphates and silicates of zirconium currently in use, a special place is occupied by materials produced by sol-gel methods.

Our Institute has a long history of sol-gel synthesis of gel zirconium phosphate and silicate in the form of spherical granules of the necessary size, which is especially valuable for practical usage in sorption columns. The granulated gels developed by us have significantly higher specific surface area, mechanical strength of granules, higher selective absorption towards certain ions, higher sorption capacity than traditionally used crystalline powders of zirconium phosphates and silicates.

We have developed the zirconium phosphate gels which have high thermal stability. These materials have a specific surface area of about 600-800 square meters per gram to the temperature of 900 C deg. This thermal stability determines their value as adsorbents, catalysts and carriers.

The phosphates and silicates of zirconium which were significantly improved by us have a lot of advantages in comparison with traditionally used ones for wastewater treatment from heavy metals both in terms of the technology simplification also in the efficiency of wastewater purification.

It is necessary to note that we have elaborated the high effective phosphates and silicates of zirconium for purification of radioactive waste, in particular the "Shelter" object in Chernobyl. Utilizing our sorbents we have purified radioactive effluents from cesium and strontium isotopes to trace residual concentrations.

Especially it is necessary to mention the medical usage of our zirconium phosphates and silicates. Our gels in granular form are far more effective than currently used for the purification from ammonia of human blood plasma. Moreover, we were able to purify the blood directly from the urea itself, thus eliminating the step of fermentative decomposition of urea to ammonia.

MONITORING FOOD SUPPLY AND FEEDING HABITS OF IMPERILLED SPECIES

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Nowadays, monitoring and managing restoration of imperiled species is a central problem of wildlife management. We used the red fox *Vulpes vulpes* L. as a modell to assess a cost- and time-effective methodology which can comprise the food supply and food availability. Without knowledge of species' diet, food availability and supply of restoration sites the positive results will not be guaranteed. Mammalian predators rely on food supply which may change seasonally and locally. That suggests predators should be opportunistic and their feeding habits will show spatiotemporal changes. In our study we investigated whether the food choice of the generalist red fox depends on food availability. As the published methodology used in diet analysis varies from study to study, we optimised the methodology, considering all steps from collecting faeces to statistical analysis of the data. In order to obtain accurate and reliable results, it is necessary to use a dependable methodology that ensures reliability at all steps. We determined the minimal sample size, the minimal distance between collecting points and the minimal number of fragments needed for identification. Then we collected fox scats and estimated the relative role of prey species in the diet such as *Microtus sp*., *Apodemus sp*., *Capreolus capreolus*, *Cervus cervus*, *Lepus europeus*. We found that variation in scat composition is most affected by the individual scat composition; other factors (within-scat variation, error in identification, within or between observer reliability) are negligible. As a result, we proposed a methodology providing minimal overall error. We also studied the prey availability with different methods, and tested the reliability of spotlighting, one of the main methods in density estimates. We tested experimentally the effect of visibility on the result of spotlighting and found that eyespots reflecting the spotlight

are crucial in noticing the target. Having developed our methodology we collected field data over a period of three years to determine how fox diet reflects food availability. The diet was dependent on both site differences and seasonal changes of food supply, the availability of potential prey species, the choice and preferences of individuals.

AUTHOR INDEX

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