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Visualization of Humic Acids Penetration in Higher Plants Vascular System Using Tritium Autoradiography

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Stimulatory effect of HA on the plant growth and germination is well known. Nevertheless, the mechanism of that effect is unknown, as well as the HA distribution in the plant tissues. Recently, a new method of direct labeling of humic substances with tritium was developed that allows producing labeled preparation completely identical in their properties to the native preparations [1] and an opportunity to use the produced humics to study their behavior in living cells of bacteria has been demonstrated [2]. The objective of the study was to estimate uptake of HA by higher plants and to obtain direct evidence of HA penetration in higher plants vascular system using tritium autoradiography.

Coal HA was isolated from potassium humate produced from leonardite (H/C 0.87; O/C 0.5; C/N 53; Mn = 2.1). Seedlings of wheat *Triticum aestivum* L. were used for the experiments. Eight-day old plants were transferred into the vials containing 15 mL of HA at concentration 5 $\mathrm{mg \cdot L^{-1}}$ with specific radioactivity 0.057 $\mathrm{Curie \cdot L^{-1}}$. Three plants were used per one vial. Absorption time was 24 hours. All the experiments were performed in five replications. The HA distribution study in the plant was performed using tritium autoradiography. For the microautoradiography studies, the sections from wheat shoots and roots was excised and fixed in Navashin buffer according to [3]. Then plant samples were subjected to autoradiography. The nuclear emulsion was used for microautoradiography. Labeled samples getting and purification them from exchange position tritium were held under regulations of [1].

Obtained autoradiogram showed that HA intensely adsorbed on the root surface and accumulated primarily in the cortex area. HA absorbed by plants arrive in the central cylinder zone mainly from apoplast. In the central cylinders HA found in the xylem vessels, which indicate a possibility of acropetally transport. It is important to note that the using of nuclear emulsion allowed us to obtain a much better resolution. In this way the presence of HA in the cortex was shown, as well as within the xylem vessels.

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Investigation of Organic Xenobiotic Chemicals in Soils: A Method of Paramagnetic Probes to Assess Mechanisms of Binding

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In the agro-industrial complex that uses manure to fertilize soils, xenobiotic substances represent a large problem. A variety of xenobiotics (Xe), such as veterinary pharmaceuticals, is inserted into soil together with manure. As a result of binding of Xe to soil constituents, the non-extractable residual (NER) is formed. As shown by some researchers, NER of Xe doesn't lose its toxic effect. It indirectly exerts adverse influence on some soil microorganisms and reduces their quantity. The dynamics of binding of Xe to soil constituents is well known, whereas its mechanism still remains unclear. Risk assessment of NER of Xe on soil biota and the method of the removal of NER from soil are still difficult, because knowledge of its chemical form is lacking.

Xenobiotic metabolism in the human body is influenced by hepatic enzymes and comprises their deactivation via oxidation, reduction, hydrolysis, and hydration. Then, active secondary metabolites conjugate with glucuronic or sulphuric acid, or glutathione, followed by their excretion. In soil, we observe a rapid abiotic binding of Xe to humic substances (HS). The electron paramagnetic resonance (EPR) analysis of contaminated soils using the method of paramagnetic probes (PP) points at similar general mechanisms of unknown binding of Xe to HS, as for example deactivation via disintegration of Xe, followed by conjugation, e.g. covalent binding, with soil constituents.

The experiment includes several EPR measurements of a sample of pure moistened soil, the same soil sample moistened with aqueous solution of PP, and the same soil sample moistened with aqueous solution of PP and Xe. Only in the last case, a cardinal change in the direction of the process from an initial sharp decrease in the concentration of PP radicals to a complete return of the paramagnetic substance to its original radical state after a while is observed.

An interpretation of this phenomenon observed for the first time at our experiment requires discussion of the nature of organic radicals (OR) in HS and the mechanisms of interaction between HS, PP, and Xe. Hypothesizing a structure $O-H\cdots O$ in HS, which is similar to part of quinhydrone, as the source of OR, we model the quantum state of the considered group of atoms as stable if the distance between the outer oxygen atoms R_{OO} is less than the critical value. The group $O-H\cdots O$ represents a weakly bound system that consists of an OR, *i.e.* phenoxyl, proton electron pairs (Proton-Coupled Electron, PCE), and a structure including carbonyl group or quinone, if the distance R_{OO} exceeds the critical value. Due to the nature of HS always, several groups $O-H\cdots O$ with phenoxyl can be found in HS.

According to our model, the first step of the considered mechanism is a transfer of PCE from the above-mentioned weakly bound systems of HS to PP and Xe. The transfer of pairs to PP is measured by a decrease in their radical concentration, whereas the transfer of pairs to Xe is hypothesized to be based on a cardinal change in the direction of considered process from a decreasing of the concentration of PP radicals to a return to their initial state. The strong influence of Xe on the molecular environment in soil deals with a change in the spatial distribution of the electrochemical potential μ that occurs, because of the presence of some atoms with great values of electronegativity in molecule of Xe. It causes a transfer of the significant quantity of PCE to Xe from HS immediately and from PP after a while. This induces breakup of Xe into several parts, which can be bound to active quinones of HS, released via loss of PCE from the group $O-H\cdots O$.

Lignohumate – New Results of NMR and MS

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Semi-sinthetic nanosized humic substances "Lignohumate®" produced from the waste of cellulose industry. These "green chemistry" products used as biologically active substances in a wide range of applications, for example, as growth-stimulating agents in agronomy. A lot of questions related to their structure, composition and biologically activity are still open. Mass-spectra (EI, 70 eV), ^{13}C (150 MHz) and ^{1}H (600 MHz) NMR spectra of "Lignohumate®" and its fractions were studied and following conclusions were made:

^{13}C and ^{1}H NMR spectra of lignohumates are more informative than of humic substances produced from coal, peat and soils because of low-molecular components in their structure.

Quantitative ^{13}C NMR spectra of lignohumates can be successfully used in raw material refinery control in technological processes and express diagnosis of growth-stimulating activity of the final product.

Mass-spectrometry and NMR spectroscopy allows to determine the composition of some low-molecular components of fractionated lignohumates.

Evaluation of Organic Contaminants Properties in Drinking Water

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In the late of 90's it was proved that the major source of carcinogenic halogen compounds in chlorinated water are humic (HA) and fulvic (FA) acids, so that the structure and properties of these compounds have been studied by various methods of analysis. Chloroform was chosen as a marker of the presence carcinogenic properties. In practice, the content of total organic carbon (TOC) in plumbing drinking water supply is from 6 to 12 mg/L and the content of identified organic compounds - not more than 4% of the TOC. Therefore, it is advisable to evaluate the most important properties of the summary measures.

The most important property of humic (HA) and fulvic (FA) acids – their ability to form complexes. Our practical interest is the assessment of the interaction of natural organic impurities present in drinking water, with drugs that are able to form complexes with biometals. In applying the drug "Glutamic acid" there is a side effect of reducing the hemoglobin, which is possible due to the fact that it forms complexes with Fe (III) or Cu (II).

The purpose of research – to evaluate the effects of organic contaminants of drinking water on the complexing properties of glutamic acid to iron (III) and copper (II).

The assessment of the strength of the complexes of glutamic acid with Fe (III) or Cu (II) was performed by spectrophotometry. The essence of the methodological approach is reflected by the following reaction:

$2[CuL_4]^{2-} + 4I^- \rightarrow 2CuI + I_2 + 8L^-$, where L is the organic ligand.

To quantify the process was built calibration relationship between the content of iodine in the system and the optical density measured at a wavelength of 285 nm.

According to preliminary data found the natural drinking water from different manufacturers that are involved in the experiments, contain 2 to 3 mg/L of total organic carbon. In the presence of the drug "Glutamic acid" properties of water system are change strongly.

We can conclude that the effect of reducing the capacity for reduction of iron (III) and copper (II) depends on the properties of organic compounds in solution. For example, glutamic acid in solution in distilled water at a concentration of 50 to 250 mg/L (TOC) has no effect on the recovery of iron, despite the fact that there is a formation of iron - glutamine complexes. However, if the solution of this amino acid is prepared in various kinds of natural drinking water, then there is a striking effect of reducing the ability to recover of iron by 73-100%.

The same trend is observed with respect to the copper (II), when the solutions of glutamic acid, prepared in natural water, reduces the ability of copper to the recovery on 53-88%. Interaction of the copper (II) with glutamic acid, prepared with distilled water, reduces the ability of Cu(II) to recovery by 9% and 39% at a concentration in solution of 50 to 100 mg/L (TOC) respectively.

Thus, in the natural drinking water is necessary to control the total organic carbon and complexing properties of organic impurities. This methodological approach can be used as a method for estimating complexing activity of organic impurities in natural water and drugs in vitro predictive effect on the process of hematopoiesis.

Binding of Heavy Metals by Humic Acids: pH and Ionic Strengths Effects

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Being the main component of the soil organic matter, humic acids (HA) perform important biospheric duties, including regulation of the flows of macro- and microelements, occasionally acting as environmental pollutants, e.g. heavy metals (HM). Thus, studying the interaction between HA and HM is an acute task.

The objects of the present study are HA, isolated out of the oligotrophic peat of Arkhangelsk region according to the technique, stated in study [1]. The elemental and functional composition of the studied sample is presented by authors earlier [2]. The equilibrium characteristics of the binding process were studied by potentiometric titration of the powdered HA using ionometer “Expert-001”, equipped with ion-sensitive electrodes ELIS-131-Pb and ELIS-131-Cd, under changing pH and ionic strengths and stable temperature 25±0,25°C. pH stability during an experiment was preserved by adding 0.05N NaOH to the bulk solution. Sorption capacity of HA was calculated using Langmuir’s equation. Being the function of pH, HA solubility rate was evaluated by studying the content of soluble HA fraction after filtration using spectrophotometer UV 1200 (Shimadzu). Results are presented in Figure 1.

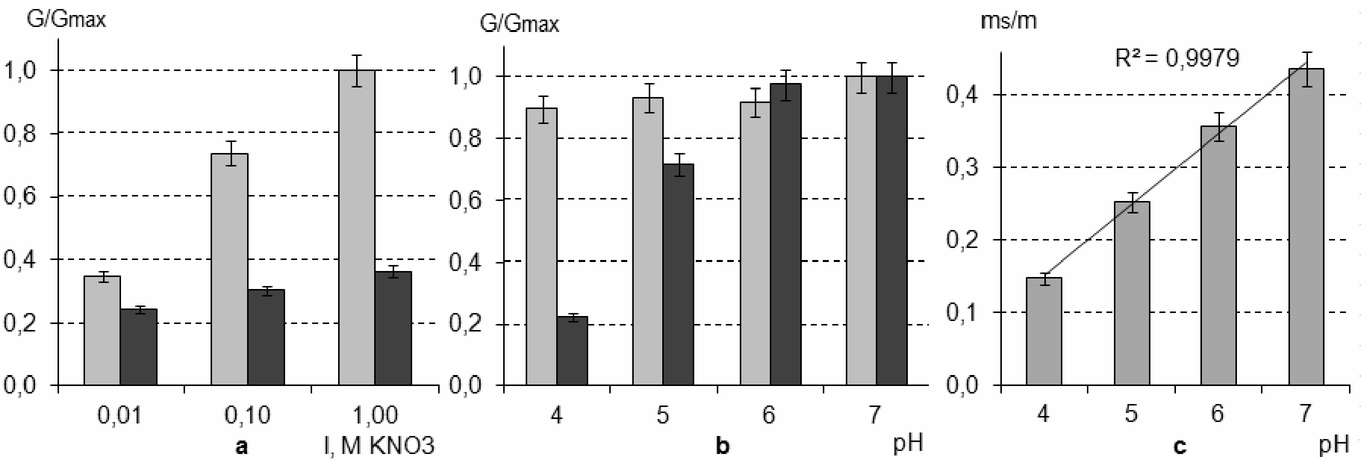

Figure 1. Binding (G) of HM ions (light-grey – Pb (II), dark-grey – Cd (II)) under changing ionic strengths (a) and pH (b); content of soluble HA fractions (ms) under changing pH (c).

According to the Figure 1 it may be stated that HA are partly soluble even at low pH. Thus, it may be assumed, that higher binding of HM under increase of pH is observed due to both adsorption of HM by solid HA’s surface and to the formation of complexes between HA and HM. Highest sorption of Pb(II) = 2.61 mmol/g and Cd(II) = 1.07 mmol/g is observed under 1 M KNO_3 ionic strength. Having a bigger radius, lead ion is less prone to the formation of the hydration shell and thus is better bound by the charged sorbent’s surface. At the same time, increase of binding of HM under increasing ionic strength is due to desalinization effect.

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Chitosan and Its Derivatives in Drinking and Waste Water Treatment

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Due to a combination of unique properties chitosan is one of the most promising biodegradable and non-toxic polymers to be applied at an industrial scale as a flocculant for treatment of drinking water and liquid wastes. Thanks to the presence of amino groups chitosan significantly surpasses other carbohydrate-based polymers in many fields of sorption and separation. Despite obvious advantages, in many countries the chitosan introduction as a flocculant is limited by the absence of sanitary certificates, relatively high costs, and certain inconvenience of application related to poor solubility of chitosan in water. One of the possible steps forward to expanded chitosan application is a development of ready-to-use flocculation compositions based on powdered water soluble salts of chitosan. Combining chitosan salts with inorganic coagulants of new generation and/or chemical modification of chitosan toward enhanced efficiency in removal of hydrophobic pollutants can yield a range of products to fit specific requirement of certain industrial fields regarding excellent performance and affordable price. Here we report on the development, testing, and experience of introduction of chitosan based flocculation compositions “InstaFloc”, “ChitoFloc” for drinking water treatment, treatment of oily and liquid radioactive wastes containing latex dust-suppressors and colloids of transuranic elements.

To meet sanitary standards for drinking water, natural waters must undergo deep purification stage providing complete removal or significant reduction of organic and inorganic pollutants contents. Evaluation of chitosan-based flocculant “InstaFloc” at an industrial scale has been demonstrated at water treatment facilities of a milk factory (Vladivostok, Russia). The initial line productivity with aluminum coagulant was limited to 4-5 m^3/h due to the required stage of floc sedimentation in intermediate tank. Application of “InstaFloc” at the same technical setup allowed a 4-fold increase of filtration rate and line productivity together with improvement of output water quality.

High potential of chitosan is not limited to the drinking water treatment; processing of oily wastewaters is another important field of chitosan application. Comparison of flocculation efficiency of oil-in-water emulsions using different chitosans showed that polymers with deacetylation degree (DD) 80-85% and molecular weight in a range 30-500 kDa had comparable demulsifying properties, although soluble chitosans with DD 50-60% were notably less efficient. Compared to synthetic flocculants, the application of chitosans and “InstaFloc” provides significantly higher efficiency and two-threefold reduction of the residual oil content at lower flocculant doses. Introduction into the chitosan backbone low amount of pending alkyl-chains results in substantial increase of flocculation efficiency in oil-in-water emulsions stabilized by ionic surfactants.

Because of the cationic character chitosan can be applied to the removal of virtually any negatively charged colloid contaminants. We show the results of pilot tests of flocculation/precipitation setup for dust-suppressor (DS) and transuranic elements (TRU) removal from wastewaters of Chernobyl Nuclear Power Plant (ChNPP), including those of the Object “Shelter”. Although laboratory tests have shown the comparable efficiency of chitosan and synthetic flocculants with medium charge density, formation of the gel-like structure in the latter case and fast filter clogging prevents hampers of synthetic flocculants application in flow-type systems based on flocculation/filtration setups.

Sorption Preconcentration of Radionuclides Using Detonation Nanodiamonds

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Nanodiamonds (ND) obtained by detonation of explosives (eg, TNT and RDX) with a negative oxygen balance, are potentially promising carbon nanomaterial with a highly developed surface (250-300 m^2/g or more), a large number of oxygen-containing functional groups on it, chemical and radiation resistance, economically viable and relatively easy production [1]. These unique properties of ND can be used to isolate alpha-emitting radionuclides from liquid radioactive waste for further vitrification and actinides subsequent separation for analytical purposes.

The aim of this work was to establish the sorption behavior of radionuclides (Tc(VII), U(VI), Np(V), Th(IV), Pu(IV), Am(III), Eu(III) and Sr(II)) on detonation ND and to determine the effect of functionalization of the surface on the sorption.

Kinetics of sorption shows that steady state condition is achieved within first 30 minutes of interaction.

Figure 1 shows dependence of actinide sorption on pH suspension. The sorption is very high for U(VI), Th(IV), Am(III) and Pu(IV) even in the range of pH 1-3. The high sorption of Tc(VII) on ND in 1-6 M solutions of hydrochloric and nitric acids was obtained. The sorption capacity of ND was defined. It is comparable with respect to U(VI) to the values typical for other carbon materials.

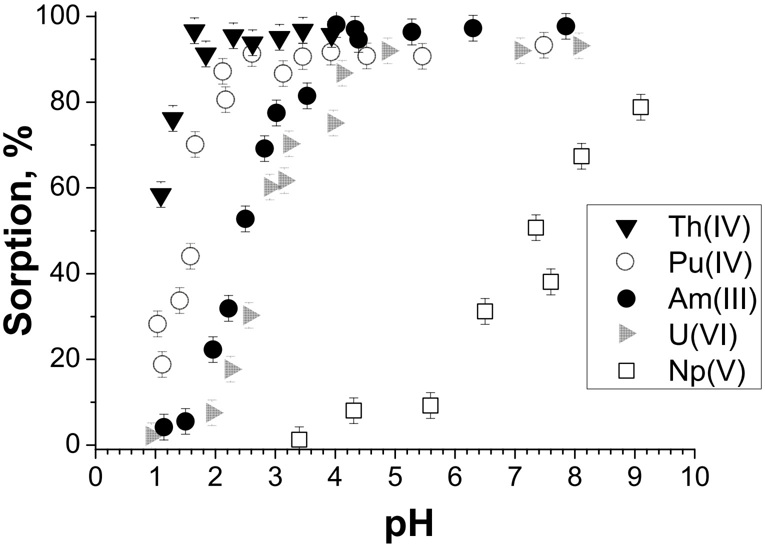

Figure 1. pH-dependence of actinide sorption on non-modified ND.

In our experiments different types of ND were used: treated with hydrogen (800°C, 5 h) ozone, air (400°C, 5 h), acids and ND functionalized with different groups by covalent grafting (glycine and CN-group). The different types of ND were characterized by IR spectroscopy, X-ray photoelectron spectrometry and measurements of ζ-potential at different pH of the suspensions and the particle size using Dynamic Light Scattering.

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Radiochemical Approach in Modification of Carbon Based Nanomaterials with Biopolymers

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Non-covalent modification of carbon based nanomaterials with biopolymers is of fundamental importance to improve the profile of its technological and environmental application. Modern developments of chemistry of nanomaterials pointed us at the study of sorption ability of carbon-based nanomaterials to globular proteins and humic substances and to determine properties of formed complexes.

Three types of carbon-based nanomaterials with different hydrophobic properties were under the test. They are graphene, single-walled carbon nanotubes and detonated nanodiamonds. The adsorption capacity carbon-based nanomaterials was studied in relation to brown coal humic acids (commercially available preparation Powhumus (Humintech, Germany)) and fulvic acids separated from Suwannee River (recommended as a standard by IHSS) and two globular proteins lysozyme from chicken egg white and human serum albumin (MP Biomedicals). Tritium label was used to determine or “trace” the amount of biopolymers adsorbed on solids. For this purpose tritium labeled humic substances and globular proteins were obtained by means of tritium thermal activation method [1, 2].

5-12 mg sample of nanomaterial powder was placed in the Eppendorf tube followed by the addition of 0.8 ml of ^{3}H-compound solution in phosphate buffer. The bulk radioactivity of compounds solutions was ca 55 MBq L^{-1}. Ultrasonication of the dispersion was carried out for 2 hours using a bath sonicator (GRAD, Model 28-35, Russia) with rated power of 110 W followed by incubation at room temperature for 24 hours. The solutions thus obtained were subjected to centrifugation at 2400g (Vortex) for 60 min. The upper 75 % of the supernatant after ultracentrifugation was filtered through 13 mm syringe filter with 0.2 µm PVDF membrane (Acrodisc LC, Life Sciences). A sample of filtered solution was stirred in 7 ml of scintillation cocktail OptiPhase HiSafe 3 (PerkinElmer). Counting rate was measured by liquid scintillation spectrometer RackBeta 1215 (Finland). Adsorption Γ was calculated according to following equation

$$\Gamma = \frac{\left(c_0 - {}^{I}/_{\varepsilon a_{sp} V_a}\right) \times V}{m}$$

Here I is counting rate, ε is registration efficiency of tritium β-radiation (from 40 to 50%), V_a is volume of an aliquot, V = 0.8 ml, asp is specific radioactivity of the compound, c_0 is initial concentration of the compound solution, m is mass of solids.

Since radiotracer method was used adsorption isotherms were obtained in wide concentration range from 10 to 3000 mg L^{-1} for proteins and from 0.02 to 200 mg L^{-1} for humic substances. The values of the adsorption in plateau regions (in the cases of the Langmuir type adsorption isotherms) were about 0.5-1 g g^{-1} for proteins and reaches 40 g g^{-1} in the cases of humic substances. Besides determination of nanomaterial-conjugate composition, each nanomaterial-conjugate sample was subjected to dynamic light scattering analysis that allowed us to reveal the aggregation stability suspensions on nanomaterial-conjugate composition.

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Stability and Interactions of Engineered Nanoparticles in Aquatic Systems

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Nanotechnology has turned out to be one of the most promising approaches for obtaining new forms of materials. The outstanding physical-chemical properties of these nanomaterials such as engineered nanoparticles (ENP) are convincing, which is currently leading to a tremendous increase of their use in industrial, technical, medical, pharmaceutical, cosmetic and life science applications. In particular, ENP are highly attractive for improving environmental quality when utilized, e.g., in water treatment processes or in ground water remediation. However, there is also concern about the environmental risks associated with the widespread use and production of ENP. ENP are likely to be emitted into environmental systems and have been shown to be of toxicological relevance. In contrast to most other chemical compounds, there are nearly no environmental data regarding the occurrence, the behavior and the fate of ENP in aquatic systems[1]. Being aware that ENP can undergo alterations and ageing in the aquatic environment, it is very likely that a good part of emitted ENP in aquatic systems will not persist as such, leading to camouflaged species or even new products. Apart from pH value and ionic strength, organic matter (OM) plays the key role regarding the stability and the reactivity of ENP in aquatic systems. OM such as refractory organic matter (ROM) is omnipresent in environmental and technical systems. It is known that OM might adsorb onto ENP, which can lead to an inhibition of their coagulation potential owing to steric stabilization. However, the presence of OM might also lead to flocculation of ENP and thus to the formation of larger agglomerates, especially in the presence of divalent ions such as calcium[2].

This contribution gives a critical overview of the interactions and the stability of ENP in environmental and technical aquatic systems. Analytical methods for the highly sensitive detection and quantification of ENP in aqueous suspensions and for the examination of their interactions with environmental matrices are presented. In particular, analytical coupling techniques such as Asymmetric Flow Field Flow Fractionation or Size Exclusion Chromatography coupled with highly sensitive detectors are addressed[2]. Regarding the interactions of ENP in aquatic systems, the focus will be on the impact of OM on the stability of silver nanoparticle suspensions at different ionic strength[3]. Additionally, the role of OM quality (e.g. humic acid, fulvic acid, humic acid-like substances) in these reactions will be considered. A profound understanding of these molecular interactions is key for the assessment of the mobility and transport behavior, the bioavailability and (eco)toxicity, the reactivity as well as the technological applicability of ENP in the aqueous phase.

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Comparative Study on Molecular Profiles of the DOM Isolated from the Kolyma River in the Russian Arctic Using XAD-8 resin, DEAE-Cellulose, PPL-, and C18 – Cartridges

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Although modern methods of structural analytics enable acquiring high quality and high resolution spectroscopic data, they usually set strict demands to the purity of the samples. This is particularly true in case of dissolved organic matter (DOM) which represents a complex mixture of natural organic compounds. Application of high resolution magnetic resonance techniques for molecular analysis of natural heterogeneous objects, such as DOM, is very demanding with respect to the sample preparation procedures. The objective of this study was to characterize the operationally-defined molecular features of the DOM samples isolated from the Kolyma River in the Russian Arctic using high resolution magnetic resonance techniques and to compare DOM extraction techniques for acquiring the most representative DOM samples from the Arctic Rivers. To achieve this goal, DOM was isolated from the Kolyma River with a use of four sorbents differing in polarity and sorption mechanism. The sorbents included weak anion exchanger diethylaminoethyl-cellulose (DEAE), moderately polar Amberlite XAD-8 resin composed of poly(methylmetacrylate) polymer, moderately polar PPL cartridge packed with modified copolymer of divynylbenzene and polystyrene, and non-polar C18 cartridge packed with alkylated silica gel. To enable comparative study of the obtained DOM isolates, we implied molecular level analysis using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry with Electrospray Ionization (ESI FTICR MS) and 1H NMR spectroscopy. The DOM samples were isolated from the main stem of the Kolyma River near Cherskiy village (Russian Republic of Sakha-Yakutia) situated about 200 km from the rivermouth. FTICR MS data were processed using the self-designed Transhumus software (A. Grigoryev). In this study, we used only CHO identifications for more precise analysis. For all samples, we analyzed common and unique identified formulas. The total number of common formulae was 1658. A number of unique peaks was 173, 319, 266, and 343 for PPL, C18, XAD8, and DEAE isolates, respectively. Unique peaks for C18 sample demonstrated highly aliphatic character with significant hydrogen enrichment, XAD sample demonstrated mostly lignin-like unique formulas, DEAE demonstrated a distinct shift towards oxygen-rich, tannin-like compounds. PPL sample did not demonstrate a substantial specific affinity: unique peaks were distributed among different compound classes. Although FTICR MS allows identification of single ions, it is not a quantitative technique. For quantification studies we used 1H NMR spectroscopy. It demonstrated significant differences in proton distribution within functional groups of the DOM samples isolated by different techniques. PPL isolates demonstrated the highest proportion of aliphatic protons and the lowest one - of carbohydrates. The XAD isolate showed the highest proportion of aromatic components, which is in a good agreement with the FT ICR MS data. The DEAE sample was characterized with the highest content of carbohydrate-like units. Therefore, the choice of extraction technique strongly influenced the quality of the DOM sample. For biomarker studies, we suggest to use PPL or C18 extraction because of high purity of the isolates and softness of the method. Also PPL and C18 cartridge methods are simpler in use, especially in the field laboratory. In case of analysis of specific components we suggest to use XAD or DEAE extraction method, XAD is preferable because it is a standard method of the International Humic Substances Society.

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Nanostructural Organization of Soils

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Currently, it is commonly recognized that the soil colloids in a form of gels cover soil particles and bind them with each other, thereby forming the soil as a system with a certain set of properties.

Moreover, soil gels are considered to be jellied humus reinforced with various particles.

Note that the humus jelly in the framework of this approach has been regarded as a certain uniform substance, representing a matrix that houses mineral particles. However, such a model concept contradicts recent data on the behavior of polymeric systems and requires revision.

Examination of the soil samples and the soil gels isolated from soils with electron and tunnel microscopes has demonstrated that the soil gels consist of aggregates with a size varying from several tens to several hundreds of nanometers.

Comparison of these data with the results of analysis of the soil colloid component with the use of a transmission electron microscope, soil gels with the use of a scanning electron microscope, and solutions of humic substances (HS) by photon correlation spectroscopy and small angle neutron scattering (SANS) suggests that these are organic aggregates.

It is evident in the images recorded with a tunnel microscope that the observed aggregates

consist of smaller particles, the size of which has been earlier determined and vary for soils of different types, amounting to 8–12 nm for chernozem and 2–5 nm for sod podzol soil.

Thus, the organic matrix of soil gels consists of the aggregates with a size ranging from several tens to several hundreds of nanometers, which, in turn, are formed by merging of the primary HS particles with a size of several nanometers.

It is possible to get an insight into the structural arrangement of primary HS particles in larger aggregates (hereinafter referred to as clusters) with a size of several tens to several hundreds of nanometers by comparing the SANS data on HS solutions and soils. In both cases, a fractal arrangement of the clusters in HS solutions and the colloid soil component was observed.

Comparison of the data obtained when studying HS solutions by SANS and the data on the fractal arrangement of the soil colloid component obtained by the same method suggests

a justified conclusion that the clusters of HS particles in soils are also arranged according to the fractal pattern.

Humic substances have been for a long time regarded as a set of macromolecules; correspondingly, the soil gels from this standpoint should be regarded as systems based on fractal clusters of macromolecules. However, fundamentally different approaches to the HS structure have appeared during the past decade and become commonly recognized. They refute the traditional idea that the HS have a polymer nature. It has been demonstrated based on experimental data obtained with the help of many modern methods that HS are associates of relatively low molecular weight components formed during degradation and decomposition of biological material that are dynamically united and stabilized mainly via weak interactions. This is the most important feature in the HS structure. It has been proved that HS are supermolecular structures.

Thus, soil gels, which unite and bind soil particles determining many soil features, appear when fractal clusters of HS supermolecules are united.

All these data suggest several levels of the HS arrangement in soil gels and soils (table):

(1) Molecules of low molecular weight substances formed as a result of degradation of biological remains entering soil.

(2) Supermolecules of humic substances.

(3) Fractal clusters of supermolecules of humic substances.

(4) Soil gels formed via merging of the fractal clusters of supermolecules of humic substances.

Comparison of Different Methods of Extraction and Cleanup of Polycyclic Aromatic Hydrocarbons from Soils

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Polycyclic aromatic hydrocarbons (PAHs) are widespread organic compounds in common soils. Although there are hundreds of PAH compounds, the U.S. Environmental Protection Agency (EPA) lists 16 PAHs as prior pollutants. Strong interactions of the compounds with the soil components cause problems of low and variable extraction efficiency, extraction of related organic compounds, which, in turn, cause interference in instrumental analysis. Therefore, many efforts are spent on the development of new extraction and purification of extracts from the accompanying components procedures.

Method of extraction by Soxhlet is the most widely used traditional technique, but it requires a significant investment of time and reagents. Ultrasonic extraction methods, from the literature, are less effective than traditional methods, but they can minimize consumption of solvents and extraction time. All of the methods use organic solvents. The further purpose of researches is to find alternative extract procedures to reduce amounts of solvent used. However, with increasing the number of extraction techniques, comparisons between PAH in soils may be questionable. Although the prospects of standardized methodology development are not so clear, the relative merits of different extraction procedures of the extraction of PAHs from soil should be evaluated before choosing one or several of them. The objective of our study was to compare different methods of extraction of PAHs from soil (soxhlet, ultrasonic), to identify the best method of extraction and to investigate the effect of the purification procedure for the loss of PAHs.

Different methods of extraction and separation of PAH have been used guided by both Russian methods of measurement (PND F 16.1:2:2.2:3.39-03) and methods recommended by the United States Environmental Protection Agency (US EPA 8310). For each method's comparison we have used standard sediment NIST 1944 (USA). Allocation fraction of PAHs has been performed by column chromatography with aluminum oxide or silica gel. Evaporation of the extracts as well as the stage of the solvent immediately before the analysis has been performed using the Kuderna-Danish evaporator. For the preparation of standard solutions EPA 610 PAHs Mix from Supelco has been used, with the concentrations of each component 0.1-20 µg/cm3. PAH content in the samples has been determined by reversed-phase gradient HPLC with spectrofluorimetric detection.

Comparing of the PAHs mass fraction value, obtained by different extraction methods, shows the greatest match in comparison with certified values with respect to the Soxhlet extraction - 70-80% recovery of PAHs. In the extraction using ultrasound extraction degree of test substances falls to 50%.

The methods of prepared PAHs concentration and the change of solvent immediately prior to analysis have also been compared. Russian techniques offer evaporation of prepared extracts, which have passed all stages of extraction and separation, to dry consistent and addition of another solvent to the dry residue. This results in almost 100% losses of the most low molecular PAHs (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene) and 10-40% losses of high molecular polyarenes. In foreign techniques on the stages of the concentration and the solvent change in the extracts, containing such semi-volatile organic compounds as PAHs, it is recommended to use Kuderna-Danish evaporator. The researches show almost no losses (no more than 5%).

Use of column chromatography with different sorbents, such as alumina and silica gel, shows no significant differences. Silica gel gives opportunity to allocate a fraction of saturated hydrocarbons for further analysis or more complete cleaning fraction of PAHs.

Efficiency of Combined Application of Lignohumate with Microbiological Product BAC on Cleaning Rate of Soil after Oil Pollution

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Every year, the amount of the grounds disturbed while hydrocarbon extraction, their transporting, processing and application is growing.

Due to the large depreciation of the pipeline the number of oil spills and oil products is increasing. The soil is like a sponge. Due to its powerful ability to adsorb it accumulates most of the oil pollution. In the process, its physical, agrochemical and microbiological characteristics change. As a result the value of agricultural landing is lost. In this regard, environmentally safe and economically viable methods to intensify the processes of biodegradation of hydrocarbons and restore fertility of agricultural lands are needed.

There are several physical and chemical methods of soil reclamation. Biological method is efficient, which is to enhance the directional micro-flora of the soil, making microbial agents which decompose hydrocarbons.

In 2004, under the leadership of the company EcoProm the production testing of the biological product BAC and Lignohumate for cleaning soil from the oil were held.

Oil and petroleum products in the soil are decomposed, directly under the action of living organisms that are part of a biological product BAC, and under the explosive development (qualitative and quantitative) of native flora. Utilization of hydrocarbons goes in line with the transformation of them into organic compounds of natural humus with positive efficiency on soil fertility of disturbed lands.

The experience has shown that a combination of BAC and complex biological humic product Lignohumate can significantly reduce oil pollution of soil by stimulating natural soil and the imported flora. The rate of decomposition of oil in the soil under the influence of pure product BAC increases by an order, and at the combination of products increases by 25-35%.

In the production area (military unit, the Transbaikal Military District) it is demonstrated that a binary mixture of drugs for one growing season significantly reduces oil pollution of soil (oil - from 100 mg/g to 0.15 mg/g of soil). Practical recommendations for the use of the microbial product BAC and Lignohumate for soil reclamation are prepared.

The product BAC contains oil destructors in its composition – the bacteria species *Rhodococcus* and *Acinetobacter*. Lignohumate is a complex humic product with properties of a growth regulator, which accelerates the growth and development of both plant and microbial co-society (in particular the complex bacteria-oil destructors).

So, the use of a mixture of the products can actively reclaim large areas of relatively low (compared to other technologies) cost of works at a weak negative impact on the environment. Land recovery time in this case reduces up to 3-4 times.

Effect of Potassium Humate on Nanodioxide Titanium Toxicity

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The objective of this study was to determine the bioactivity modification of nano-TiO_2 by humic substances (HS) application.

In this work we used metal-containing nanomaterials - nanodioxide titanium (nano-TiO_2), which are characterized <75 nm in size of particles in 10 weights % of water suspension, manufactured in the company «Sigma-Aldrich», USA. Nano-TiO_2 represents oxide the titanium (IV), the mix of two known crystal modifications of dioxide titanium – anatase and rutile. Among HS we have chosen "Pow-Humus" (Le-PhK) (K-humate, originated from leonardite), manufactured by German firm "Humintech". Concentration of nano-TiO_2 was varied in range 5-500 mg/l; concentration of humate Le-PhK was 5 mg/l in water medium.

Bioactivity of preparations was examined by early seed root elongation assessment related to *Brassica juncea* L. as a test-organism. We have used a modification of the method «Phytotoxkit - Seed germination and early root growth», developed by Belgian scientists [http://www.microbiotests.be]. Seeds were preliminary presoaked in suspensions with tested nanoparticles within days, then were transferred to transparent plastic containers on paper substrate from an inert material (the filter «a white tape»), impregnated with a tested solution, and were incubated during 4 days in the thermostat at 25°C. The effect of bioactivity of test materials was estimated by change of roots length of sprouts in test samples concerning control, in which seeds were sprouted in the distillate. The probe is considered toxic if the deviation from the control of average roots length is 20 and more %.

Depressing effect of nano-TiO_2 on early root growth (4 days of germination) was marked already at 5 mg/l (Fig.1).The most effect was shown at the higher concentration: probe with nano-TiO_2 500 mg/l was toxic because the deviation of average roots length was more than 25 % from control.

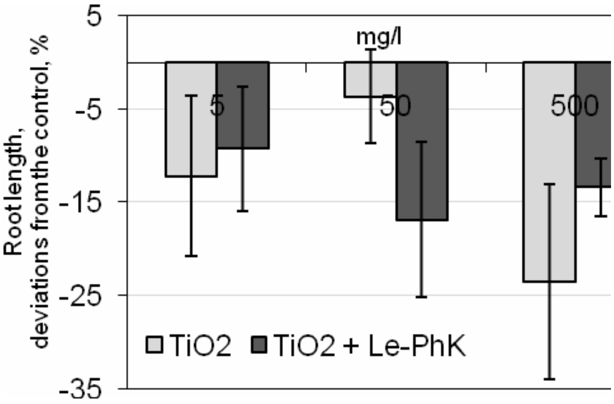

Figure 1. Influence nano-TiO_2 and nano-TiO_2 with humate on the root length of *B. juncea.*

Inhibitory effect of 5 and 500 mg/l nano-TiO_2 was reduced in presence of 5 mg/l humate Le-PhK. Samples with nano-TiO_2 500 mg/l after humate application was qualified as nontoxic because the deviation of average roots length was only 14 % from control.

The obtained data has shown that: 1) higher plants are sensitive to the nano-TiO_2 presence in growing medium; 2) the degree toxicity of nano-TiO_2 depends on the concentration of nanoparticles; 3) humus substances eliminate the toxic effect of nano-TiO_2 in water suspension which inhibits root growth.

Further research is required for the evaluation of humus substances influence on the nanomaterials which are more and more widely distributed in the environments including the natural soils.

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Soft Chemistry in Preparation of Therapeutic and Diagnostic Nanoparticles

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Nowadays biomedical diagnostics and targeted therapy become the most important areas of activity in nanochemistry. This is naturally connected with tunable physical and chemical properties of magnetic, plasmonic and other types of nanoparticles caused by the size – factor and peculiarities of nanoparticle interactions with surroundings. The report discusses soft chemistry approaches for the preparation of therapeutic and diagnostic nanoparticles. In particular, examples of superparamagnetic iron oxide nanoparticles for hyperthermia and magneto- resonance tomography (SPION) and nanostructured silver materials for surface enhanced raman spectroscopy (SERS) studies of living erythrocytes are given and analyzed in terms of nanoparticle preparation, stability, toxicity and functional properties expecting their practical applications. As a special focus, an application of humic substances for modification of nanoparticles is presented.

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Stabilization of Oil-in-water Emulsions Using Organoclays Consisting of Kaolin Modified with Humic Substances: Remedial Prospects

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Formation of oil-suspended particulate matter aggregates (OSAs) is a natural attenuation process which takes place in the marine waters polluted with oil in the presence of organo-mineral fine sediments. It includes disaggregation of oil slick into the droplets and their encapsulation into organomineral shells. The formed OSAs have negative buoyancy and slowly sink onto the bottom. As a result, multiple efforts have been directed towards creating clay-based solid dispersants for cleaning oil-polluted waters. The advantage of clay dispersants is a lack of toxicity which is inherent to molecular dispersants based on chemical surfactants. In addition, they accelerate biodegradation of encapsulated oil droplets. The disadvantage of clay dispersants is a relatively narrow range of their applicability – they work the best on freshly spilled polar oils. The formation of OSAs is highly effected by the properties of suspended particulate matter (SPM) such as particle size, surface area, concentration, and surface chemistry. The dominating forms of SPM in the aquatic environments are organoclay colloids consisting of clays modified with humic substances (HS). HS are natural polyelectrolytes whose sorption onto clay minerals can significantly modify their surface chemistry by changing hydrophobic-hydrophilic balance of clay particles. This may impact greatly interaction between oil and fine clay particles suspended in water.

The objective of this study was to investigate stabilization of oil-in-water emulsions by clay particles modified with HS of different origin. For this study, clay mineral (kaolin) coated with HS from different environmental sources (water, soils, peat and coals) was used. In addition, the clay particles modified with silanol-derivatives of HS were used. HS were characterized by C, H, N content, molecular mass distribution as measured by size exclusion chromatography, and structural fragment distribution measured by 13C NMR spectroscopy. Prior to modification with HS, kaolin clay was dispersed using ultrasonic treatment with subsequent removal of coarse particles (> 1 μm) by centrifugation. The fine kaolin particles suspended in the supernatant were saturated with Ca^{2+} at pH 5.5. Then, HS were sorbed onto Ca^{2+}-saturated kaolin particles under bath conditions at pH 5.5 and 1mM $CaCl_2$. For experiments on oil stabilization, four different raw oils were used with densities ranging from 0.81 to 0.86 g/cm^3. To produce oil in water emulsion, the oil was added to the dispersion of clay in water containing 0.1 g/L of clay. The system was placed into ultrasonic bath, and then clay dispersion from the depth of 3 cm was sampled to measure optical density at 535 nm. The measurements were made after 1 and 24 hours of exposure to the ultrasonic treatment.

The results showed that the stability of oil emulsions in the presence of clay-humic colloids was much higher as compared to oil-water system. The emulsion was stabile up to 24 hours exposure. The highest stabilization of oil-in-water emulsions was observed for clay complexes with coal HS and peat HS. A use of silanol derivatives of HS for clay modification was less efficient as compared to natural HS. The obtained results show an opportunity to use artificially prepared HS-kaolin organoclays as solid dispersants for stabilization of oil-in water emulsions for cleaning up oil-polluted aquatic environments.

Photocatalytic Efficiency of Fe_3O_4@TiO_2 Core-Shell Magnetic Microspheres in Degrading Micropullutants in Water Interface

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Photocatalytic degradation of an herbicide from imidazolinone family is investigated in water interface using TiO_2, H_2O_2 or their combination under simulated sunlight irradiation. The effect of parameters such as amount of catalysts, concentration of herbicide, and pH were investigated by calculating the rate constant of degradation and a pseudo-first-order kinetic was observed. Mulliken charge distributions calculated by the density functional theory (DFT) method B3LYP/6–31+G(d) level of theory for key cationic, anionic and neutral structures of the herbicide give interpretation for the dependency of photodegradation rate constant on pH. Parallely, degradation products were putatively identified using high resolution mass spectroscopy (FT-ICR-MS) based on precise chemical formula assignments and strategies in organic chemistry [1, 2]. In the same conditions, a titanium dioxide coated magnetic nanoparticles (Fe_3O_4@TiO_2 microspheres) [3, 4] was found suitable for the degradation of this herbicide. The kinetic degradation of the herbicide was followed by Ultra-high performance liquid chromatography (UHPLC) and the effects of Fe_3O_4@TiO_2 microspheres doses as well as pH of the solutions were investigated. The approach enabled rapid and easy phase separation of the active nanoparticles from the water phase by applying external magnetic field and the photostability of Fe_3O_4@TiO_2 microspheres (after successive cycles) shows that the removal efficiency of the herbicide was maintained between 94 and 100%.

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Photocatalytic Oxidation of Organic Dye With Use the Electrochemical Synthesis of Cu_2O and Fe_2O_3 nanoparticles

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Recently, much attention has been paid to photo catalytic methods for dye containing sewage decoloration using nanodispersed catalysts TiO_2, ZnO, etc. These methods use light energy to initiate chemical reactions in the presence of photocatalysts that are mostly semiconductor materials. The photocatalytic processes used are based on visible light absorption by a dye sensitizer which, being transferred to the excited state, are exchanged by charged particles with a photocatalyst.

In this work the photocatalytic oxidation of dye with use the electrochemical synthesis of Cu_2O and Fe_2O_3 are investigated.

The synthesis of the copper (I) and iron (III) oxide was as follows: the electrolysis of a saturated sodium chloride aqueous solution was carried out with the use of two copper or iron electrodes (working as a cathode and an anode) at a current density of 0.2 A/sm^2. When the current flows, the dissolution of the copper electrode occurs with the Cu_2O formation. The obtained precipitation was filtered and air dried. Depending on the conditions of the synthesis, the product went from brilliant orange to red and it was cuprite (Cu_2O).

The iron (III) oxide solution was prepared using electrolysis with iron electrodes. During electrolysis the $Fe(OH)_2$ is probably formed followed by slow oxidation on air before $Fe(OH)_3$. The final product to identified mostly α-Fe_2O_3 is formed at heated $Fe(OH)_3$ at 300°C.

The samples were produced under a different current density characterization using the scanning electron microscopy, X-ray diffraction. The specific surface of the patterns was determined via dye adsorption. The adsorption investigation of the dye on the samples surface took place in darkness to prevent its photocatalytic oxidation.

At photocatalytic oxidation with use different concentration catalyst the dye concentration rapidly decreases in the first 10 min. The degree of solution decoloration varies at different catalyst concentrations before 50%.

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Sorption Capacity of Peat Mechanoactivated in The Presence of Iron Oxyhydroxide

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Recently, much attention is paid to the use of peat for wastewater treatment – industrial and domestic. When evaluating the absorption capacity of sorbents with respect to organic wastewater contaminants, researchers face the difficulty in choosing a model substance. Methylene blue is widely used in the practice of adsorption measurements in aqueous solutions; it is used not only to describe the activated carbons, but also a number of granular filter materials and clay minerals. One advantage of the technique of methylene blue adsorption is getting rid of the long experiments on filtration through the absorbent until it reaches saturation in dynamic environments.

The aim of this work is to investigate the sorption properties of peat modified by mechanical activation.

Mechanical activation of peat was carried out in a planetary mill. Iron oxyhydroxide, a thermally activated sludge produced during cleaning of underground water from iron was used as modifier.

The adsorption of the dye by peat was investigated using the technique of methylene blue adsorption intended to determine the adsorption activity of powdered activated carbon.

The adsorption activity of peat was found to increase with increasing dye content in a solution, being 40% higher for mechanically activated peat than for initial peat and for that mechanically activated in the presence of iron oxyhydroxide it was higher by 60-70%.

The investigation of the kinetics of the methylene blue extraction process for the initial peat and that mechanoactivated has revealed that the treatment of peat via mechanoactivation affected its kinetic and sorption characteristics. So, for the initial peat the sharp rise in adsorption activity fell on 30 min and was 112.5 mg/g while the adsorption activity of the treated peat over the same time period in comparable conditions was within the range of 145-180 mg/g and the process was intensified since the first minutes. For all cases, the equilibrium of the process was set after 60 minutes.

The results of metal sorption from sulphate solutions of salts under static conditions also testify to the efficiency of use of aluminum for peat sorbent obtaining, so the average purification efficiency was 93% for Cd^{2+}, 75% for Ni^{2+}, and 91% for Cu^{2+}.

Changes in the composition and structure of sorbents obtained were characterized using NMR spectroscopy, IR spectroscopy, group and elemental analysis.

These investigations indicate that the sorption of pollutants in the interaction with a peat mechanoactivated in the presence of iron oxyhydroxide is due to dispersion forces, electrostatic forces, and hydrophobic interactions between the adsorbates and the sorbent surfaces. The characteristics of peat as a sorbent of organic pollutants and heavy metals are significantly improved due to such a treatment.

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Contact Angles of Humic Substances are Complexes with 1:1 and 1:2 Clay Minerals

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The natural organic matter consists of 60-90 % of humic substances (HS). The most stable forms of organic matter in environments are the clay-humic complexes. Clay-humic complexes are presence in various environmental compartments, such as soils, sediments and aquifers.

HS are sorbed onto clay mineral significantly change their surface properties: affinity, surface area, free energy etc. Measuring of contact angle allows obtaining data about affinity and surface energy of object easy and expresses.

For this study aluminum silicate clays with 1:1 (kaolin) and 2:1 (smectite) layered were used. Clay minerals were coated HS from different sources (soils, peat and coals) and contact angles obtained clay-humic complexes were measured by static sessile drop method. HS were characterized by C, H, N content, molecular mass distribution by HPLS and structural fragment carbon distribution by liquid-state 13C-NMR.

Clay minerals were dispersed by ultrasonic treatment with subsequent removed coarse particles > 1 µm by centrifugation. Then suspension of fine particle clay minerals was saturated Ca^{2+} at pH 5.5.

HS were sorbed on clay minerals in bath conditions at pH 5.5 and 1 mM $CaCl_2$. Weak sorbed HS were remove by six fold washed by 1 mM $CaCl_2$. Contact angles of obtaining humic-mineral complexes and pure minerals were measured.

For the sessile drop method, a microscope slide glass cleaned with acetone and distil water, was coated with clay-humic colloids. Clay-huimic stock suspensions in a concentration of about 1–2% wt/vol were intensive shaken during several minutes. Immediately 40 µL suspension was placed on the microscope slide and evaporated for several days under normal conditions. Finally suspensions were dried in an oven at 105°C for 2 hours directly before contact angle measure. Glass slides were kept horizontal during the drying process. The contact angles were determined using a goniometer DSA100 (Kruss, Germany).

Contact angles of pure kaolin and smectite were significantly lower in compare HS-mineral complexes (here and below significant estimating by t-test at a = 0.01, n = 14). However contact angle values between HS-kaolin (with different HS: soils, peat and coals) there were not significant differences their range was 30-32°. In contrast contact angles of all HS-smectite complexes were significantly different from each other. Values of contact angles were range from 49 to 83° and row in order HS are used for sorption: Chernozem soil HS < Coal HS < Peat HS < Sod-podzol soil HS. This range coincide by alkyl group contain in HS.

Results of the study suggest more profound modification by HS of smectite surface in contrast kaolin. It can be assumed that in case of smectite take place sorption HS on specific hydrophilic sites resulting in hydrophobic parts of HS molecules turn on external layer of HS-smectite complexes surface. In contrast, in case of kaolin, HS sorbed by unspecific mechanism and contact angle depend on only surface area of mineral.

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Interaction of Coal Humic Substances with White Rot Fungi: an Approach with Tritium Labeled Preparations

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Humic substances (HS) are defined as the products of complex transformation of organic residues with both biotic and abiotic factors being involved in this process. Among the biotic factors much attention has been paid recently to xylotrophic microorganisms with particular emphasis on white-rot fungi as they produce a wide spectrum of extracellular oxidoreductases providing HS transformation. However, interactions of white rot fungi with HS are poorly elucidated. In the current study uptake of HS by Basidiomycete was investigated under different carbon source availability (nutrition media with or without glucose were used).

Experiments were performed using pure culture of Basidiomycete *Trametes maxima 0275* (Wulf. Ex. Fr) Quel. and tritium labeled leonardite HS ([^{3}H]HS). After 7 d of *T. maxima* submerged cultivation [^{3}H]HS were added into the medium to final concentration 50 mg l^{-1} followed by subsequent cultivation for another 24 h. Performed experiments showed that HS were easily sorbed by fungi mycelium, and a significant portion of HS introduced could be found in the intracellular space of fungi (Fig. 1).

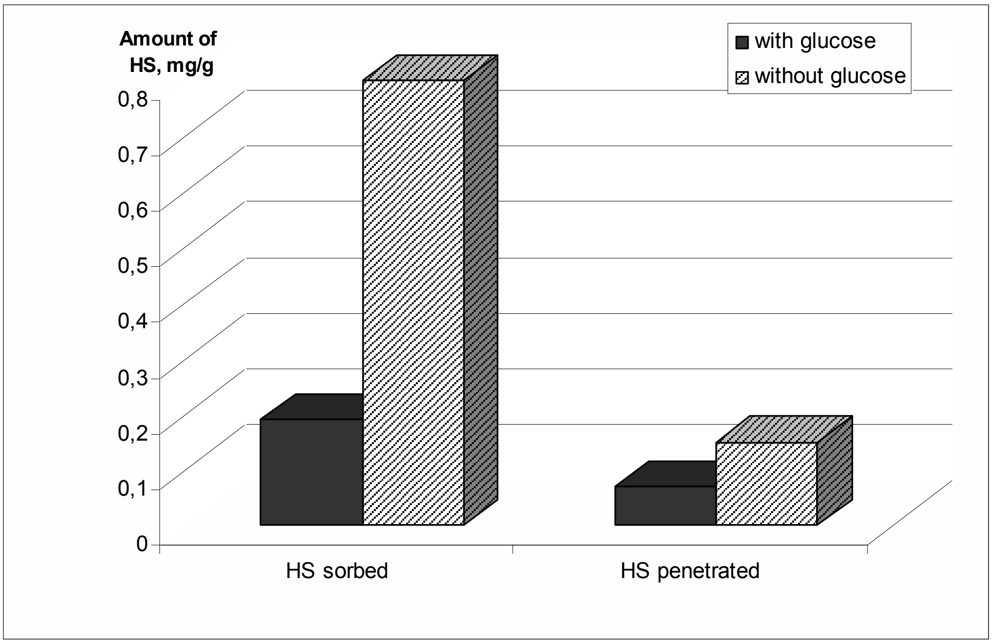

Figure 1. Intra/extracellular distribution of [^{3}H]HS in *T. maxima*.

Amount of HS sorbed by fungi was estimated as 0.52±0.05 and 1.1±0.3 mg g^{-1} of fresh mycelium weight for the case of nutrition medium with and without glucose respectively. It should be noted also that along with increase of the amount of HS sorbed under carbon deficiency conditions the value of HS penetrated cells raised as well. When glucose was added, the value of HS penetrated the cells was accounted for 0.17±0.02 mg g^{-1} of fresh mycelium weight whereas in case with absence of glucose that value increased to 0.56±0.09 mg g^{-1}. So, our experiments demonstrated that depending carbon source presence or absence the amount of HS penetrated value varied from 32 to 51% of humics totally taken up by fungi. The latter was evident for the fact that HS were seemingly to be utilized by fungi as an alternative carbon source.

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Perspectives of Use of Humic Preparates as Mechanism to Control the Plants Productivity

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Humic substances became more involved in agricultural practice as a tool for bio productiveness management. On the base of All-Russia selection institute we have asses the reaction of different sorts and species of plants on different humic substances. Kinetic dependencies were revealed for humic substances, extracted from different sources and this allows to create species dependent and sorts affected humic based correctors of bioproduction process.

On the base of effectiveness of different humates affects the technology new humic-like substance were elaborated. This technology based on application of new liquid organic-mineral fertilizer “Stimulife” (Certificate of Government registration of agro fertilizer №1264-08-206-317-0-0-0-1, technical conditions 2186-016-79850210-2007, medical certificate №77.99.30.099.A.000560.11.07) was studies as a tool for regulate of plant growth in agriculture, pharmacy, design and forest management.

New agro fertilizer was elaborated on the base of modeling of humification process in conditions of technological control and use to be processed in conditions of oxidation ammonium destruction of turf by manufacture of AFI (Agrophysproduct LTD).

Technologies developed was adopted to processing conditions and use to be applied for agricultural machines of new generation as well as to current technical equipment of farms. Optimization of biological productivity of crops recognized as achievable due to application of program of prognosis of plant condition. This allows to select an optimal dates of plants processing in critical ontogenesis phases by growth-regulate powder “Stimulife” in concentrations, which are optima for every culture.

Application of “Stimulife” substance results in quality of crops and increases the crop production in sense of grain, technical, vegetable, pharmacy plants up to 10-30 %. Medium economical effectiveness of leaf (non root) amendments of “Stimulife” was revealed as up to 10 rubles to one ruble of spends.

A technology was experienced in farms of Leningrad region.

Specification of production: technological documentation, consulting, bio preparations.

Consumers: producers of different marketing strategies, forestry, biotechnologies pharmacy and decorative plants.

Comparative Studies of the Kolyma River and Permafrost DOM Using FTICR MS

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One of the largest organic carbon reservoirs is stored in the Arctic region. The enhanced discharge of freshly liberated dissolved organic matter (DOM) into the Arctic Ocean will affect greatly the physical, biological and chemical environments. To track these changes, much deeper molecular understanding should be achieved on the specific structural features characteristic to the permafrost DOM. To address this challenge, a broad set of DOM samples was isolated from the region of the East Siberian Arctic including the mainstream of the Kolyma River, its tributaries and permafrost mud streams for further Fourier transform ion cyclotron resonance (FTICR) mass spectrometry analysis.

Dissolved organic matter (DOM) was sampled in the Kolyma River Basin, North-East of Russia using the isolation protocol as described by Dittmar T et. al. in Limnology and Oceanography: Methods 6, 230–235. The isolation procedure includes a use of PPL Bond Elute Varian cartridges. Fresh water is acidified and discharged through the cartridge. Methanol is used to elute the adsorbed DOM. The isolated samples have very low ash content and are suited for high resolution spectroscopic studies. MS analyses were performed at the 7T LTQ FT (IBCP, Moscow, Russia) and 9T FTICR MS build in house (NHMFL, Tallahassee, FL, USA). MS data processing was performed using self designed software.

A representative set of samples from different sources in the Kolyma River basin was isolated during the Polaris Project expedition in 2010. The samples were analyzed using elemental analysis and 1H NMR spectroscopy which displayed higher aliphatic character and enrichment with nitrogen as compared to the low latitude DOM. Of particular importance is a difference observed between the DOM isolated from the mainstream of the Kolyma River and the permafrost mud: the latter were characterized with higher aliphaticity and the content of nitrogen. It was suggested that this might be indicative of the presence of higher amounts of the protein-like compounds in the permafrost samples. To examine this phenomenon thorough FTICR MS investigation was performed using atmospheric pressure photoionization (APPI) and negative electrospray (ESI). All identified compounds were sorted according to the same heteroatom content and Double Bond Equivalents (DBE). Nitrogen containing compounds were successfully identified. Much higher content of N2Ox and CH classes observed in permafrost sample. This confirms the validity of the structural trends and substantially different character of the permafrost and riverine DOM.

Complex Analytical Study of NOM with an Example of Dissolved Organic Matter Isolated from Lake Waters of Ural Region

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Two NOM samples from Irtyash and Tatysh lakes (South Urals, Russia) sorbed on XAD-8 resin according to the conventional technique were characterized using different analytical methods, such as: elemental analysis, size-exclusion chromatography (SEC), UV-vis spectrometry and ^{13}C NMR spectroscopy.

C, H, N and ash contents were determined using Carlo Erba Strumentazione elemental analyzer (Italy). UV-vis spectrometry analysis was conducted using spectrometer Cary-50 (Varian, USA). SEC analysis was conducted using HPLC system with UV-detector under conditions standard for NOM analysis. Solution state ^{13}C NMR spectra were acquired using Avance 400 spectrometer (Bruker, Germany) on the samples dissolved in 99,9% D_2O.

The samples characteristics obtained are typical for those of NOM of low colored surface waters (Tables 1–4). Specific UV absorbance (SUVA), that is defined as the UV absorbance of a sample at a given wavelength normalized to organic carbon content, was calculated at 254 and 280 nm that correspond to wavelengths characteristic of aromatic groups absorbance. The results obtained conform well to H/C and aromatic to aliphatic carbon percentages ratios that indicate NOM unsaturation and aromaticity degrees correspondingly (Table 4).

Thus, complex analytical method of NOM using different physicochemical techniques was demonstrated with an example of lake water dissolved organic matter.

Table 1. Elemental composition determined, corrected to ash and moisture

Sample	C	H	N	O	O/C	H/C	C/N
	mass %				atomic ratios		
IRT	57.20	4.88	1.86	36.06	0.47	1.02	35.83
TAT	56.68	5.06	2.27	35.99	0.48	1.07	29.10

Table 2. Molecular-weight characteristics of NOM according to SEC study

Sample	Mw, Da	Mn, Da	Mw/Mn	Column recovery
IRT	6800	3400	2.0	82 %
TAT	6300	3000	2.1	84 %

Table 3. Structural composition of NOM according to ^{13}C NMR study

Sample	Structural fragments of NOM					
	CHn	CH-O,N	OC-O,N	C(arom)	(C=O)-O,N	C=O
IRT	42.0±0.8	11.3±0.5	1.4±0.3	25.3±0.7	16.8±0.7	3.2±0.3
TAT	39.5±1.0	13.6±0.5	2.9±0.4	24.1±0.4	15.0±0.4	4.7±0.2

Table 4. Correspondence between H/C, aromatic to aliphatic carbon ratio and SUVA

Sample	H/C	C(arom)/C(aliphat)	SUVA, L/(mg[Carbon]·cm)	
			254 nm	280 nm
IRT	1.02	0.5	0.00270	0.00190
TAT	1.07	0.4	0.00263	0.00185

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Lignin as a Precursor of Humic Substances in Soils (According to ^{13}C NMR Spectroscopy)

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A characteristic feature of lignin structures are their tendency to condensation reactions, which can lead to the formation of new stable C-C bonds. This lignin property with its high resistance to degradation divides it from other natural polymers and largely determines its action in biochemical processes, including the formation of humic acids. Lignin, performing protection function in plants, must provide different effects on the properties of humic substances, which are defined by phylogenetic origin of plants. Therefore humus substances have a different protection effect in different ecological conditions.

The determination of lignin in plants, soils and humus acids involved the alkaline oxidation with copper oxide at 1700°C under pressure in nitrogen environment. It was shown that the degree of oxidation of the biopolymer during the transformation of organic matter increased when going from the living plant tissues to humic acids in surface and buried soils [1]. The portion of lignin fragments remained unchanged during the biopolymer transformation in the following series: plant tissues–falloff–litter–soil–humic acids–buried humic acids. It was also shown that the biochemical composition of the plants had a decisive effect on the structure of the humic acids in the soils.

The quantitative analysis of lignin phenols and ^{13}C-NMR spectroscopy proved that the lignin in higher plants was involved in the formation of specific compounds of soil humus, including aliphatic (peaks at 56 ppm) and aromatic (peaks at 147 ppm) molecular fragments. In the humus acids of Greyzems Haplic and alpine Leptosols Umbric the peak areas of lignin structures are mostly in the aliphatic part of 13C-NMR spectrum. Correlation between the lignin content (VSC) in the humus horizons of humid landscapes soils and peak area of the lignin origin at 56 ppm is about 0.94 ($P = 0.95$). In the humic acids of Chernozems, the contribution of aromatic lignin fragments to the nuclear part of the molecule is double that in the peripheral part of the molecule. In the buried horizons, the peak areas of lignin compounds in the nuclear fragments of humic acid molecules are larger than their halos for humic acids of the surface horizons by 5 times. The peak areas of lignin structures in the aromatic and aliphatic fragments are similar for the humic acids from Fe-Mn concretions and Gleysols Mollic of accumulation landscape positions.

Comparison of ^{13}C-NMR spectra of native lignin preparations, isolated from different species of tree and herbaceous plants, with a spectrum of humic acid diagnosed that, the number of peaks at 102, 115, 119, 131, 152, 166 ppm also have a lignin genesis. Secondly, heterogeneous set of peaks in the spectra of different plants and, consequently, in the molecules of humic acids of different soils, must also be different. Thirdly, lignin of southern taiga trees is the source of more advanced in space molecules of humic acid with developed aliphatic part. Cinnamilic phenols from steppe plants form a spatially compact structure of Chernozem humic acids.

That is way, in Chernozem and Krasnozem, as in soils with high biochemical activity the more possible pathway of humifiation is the deep and quick fermentative degradation of high-molecular compounds to monomers. The role of humic acids abiotic condensation from simple free monomers is more considerable in lowlands hydromorphic conditions and in high mountain soils, where microbial activity is lower and ferment amounts is also low. High-molecule compounds preserve and gradually change into humic acids by the way of biopolymer degradation. Thus the total production and composition of lignin fragments in humic acids reflects the proprieties of plant souse of lignin and biochemical conditions of humification.

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Unexpected Role of Humic Acids in Wax Biosynthesis of Higher Plants

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The beneficial effects of humic acids (HA) have been numerously reported. According to a modern view on biological activity of HA they can affect plant growth by different ways such as increasing respiration, enhancing mineral nutrition, and/or stimulating hormonal activities Although a large dataset of evidence indicates that HA can directly affect plant development in several metabolic pathways, relatively little attention has been paid to uptake of HA by plants. However, realization of the above mentioned mechanisms requires HA entering plants and translocation from their roots to shoots. Therefore, uptake of HA by plants is a keystone in understanding nature of HA activity. Recently it was demonstrated that endodermis possessing hydrophobic character due to cell wall suberinization was seemingly the main control point for HA transport in plants [1]. The objective of this work was to study distribution of HA in plants lipid fraction using tritium labeled humics.

Tritium-labeled coal humic acids ([^{3}H]HA) were prepared as described in [2]. Seedlings of wheat *Triticum aestivum* L. were used for the experiments. Eight-day old plants were transferred into the vials containing 15 mL of HA at concentration 50 $\mathrm{mg{\cdot}L^{-1}}$ with specific radioactivity ~0.7 mCi $\mathrm{L^{-1}}$. After 24 h plants were taken out from the solutions and wheat shoots were subjected to lipid extraction and separation by thin layer chromatography (TLC) procedure followed by autoradiography of the chromatograms. Then the band where the highest radioactivity was observed was subjected to GC-MS analyses.

Compounds of the [^{3}H]HA band of plant lipid extract determined using CG-MS analyses were found to be mainly hydrocarbons including normal and branched alkanes (about 73% of total amount of compounds) and normal alkenes (about 19% of total amount of compounds). In case with lipid fraction of humics, alkanes (normal and branched) and normal alkenes totally accounted for about 54% of determined compounds. It could be therefore hypothesized that compounds from HA (or at least part of them) must not be metabolized by plants before assimilation but assimilated *in crudo*.

Alkanes can be usually found in plants in waxes which are associated with cuticle and suberized tissues, and the determined composition of HA in lipid fraction might therefore reflect their role as part of the waxes associated with suberized tissues. In most plants there are two principal wax biosynthetic pathways: an acyl reduction pathway, which gives rise to primary alcohols and wax esters, and a decarbonylation pathway, leading to the formation of aldehydes, alkanes, secondary alcohols and ketones. It is the decarbonylation pathway providing principally wax biosynthesis, and the principal step of the decarbonylation pathway is the hydroxylation of alkanes to secondary alcohols. Therefore, HA-derived hydrocarbons could be hypothesized to be involved in the wax biosynthesis as precursors for secondary alcohols.

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Rational Design of Engineered Nanomaterials for Water and Soil Remediation

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Metallic nanoparticles are being increasingly used in various industries. The nanosized monometallic or bimetallic particles can be either supported (or encapsulated) onto an appropriate matrix (polymer, carbon, metal oxide, zeolite etc.) or used as free-standing (naked) forms. The decreasing costs of metal nanocomposite materials and increasing understanding on the advantages of the nano-size effects lead to many new applications of metal nanoparticles. Recently nanomaterials are considered among the forefront leaders for environmental applications, including water and soil remediation. Iron nanoparticles are capable of destroying diverse chlorine-containing carcinogens such as polychlorinated biphenyls (PCBs), DDT, lindane and virtually all chlorinated organic solvents. The catalytic effects of surface modification of iron nanoparticles have been also reported. Both metallic and oxide iron nanoparticles were found to remove also heavy metals (Hg, Cu, Cr), arsenic and nitrates from water. Chitosans and derivatives of cellulose were used as biocompatible supports for metallic an oxide iron nanoparticles used in water remediaion.

The possibility of using metal nanoparticles in environmental protection for remediation of soils and water resources polluted by ecotoxicants, such as chlorinated organic compounds rises the question of the character of the impact of the nanomaterials (to be used for remediation) on the biocenosis of the ecosystem, which is in the contact with the nanomaterials. The possible toxic effect of the metal nanoparticles and the products of their reaction with the toxic organic compounds (the forms of the metal nanoparticles formed after the remediation process) should be eliminated or reduced to zero if possible. The effect of nanomaterials on the hydrobiotic forms and seaweeds is still more important taking into account that they are the starting link of the trophic (food) chains, in which the toxic compounds can be accumulated and can enter the higher organisms, including the human being. The low toxicity of iron based nanomaterials applicable in environment remediation has been demonstrated for a number of hydrobionts (daphnia, algae, mussels, planaria flatwarms).

Chemical Analysis of Water – Quality Assessment of Water Treatment

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In general, the effectiveness of some of the traditionally used in water treatment technologies, which include flocculation and sorption, flotation, can be significantly increased through the introduction of nanotechnologies. Membrane technology, according to experts, is one of the important spheres of development of nanotechnologies in the field of water purification and water treatment. Moreover, nanofiltration provides ultra pure water of high quality, which is used in medical, pharmaceutical, electronic, food and other branches of industry.

Choice of the method of processing of water is always defined its original composition, and evaluate the efficiency of water treatment is possible only according to results of research of initial and treated water. That is why the data of the integrated analyses of water are crucial for water treatment in general and in the use of nanotechnologies in particular. In the latter case, it is important to know the content of organic substances which may be present in the water as in the form of humus substances, and in the form of individual organic pollutants (pesticides, drugs, surface-active substances, etc.).

Assess the content of organic substances can be at the value of oxidation: for waste water - COD, for drinking and natural water - permanganate index, as well as BOD. Thanks to the simplicity and availability of the equipment these methods are available for any analytical laboratory. An enduring characteristic of the content of organic substances is total organic carbon. In Russia the content of TOC is only for bottled drinking water, for this reason, and also because of the relatively high cost of equipment determination of TOC method is used only in some Russian laboratories.

Even more difficult is the control of the content of individual organic compounds, which is possible only with the help of modern expensive chromatographic methods of analysis.

An important indicator of the quality of drinking water and the characteristic of the degree of cleaning of waste water is the content of heavy metals. According to requirements of normative documents on water quality, heavy metals (lead, cadmium, mercury,...) can be present in the natural, drinking and purified water at the level of very low concentrations, therefore, to control their content should use highly sensitive methods of analytical control, ICP, ICP-MS, GF AAC.

In many regions drinking water contaminated with arsenic causes significant problem. The effect of arsenic on human has been known for a long time, the maximum allowable concentration of arsenic in natural and drinking waters is at 10 μg/l. However, it’s difficult to solve the problem of water purification from arsenic. According to the literary data the use of nanotechnology allows the purification of water from arsenic, which involves analytical control of this element in the water.

The use of nanotechnology is the most appropriate method for removal from water of manganese and iron, which, as a rule, are present in the underground water in high concentrations.

Thus, the introduction of nanotechnology is impossible without establishing a system of analytical control of water quality with the use of modern methods of analytical chemistry.

Influence of Cut on Humic Substances of Podzolic Soils in the Spruce Forests of European North-East

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Humic substances (HSs) are a special unique part of soil organic matter (SOM) that provides for stable functioning of soil and all components of terrestrial ecosystems. The impacts of clear-cutting on SOM, HSs and properties of podzolic soils formed under spruce forests on mantle loams of the European North-East of Russia (middle taiga, the Komi Republic) has been investigated. Bioclimatic conditions of middle taiga have been shown to favor temporary bogging in soils at cut areas for first 5-10 years. Re-vegetated deciduous tree species with coniferous inclusions 36 years after cutting led to a decrease in forest litter thickness (4.1±0.4 cm), acidity (5.0±0.2 units pH_{H2O}), and increase density (0.15±0.02 g cm^{-3}) and compared with native spruce forest (5.5±0.8 cm, 4.3±0.1 units pH_{H2O}, 0.11±0.02 g cm^{-3}, correspondingly). There is a clear trend on lowering organic carbon stocks in all study anthropogenic soils from $25.5 \cdot 10^3$ (native spruce forest) till $24.4 \cdot 10^3$-$23.1 \cdot 10^3$ kg ha^{-1} (cut areas) and total nitrogen stocks in forest litter from $0.99 \cdot 10^3$ (native spruce forest) till $0.84 \cdot 10^3$ kg ha^{-1} (in “young” cut area).

Cut area soils are remarkable through increased SOM migration due to enlarged part of water – and acid-soluble substances and hydrophilic components in SOM. Generally, distribution of hydrophilic and hydrophobic SOM components at cuttings differs from that at native forest site. Forest litter and especially eluvial soil horizon of “young” cut area demonstrate an increase in hydrophilic SOM part. “Old” cutting is remarkable by a gradual increase in hydrophobic componing along with transition of O-horizon to EBh-horizon.

Other tree species and different humus formation conditions at loggings are responsible for changes in humic substances (HSs) elemental composition and simplification of HSs macromolecules structure. Carbon content in humic acids (Has) varies between 510 and 566, nitrogen between 28.2 and 47.6, hydrogen 40.6-57.1, and oxygen 334-396 g kg^{-1}. C, N, and H content in fulvic acids (FAs) have lower values of 474-514, 8.8-18.1 and 28.8-47.3 g kg^{-1}, correspondingly. O content and O:C ratio in FAs significantly exceeds that in HAs. Down soil profile, all study soils decrease in HSs carbon content.

HSs composition of native spruce forest Podzols is typical of taiga Podzols. However, cut area soils have certain changes in HSs composition. HAs in soils of cut areas contain 1.3-1.7 times more nitrogen as compared to the control (32.6-47.6 g kg^{-1} against 28.0-28.2 g kg^{-1} in HAs extracted from O and E horizons of native soil) and have a much lower C:N. FAs show the same trend of an increasing nitrogen content and a decreasing C:N in soils of “young” cut area, exclusively. For the “old” cut area, these values are similar to those of native forest soil. HAs extracted from O and Ehg (E) horizons of logging places demonstrate higher H:C ratio (1.00-1.20) values compared to the native soil (0.90-0.95). This evidences that their macromolecules increase in the portion of aliphatic fragments.

Analyzing HAs and FAs hydrolyzates (6M HCl) we have identified 15 amino acids with similar composition for all humic and fulvic acids studied. Total content of amino acids in E horizon at cut area is 4.5-4.8 times higher than that for native soil. HAs and FAs from different soil horizons of native forest differ also by proportion of main amino acidic groups, namely acid, base, non-polar and polar groups. HAs hydrolyzates are increased in portion of base amino acids (histidine, lysine, argenine) from 14.4 to 22 % and reduced in portion of polar amino acids (threonine, serine, glycine, tyrosine) from 25 to 17.3 % of amino acid total in O and E horizons, relatively.

The study is supported by Program of UD RAS, project No 12-P-4-1065 «Interrelation of structural-functional and spatial-temporal organization of soil biota with dynamic aspects of podzolic soils and SOM under the process of natural reconstruction after harvest cut in taiga ecosystems in the European North-East».

Determination of Nanodiamonds Adsorption Activity to Heavy Metals in Waters by Methods of Laser IR and Raman Spectroscopy

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It is extremely important to create new active adsorbents in order to remove impurities from waters, to have high-purity materials and drugs, to use adsorbents for biomedical purposes. It is known that due to the large specific surface area, multifunctionality of surface groups, the possibility of targeted modification of the surface, adsorption properties of nanodiamond particles exceed adsorption properties of many carbon sorbents.

This work presents the results of a study of adsorption properties of the original and modified nanodiamonds dispersed in aqueous solutions, with respect to dissolved salts of heavy metals Cu and Pb. We also made experiments with different types of anions: NO_3^-, ClO_4^{2-}, SO_4^{2-}. We investigated the original detonation nanodiamonds (DND) I6 (Fig. 1) and the modified I6 by COOH-groups. The activity of nanodiamond adsorbents was determined by the difference of concentrations of dissolved salts before and after their interaction with the DND particles. The salt content was measured by the dependence of the quantitative characteristics of absorption spectra and of the Raman scattering (RS) valence band of water in solutions on salt concentrations. Sizes of the particles and aggregates were measured with dynamic light scattering method. Comparative analysis of the activity of DND adsorption properties to hard metals in aqueous solutions was performed using IR spectroscopy. The obtained results demonstrate that the activity of DND adsorption properties depends on the primary processing of DND nanoparticles, on modification of their surface, on the size and concentration of DND in solution.

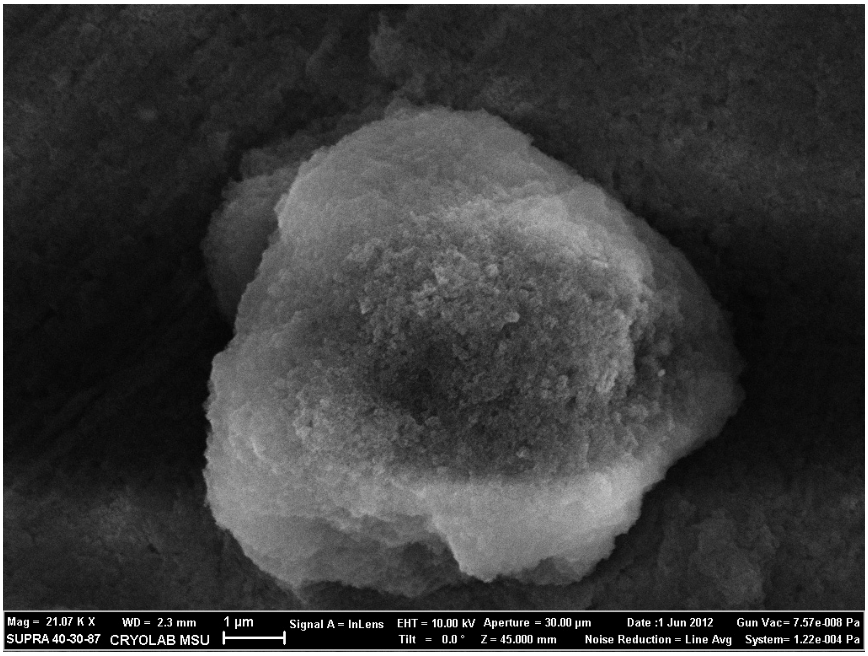

Figure 1. Photography of nanodiamonds I6, removed from water suspension with concentration 0.5 mg/ml (high-resolution tunnel microscope).

Characteristics of Humic Acids of Peat in Gorny Altai

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Since 2008 in Altai Republic fundamental and applied research of bog bio-geocoenosis of Altai Mountains within the framework of a scientific and educational complex has been carried out: the accredited Laboratory of Agro-ecology of TSPU – the Chair of Chemistry of GASU – the Analytical Laboratory of Gorno-Altaisk Research Agricultural Institute of Siberian Branch of Russian Agricultural Academy. Peat resources of Altai Mountains draw attention as a raw potential of a tourist and recreational area. The priority directions of development of high technologies in the republic are the following: a sector of balneology, sports, and health improving medicine. The extensive area of use of humic products on the basis of peat defines the research of mountain peat on target components, in particular humic substances, studying their structure and properties.

Among the representative kinds of peat in Gorny Altai the lowland sedge kind is widely spread. In comparison with the West Siberian peat the mountain sedge peat is characterized by a large amount of humic acids: 47.8 % and 37.5 % accordingly, and by a lower amount of NHR (non-hydrolyzed remnant): 7.5 % and 11.2 %. The amount of WSS (water-soluble substances), EHS (easily hydrolyzed substances) and HHS (hardly hydrolyzed substances) in lowland sedge peat of both regions is identical or close enough: WSS and EHS (29.1 % and 30.6 %) and HHS (3.0 % and 3.1 %).

According to the elemental analysis it is necessary to note a considerable amount of carbon (C) in the HA (humic acids) of the sedge peat under study (68.09 %... 70.13 %), hydrogen (H) (6.07 … 6.82 %), and a raised amount of nitrogen (N) (2.63 %... 3.77 %). The specified aspects point out the developed aliphatic structures in HA of the lowland sedge peat: an average ratio of H/C makes up 1.11; O/C – 0.31.

According to the data of IR-spectra in the structure of HA of the sedge peat the alkene substitutes (2920 cm^{-1}), carbohydrate fragments (1030 cm^{-1}), and hydroxyl groups (3400 cm^{-1}) prevail over aromatic fragments. In the macromolecules of the investigated HA the hydroxyl groups and carbohydrate fragments prevail over alkene substitutes: the corresponding correlations of the optical density make up 1.23 and 1.41 accordingly.

The use of humic preparations as the fodder additive for Siberian stags has shown a positive influence on biochemical indicators of blood, on the amount of macro- and micro-elements, and on antler-growth efficiency.

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The Study of Complexation Features of Humic Acids Macromolecules with Metal Ions by the Spectral Dependence of the Fluorescence Quenching Efficiency

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Humic acids HA are the most important component of environment. They contain in the soil, water (dissolved) and air (aerosols). The HA origin are organic material which is synthesized at oxidation of difficult natural organic molecules such as by carbohydrates, proteins, lignins and contain in the remains of lifeless plants and organisms. The structure of HA macromolecules contains many groups functionally different chemically (catechols, quinines, phtalates, fenolamines,salicilates, etc.) capable to a complex formation with metals [1]. Due to this property the HA influence on concentration of the dissolved pollutant.

Receiving constants of a complex formation of KME by a method of fluorescence is based on observation of fluorescence quenching of HA intensity by metal ions. Formally, the KME value is determined from the equation Stern-Volmer SV [2].

$$I_0/I = 1+K_{SV}\,[Q] \qquad (1)$$

In (1) [Q] – concentration of metal ions; I_0 and I – values of intensity fluorescence (integrated or on certain length of wave) at [Q] = 0 and [Q] ≠ 0 respectively. K_{SV} – a constant of SV constant quenching defining efficiency of quenching. It is necessary to emphasize especially that K_{SV} is equal to constants of a complex formation of K_{ME} only if quenching has the static (concentration) nature, but not of dynamic [3]. By means of a SV method a significant amount of works in which it was reliably established that concentration quenching takes place is devoted to studying of constants of a complex formation of HA. However in all available works there was no information on what efficiency of a complex formation of separate sites of HA. This question can be solved if to analyze the spectral dependence of quenching efficiency. In the real work it is made on an example of quenching of fluorescence of a sample of HA IHSS by Cu^{2+} and Cd^{2+} ions. In fluorescence spectra of HA two spectral components were allocated with maxima for 455 (blue component) and 505 nanometers (red component) for which SV constant were defined. It was established that efficiency of quenching blue and red components differ: with Cd^{2+} ion for 20 % while for Cu^{2+} ion this distinction makes more than 3.5 times. It means that complexing ability of HA with metal ions considerably differs, but thus the charge of an ion doesn't play a significant role. The size of radius of an ion can be one of the possible reasons of observable distinction: for Cu^{2+} and Cd^{2+} ions they are 0.8 A and 1.03 A respectively. The size of an ion can define availability of ions to a complexing site, and distinction in efficiency blue and red fluorescence components for ions can mean that ions with more big radii not always can reach complexing sites while copper ions have such possibility.

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Nanoparticle Stabilised Emulsions: Do They Offer Remedial Opportunities?

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Particle stabilised emulsions (or Pickering Emulsions) are emulsions that are stabilised by the adsorption of colloidal sized particles at the interface between two immiscible phases. The adsorption of these particles is controlled by the contact angle made by the particle at the contact line between the immiscible phases. The energy necessary to remove a particle from the interface is given by the expression:

$$\Delta E = \pi r^2 \gamma_{OW} \left(1 - \left|\cos\theta\right|\right) \qquad (1)$$

A colloidal particle of 500 nm diameter that makes a contact angle at the three phase contact line of 30° will be held at the water/TCE interface (IFT 34.5 mN m^{-1}) by an energy term of 2.2×10^5kT (where k is Boltzmann's constant and T is absolute temperature). Under these conditions the particles are irreversibly held at the interface between the immiscible phases.

The role of these particles in emulsion stabilisation is thus believed to derive from the kinetic barrier that they present when two dispersed droplets come into contact. Since coalescence presupposes particle removal.

Nanoparticles can also prove to be effective emulsion stabilisers though it is necessary to find some way to increase the contact angle to values close to 90°. This can be accomplished by the use of small amounts of surfactant. The stability of the emulsions can be evaluated using rheological measurements. Measurements made in the linear viscoelastic region can yield values for the storage modulus (G') and loss modulus (G''). The storage modulus measures the elastic response of the system to shear whilst the loss modulus documents its liquid response. Our work suggests that stable emulsions arise when G' > G''.

We have begun to investigate the use of colloidal silica (particle size 50 nm) as an emulsion stabiliser for TCE in water emulsions. So far our work suggests that stable emulsions can be formed with the addition of small amounts of salt and non-ionic surfactants.

We have further extended the work by examining the incorporation of iron powder into the emulsion systems. The emulsions formed are extremely stable but are also quite solid–like in appearance. There is some suggestion that incorporation of iron results in a rapid reaction as observed by the oxidation of iron. However it is not clear that this signifies TCE degradation. This is under further investigation.

A parallel body of work has examined the synthesis of iron-oxide nanoparticles which are also under investigation as remediation agents. These too can be used to stabilise oil in water emulsions, which have the additional interesting property of being magnetic.

Finally we present some very preliminary laboratory data on the use of particle stabilised emulsions as a way of dealing with a NAPL source zone.

Effect of K-humate on Diamond Nanoparticles Phytoactivity

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Diamond nanoparticles (DNs) have now gained world-wide attention and industrial applications. These engineered nanostructures are coming in broader contact to environment what makes actual their bioactivity research.

The objective of this study was to determine the influence of pure DNs (Cat# PL-SDND, Plasmachem GmbH, particle size 5-10 nm) and their complex with K-humate (Pow-Humus, originated from leonardite, 0.05 mg/ml) on white mustard *Sinapis alba* L. – very popular high plant species in bioassays. DNs water suspensions and DNs suspensions in K-humate solution were prepared at different concentrations of DNs (w. %), from 0.005 to 0.500, and tested on plant seedling root growth. Seed incubation was done in 2 stages – the seed wetting in testing suspension (1 day) and the seed growing (3 days). As the result it was measured the length of roots and compared with the data of control experiment, where seeds were grown in distilled water. Experiment was provided at the 25°C in darkness. Statistic relevance was achieved by 3 replications of experiment.

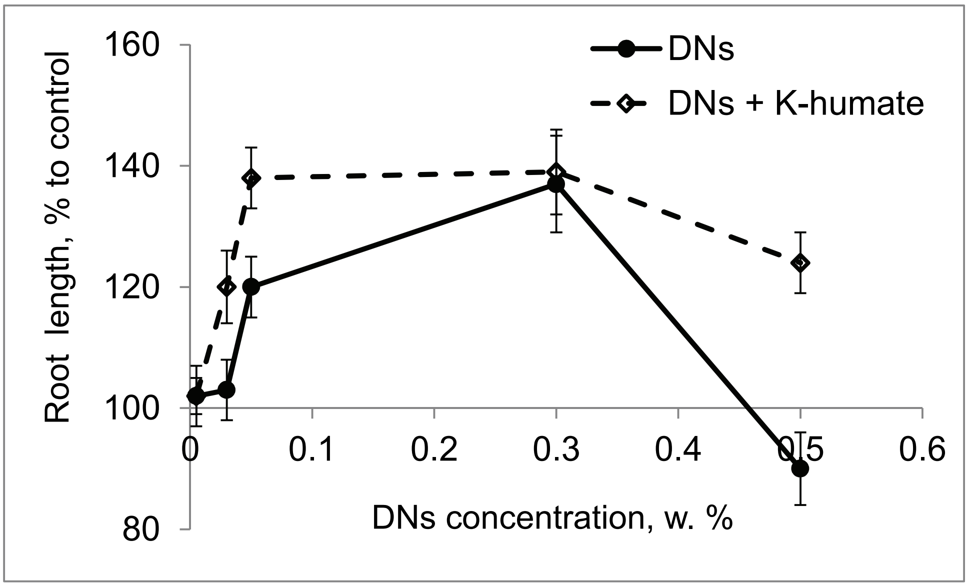

Figure 1. Phytoactivity of pure DNs and DNs complex with K-humate (tested on mustard seedlings).

It was found that DNs affect plants in different ways depending on concentration level (Figure 1). For DNs at concentrations 0.005–0.300 % the gradually increasing stimulation effect was observed; while over 0.300% the stimulating effect is sharply decreased and above 0.450 % the root inhibition effect was found. Effective concentration (EC_{50}), assumed to be around 1 % DNs concentration. DNs suspension in humate solution demonstrated significant positive effect in comparison to pure DNs suspension. The maximal stimulating influence of K-humate was observed at DNs concentration 0.030–0.050 %; while significant detoxication effect was determined at 0.450–0.500 %. It is necessary to mention that pure humate solution without DNs additives demonstrated only 111 % stimulation effect.

The influence of DNs can cause as ambiguous stimulation as an inhibition of the root growth. In general, DNs demonstrate very low phytotoxicity. Only at 0.5 w.% DNs performs slight inhibition effect on roots growth. K-humate can be perspective additive to DNs due to its high potential to increase the plant growth stimulation effect.

The authors wish to thank V. Vavilova, T. Gubarevich, A. Kalachev and Yu. Fedutik for collaboration.

Biotechnological Model of Soil Fertility of Kazakhstan

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Currently in agroecosystems the physical, chemical, physic-chemical, biochemical and microbiological processes are developed, and their in the accumulation of products and changing the properties of the soil is assessed. These processes are interrelated, so it is impossible to synthesize reliable methods and technologies for high productivity while maintaining soil fertility, reproduction [1-4].

The criterion of fertility is the biodiversity in soils and above-ground vegetation. Rule measure prohibits the conversion of natural systems in their operation to move some of the limits beyond which lost their ability to support themselves. Rule of chain reactions and “hard” control of nature creates objects that change the natural processes that are environmentally, socially and economically not acceptable in the long time interval. Biosystem, after getting in extreme conditions, simplifies and it becomes “tough”, it decreases the number of degrees of freedom [5].

Methodological basis for creation of a functional model of soil fertility constitutes a systemic analysis of complex facilities and soil balance method. This is justified by the law of minimum factor in agro-ecosystems. The most negative impact will be the factor, which is minimal with respect to the others (the principle of Liebig). This idea was developed by de Wit and Penning de Vries [6] and supported us in our investigations. Adaptation of systems analysis to the problem of restoring soil fertility include the development of efficient , environmentally sound methods of optimizing the organic matter status, power plants, the composition of the microbiota. The main stages of modeling are 1) the construction of functional physical model; 2) proxy authentication physic-chemical parameters of the model; and 3) laboratory and greenhouse testing.

The purpose of the research is to develop biotech-raising mechanisms, and reproduction of fertility in Kazakhstan.

The main research results are as follows.

1. Environmentally fertility biotechnological materials zeolites employed biomatrix humic substances and effective micro-organisms.
2. The greatest number of nitrogen fixers had options with modified zeolite with humic and effective microbial agents. These biologics significantly increased the number of microorganisms in several times.
3. The use of bio-organic fertilizers and microbial medication increased by 2 times the number of ammonifying. The highest enzyme activity of protease variants accounted for the modified zeolite – 85 ~90 %.
4. The modified zeolite biomatrix was productive (3~7.5 times) and functional over time. The mechanism of their effects was the optimization of nitrogen-fixing activity of microorganisms in water supply and nutrition.
5. Doses to the crops of rice and potatoes were 2~5 t/ha. For the modification of zeolite applied fertilizer solutions, humic-microbial drugs and stimulants, a new generation.
6. The modified zeolites on the basis of nitrogen, bio-fertilizers and microorganisms increased the effective productivity of soils up to 100%. Product modifications have optimal physical and chemical parameters, technological and economical to use for rise, vegetables and industrial crops.

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Humus Status in Technogenic Soils of Kyrgyzstan

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The extensive use of natural resources, intensive cropping and outdated agriculture due to economical reasons have resulted in the significant degradation of soils in Kyrgyzstan. Virgin ploughing and crops of cultural plants lead to sufficient changing of the ecosystem phytocomponent. Multi-species long-vegetative phytocenoses are replaced by phytoagrocenoses, *i.e.* short-vegetative, mainly one-genus types of plants. It results in the change for production process and violation of the compensated circulation of organic mass of plants.

This research is aimed to estimate humus status in soils of Northern Kyrgyzstan in terms of content, structure, fraction composition for vertical row on all over the depth of soil profile. Ratio of fractions of humic to fulvic acids depending on ecological conditions is also object of this research. The analysis of soil humus of Kyrgyzstan showed that the ploughing of virgin soils and their further intensive use in irrigated agriculture lead to sharp reduction of the humus content. It should be stressed that the most notable loss is recorded in humus-rich soils, that testifies a high speed of destruction of humus substances at crops formation.

Table. Changes in humus as a result of agricultural land-reclamation

Soil type	Depth, cm	Virgin regions	Agricultural	Loss of humus,%
Sierozem north ordinary	0–25	1.79	1.52	15.1
	30–40	1.55	1.42	7.2
	50-60	1.38	1.37	5.1
	90–100	0.76	0.74	2.6
Sierozem north	0–27	2.05	1.79	12.7
	30–40	1.76	1.64	6.8
	50–60	0.93	0.91	2.2
	90–100	0.82	0.83	0
Light-chestnut	0–25	3.77	2.64	30.0
	30–40	2.69	1.99	26.0
	50-60	1.53	1.49	2.6
	90–100	0.72	0.69	4.2
Dark-chestnut	0–31	4.07	3.04	25.3
	30-40	3.43	2.85	16.9
	50-60	1.27	1.15	9.4
	90–100	1.08	0.91	15.7

In the course of agricultural development there is also a change of fractional composition of humus. The increase in brown humic acids (BHA) is observed for irrigated mountain-valley soils, especially in the arable and sub-arable horizons. The increase in BHA is recorded also in the dry-farming chernozems, and on all over the humus horizon.

Tandem$^{12/21}$ International Long Term Program to Increase the Biological Soil Fertility and to Establish of Sustainable Biological Nutrient Resource in the Soil by Applying Phytohumincompounds (PHCs)

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The times, when high, stabile, and good quality agricultural yields could be achieved by fertilizing and chemical plant protection are over. The use of Plant Growth Regulators of a new generation consisting a combination of a small fraction of synthetic or natural phytohormones (P) and synthetic or natural humic acid (H) preparations (PHCs) is a perspective complement to the reduction of inputs of chemical fertilizers and pesticides.

Currently, the elementary processes in the application of PHCs for seed treatment, for the treatment of the plant in different stages of growth and for the treatment of the soil to be examined. The addition of a small amount of plant hormones (20 ml per 1 ton of seed or 1 hectare of crops) in the humic acid matrix provides a high efficiency of the PHCs and is completely environmentally safe (1 m^2 gets $1x10^{-9}$ of active substance). It is a substantial nanobio-ecotechnology of XXI century for agriculture and soil improvement technologies.

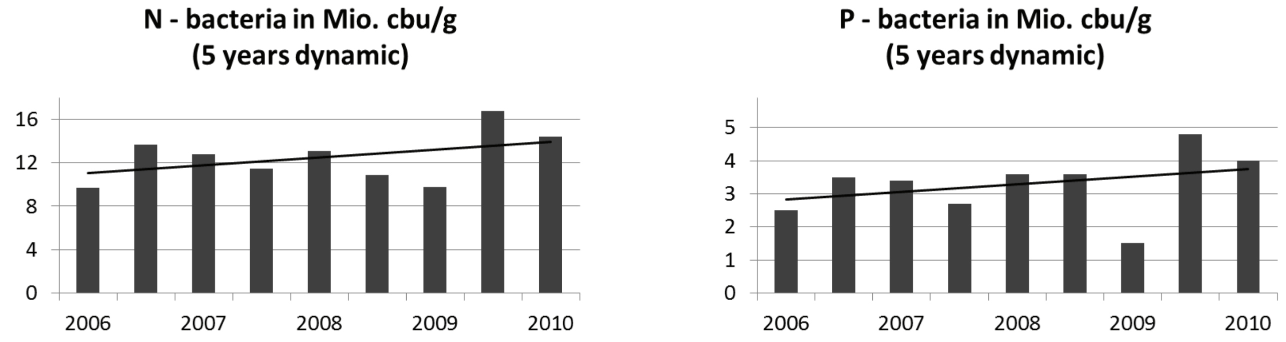

Figure 1, 2. Evolution of the concentration of atmospheric nitrogen-binding (N) and phosphorus mobilizing (P) bacteria after periodically application of plant and soil by PHCs.

In the Period 2006/11 we analyzed the PHCs "PhytoHumin 5050R" and "Future9/12" which are produced from the basic preparations Emistim C, Agrostimulin N, Biolan, Humisol, Lignohumat and RadoPin. These compounds are applied in the spring, usually with the first plant protection measures on the field. Periodical treatment of the plants increases atmospheric nitrogen fixing and phosphor mobilizing bacteria (N bacteria and P bacteria) in the soil by 25-32% within 3 to 5 years. According the YEN-model, with growing bacteria concentration the application of mineral fertilizer can be reduced up to 50-60%.

Invitation to Cooperation

In the new long term programm Tandem$^{12/21}$ – Tandem means "double". Five PHCs of different combinations are applied. Sophisticated combination of basic compounds during the spring treatment stimulates soil biology. The fall treatment then stabilizes the soil biology during the winter. We invite further international scientific partners and practice partners for long-term cooperation under the program Tandem$^{12/21}$ (www.darostim.de).

The Interaction of the Metal Iron with Humic Substances

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The humic substances (HS) are considered to be one of the most complex and diverse natural organic compounds in terms of structure and composition. HS contain aromatic skeleton, highly substituted with various functional groups. It is believed that their presence determines the ability of HS to form stable complexes, compounds and soluble composites with metal ions or their compounds. In addition, these functional groups can themselves be involved in the interaction of HS with dissolved metal compounds. In this work we studied the reaction products of HS concentrated solutions with metallic iron. HS compounds with iron are one of the most interesting, because of their prevalence in nature. Besides iron-containing HS are widely used – starting from regulators of iron deficiency in plants [1] and up to the base of nanocomposites for biomedical applications [2]. Due to the fact that these kind of iron-containing compounds are generally amorphous, heterogeneous, multiphase and nanoscale the only possible method of investigation is Mossbauer spectroscopy.

Mossbauer spectroscopy of frozen aqueous solutions showed that in the presence of air there is a transition of iron into humic solutions of alkali metals, with stabilization in the form of finely dispersed hydrated oxides of iron(III) (δ=0.45 mm/s, Δ=0.73 mm/s, 85 K). On the other hand, under anaerobic conditions, up to 60% of the iron in the solution is in the form of stabilized hydroxocompounds of iron(II) – (δ=1.28 mm/s, Δ=2.74 mm/s, 85 K). To model (simulate) the interconversion of compounds of iron(II)-iron(III) in HS solutions we conducted a similar study for EDTA aqueous solutions. It is shown that under anaerobic conditions in the model solutions of chelating ligands with metallic iron it was observed the formation of compounds of iron (II), easily and reversibly oxidized in air to form compounds of iron (III).

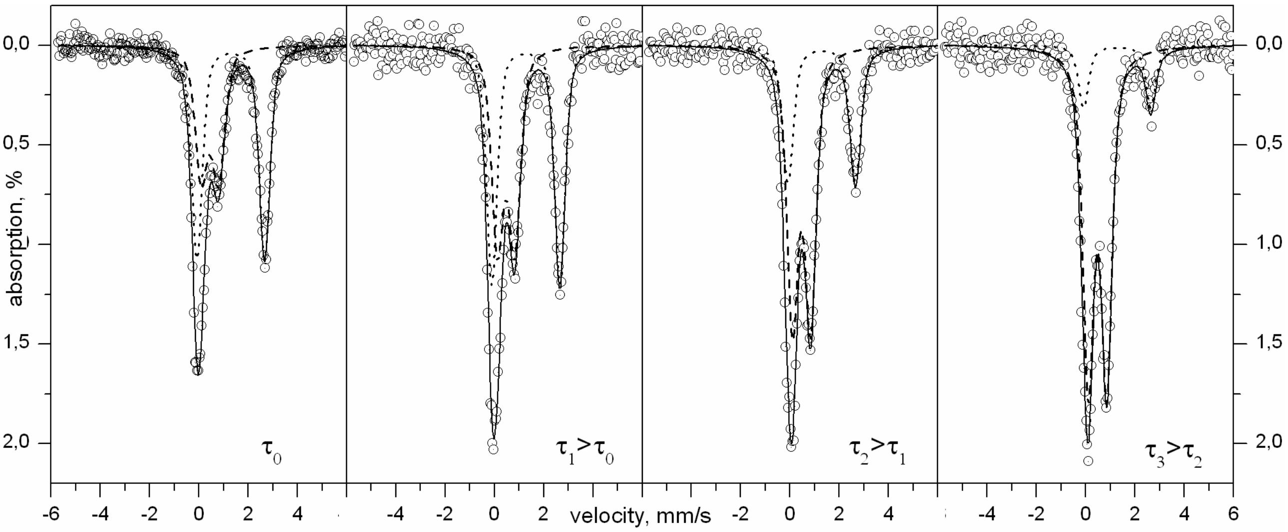

Figure 1. Changing of the Mossbauer spectra of frozen (85 K) solution of the product of interaction of metallic iron and HS from oxidation in air.

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Lignin and Humic Polymers as Natural Surfactants

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The fundamental properties of the lignin and humic polymers are amphiphilicity, polydispersity and heterogeneity of structural elements.

The most important genetic feature of peat humic substances is dependence of their composition and properties on the chemical composition of peat forming plants, in particular on the content of lignin which is the main source of aromatic fragments of peat humus.

Taking into account the similar nature of the compounds of lignin and humic nature, their important role in the natural processes, proximity of the areas of their practical application, including as natural surface-active substances, it is advisable to obtain comparative characteristics of their surface-active properties.

The solutions have been characterized by surface tension measured using Wilhelmi method and by the foaming capacity determined using cylinder shaking method (Figure 1 and Figure 2).

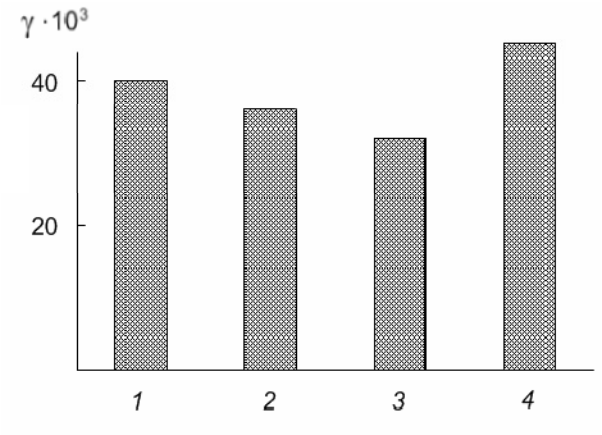

Figure 1. Maximum of decreasing surface tension (N/m)

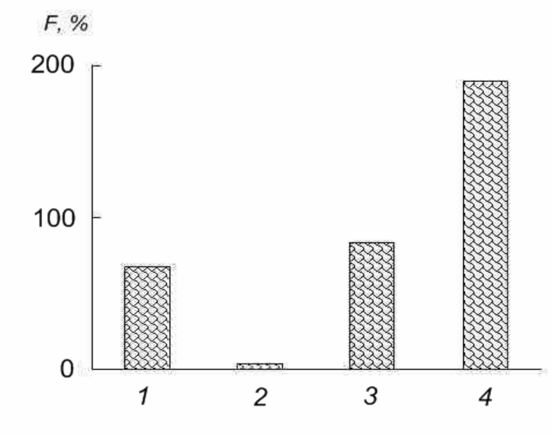

Figure 2 Foamation, %

in Solutions:
Sodium Lignosulfonates (1); Kraft Lignin (2); Sodium Humates (3); Sodium Oleate (4)

The correlation between maximum decreasing of surface tension and foam stability is observed in the solutions of investigated compounds of lignin and humic nature. This allows predicting their foaming properties.

Conclusions:

1. It was established that in the solutions of water soluble derived lignin-humic polymers, the formation of an equilibrium adsorbed layer at liquid-gas phase boundary lasts for 4–24 hours (depending on the concentration).
2. By the ability to decrease water surface tension, the lignin and humic polymers are comparable with low molecular surfactants (the maximum of decreasing surface tension reaches 35–40 mN/m).
3. Foamation of the lignin and humic polymers increases as follows: kraft lignin < lignosulfonates < humates; while decrease of surface tension: lignosulfonates> kraft lignin> humates.

The study is supported by of Ural Branch of RAS (project 12-C-5-1017) and the RFBR (project 12-03-90018-Bel_a).

Humic-chitosan Gels as Biocompatible Nanocontainers

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Humic acids represent one of the most important natural organic matters. Many studies have been and are published on their composition and chemical structure which are still not fully resolved. Though the structural knowledge is indispensable to understand and reveal the basis of humic acids function and role in nature investigation of their physico-chemical and colloidal properties, which is essentially possible even without detailed structural knowledge, is of equal importance. Humic acids may occur in various colloidal forms – sols or diluted suspensions in water, concentrated suspensions in sediments, solid particles acting through their surface and interface, gel forms in peatlands or coalfields. In our previous work it was shown that physico-chemical interactions of humic acids with, e.g., metal ions, and their kinetics is dependent on their colloidal form. We have then focused on investigation of physico-chemical properties of humic gel which represent a useful model material immobilizing humic acids yet enabling transport of interacting partners not very different from transport in water, due to high water contents in gels. This contribution summarizes results of studies on transport properties of humic hydrogels as well as on their potential applications as controlled release containers. Figures 1 and 2 show examples of hydrogels prepared by ionic gelation of humic acids with chitosan, a biocompatible biopolymer. Such materials combine water retention capability with contents of humic component serving as, e.g., soil conditioner or nutrient transport system.

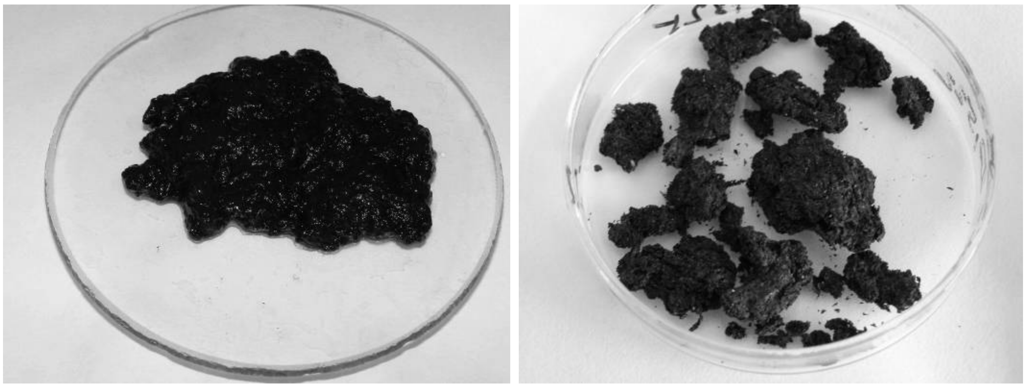

Figure 1. Chitosan/HA hydrogel before (left) and after (right) freeze-drying.

Figure 2. Chitosan/HA hydrogel beads before (left) and after (right) freeze- drying.

Influence of Peat Humic Substances and Their Si-Derivatives on Soil Structure

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Humic substances (HS) are well known to improve soil structure and water stability of soil aggregates. However, physical addition of HS produces aggregates with low stability values, and only HS adsorbed onto the soil particles significantly increase aggregate stability. Silanol modification of HS was demonstrated to be a promising approach to increase HS adsorption capacity in relation to mineral surfaces. So silanol derivatives of HS appeared to be good soil conditioner improving soil structure. The goal of this study was to estimate influence of silanol-modified HS on dry soil aggregate size distribution.

Modification of peat humic acids (PHA) was performed using 1-6-aminohexametileneaminometylentriethoxy-silane (AGM) and 3-aminopropyltriethoxy-silane (APTES), and the obtained derivatives were assigned as PHA-AGM and PHA-APTES respectively. To estimate influence of HS under study on the soil structure the laboratory experiments were performed. The soil samples were watering with humic solution (5 g/L) or distilled water (blank) up to 100% of soil water retention capacity followed by incubation at 28°C during 3 months. The dry soil aggregate size distribution was determined using dry sieving procedure.

The experiments showed that PHA-APTES did not change dry soil aggregate size distribution as compared to blank while PHA-Na and PHA-AGM decreased the content of <0.25 mm fraction from 46% to 27% and 22% accordingly, and increased the content of aggregate fraction 1-10 mm from 35% to 53% and 54% (Fig. 1).

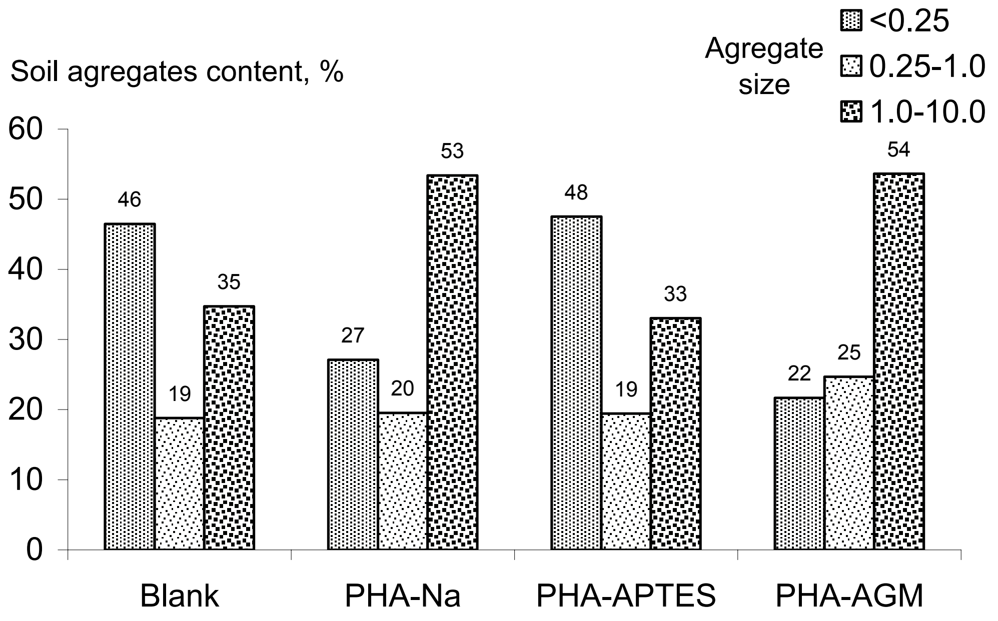

Figure 1. The influence of HS and silanol-modified HS on dry soil aggregate size distribution.

So both initial PHA-Na and modified PHA-AGM promoted formation of aggregates of 1-10 mm fraction and can be promising soil amendments. Additional experiments aimed to determine water stability of aggregates however need to be performed.

Mechanism of Humic-Stabilized Feroxyhyte Nanoparticles Formation: Mössbauer Study of Frozen Multicomponent Reaction Mixture

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In the design of biocompatible magnetic iron oxide nanoparticles (MIONs) the stability is of utmost importance. Different organic compounds are often employed to modify the MION surface during or after preparation to control the magnetic core growth, avoid agglomeration and enhance nanoparticle biocompatibility [1]. Humic substances (HS) representing natural polyelectrolytes were found to be the effective stabilizing agents for pre-synthesized magnetic Fe_3O_4 [2] and γ-Fe_2O_3 [3] nanoparticles. Our previous research showed that the using of HS as *in situ* stabilizers in one-pot synthesis of biocompatible feroxyhyte (δ'-FeOOH) led to decrease of the nanoparticle sizes up to one order of magnitude [4]. However, investigation of the stabilization mechanism remained still a great challenge. Mossbauer spectroscopy of frozen aqueous solutions (FAS) representing a powerful approach to studying of iron-containing multicomponent reaction mixtures was suggested for the stepwise investigation of this reaction system.

The one-pot synthesis examined involves addition of potassium humate and 0.1 M NaOH to $FeCl_2$ solution with subsequent rapid oxidation by 30% H_2O_2 of ultradispersed precipitate formed. According to Mossbauer spectra of frozen (78 K) reaction mixture aliquots taken at the key points of synthesis there is neither interaction between HS and ferrous ions nor formation of solid phases after addition of potassium humate into the reaction mixture.

Addition of NaOH leads to formation of ultradispersed $Fe(OH)_2$. There are two components in the spectrum of $Fe(OH)_2$ obtained in presence of HS; one of which (δ = 1.29 mm/s, Δ = 3.02 mm/s) was ascribed to bulk $Fe(OH)_2$, whereas the second (δ = 1.28 mm/s, Δ = 2.83 mm/s) can be described as a new spectral component related to an interaction of HS with the surface of ultradispersed $Fe(OH)_2$. This interaction is considered as a starting point of *in situ* stabilization and growth control of feroxyhyte nanoparticles by HS. The $Fe(OH)_2$ nanocrystals become entrapped into the HS “matrix” and $Fe(OH)_2$-HS conglomerates are formed. These conglomerates operate as the growth domains in the reaction mixture; Fe^{2+} and OH^- ions diffusing into the limited volume of such domain become distributed among several embryocrystals. Such an ion transport would be also affected by a partial negative charge of the HS branches catching cations and repelling anions. These factors lead to slower growth of $Fe(OH)_2$ particles of the domain in comparison with non-embedded embryocrystals.

So long as rapid oxidation of ferrous hydroxide embryocrystals by 30% H_2O_2 leads to topotactic $Fe(OH)_2$ to δ'-FeOOH transition, the feroxyhyte nanoparticles formed remain stabilized by HS “matrix”. Temperature-dependent Mossbauer study of the product formed shows superparamagnetic behavior of humic-stabilized feroxyhyte nanoparticles due to size effect of the *in situ* stabilization.

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Modeling Remediation of Urban Chemical Polluted Soil Using Two Types of Humic-Based Sorbents

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Nanotechnologal modification of humic acids (HA) with iron nanoparticles (Fe_3O_4) are increasingly being used for environmental remediation purposes. Their reductive and sorption properties reduce the bioavailability and thus toxicity of organic compounds and heavy metals. The aim of this work is to compare the experimental product Fe_3O_4-HA and commercial humic product effects on heavy metal polluted urban soil using plant growth test.

Polluted soil (5-20 cm depth) was sampled at the territory of Kirov industrial region on May 2012. Soil samples (400 g) were mixed with two products: Lignohumate (product based on lignosulphonates, AET, Ltd RET) and Fe_3O_4-coating with humics (Fe_3O_4/HA) (formulated by co-precipitation method *in situ,* Moscow Aviation Institute, RF) at concentrations 0.0025, 0.01 and 1 w%. The plant growth inhibition test was conducted using lawn grass mixture (*Festuca pratensis; Festuca rubra; Lolium perenne)* according to ISO 11269-2 (2003).

Remediation effect and bioavailability of humates were estimated on growth plants. The endpoint of plant tests was dry plant biomass. The results showed that plant biomass increased after treatment of soil samples by Lignohumate at all concentrations from 33±32% up to 73±18% in comparasion with control (untreated) soil. Whereas Fe_3O_4/HA in 0.01 and 1% remarkable decreased biomass growth (till 69±21%) (Fig. 1). Perhaps it appears due to negative effect of iron nanoparticles. Thus, it our previous research it was showed, that nanoparticles of Fe_3O_4 in chernosem and artificial soil mixture can depress the hydrolase activity in soil (Akulova, 2012).

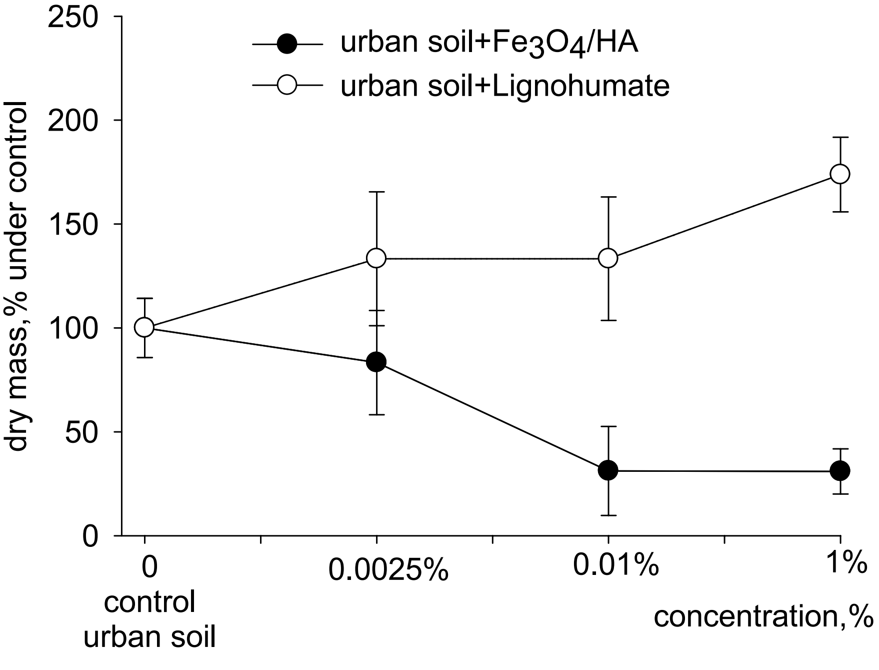

Figure 1. Effect of two types of humic-based products (Fe_3O_4/HA and Lignohumate) on plant biomass growth in urban polluted soil (after 56 days; mean values +/- SE).

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Graphene Oxide for Effective Radionuclide Removal

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Treatment of aqueous waste effluents and contaminated groundwater containing human-made radionuclides, among which the transuranic elements are the most toxic, is an essential task in the clean-up of nuclear legacy sites. The recent accident that included radionuclide release to the environment at the Fukushima Daiichi nuclear power plant in Japan and the contamination of the water used for cooling its reactor cores, underscores the need for effective treatment methods of radionuclide-contaminated water. In USA and Russia significant quantities of soils, sediments and groundwater have been contaminated with actinides including plutonium through activities ranging from nuclear weapons testing to Pu production to nuclear accident. Clearing technologies should be inexpensive, swift, effective and environmentally friendly.

During last decades the interest towards the use of new carbon nanomaterials increased significantly. Among major advantages of carbon nanomaterials are their shape, size and free surface area. Among all carbon nanomaterials, graphene oxide (GO) is well studied so far and it is proven to be non-toxic and biodegradable, and can be easily produced in vast amounts which makes it perfect for environmental applications.

In this work we show the efficacy of GO for rapid removal of some of the most toxic and radioactive long-lived human-made radionuclides from contaminated water, even from acidic solutions ($pH < 2$). The interaction of GO with actinides including Am(III), Th(IV), Pu(IV), Np(V), U(VI) and typical fission products Sr(II), Eu(III) and Tc(VII) were studied, along with their sorption kinetics. Cation/GO coagulation occurs with the formation of nanoparticle aggregates of GO sheets, facilitating their removal. GO is far more effective in removal of transuranium elements from simulated nuclear waste solutions than other routinely used sorbents such as bentonite clays and activated carbon. These results point toward a simple methodology to mollify the severity of nuclear waste contamination that has been spawned by humankind, thereby leading to effective measures for environmental remediation.

Adsorption Properties of Humic Acids of Mechanoactivated Oxidized Brown Coal of Mongolia

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The interaction of humic acids (HA) with mineral components results in the variety of compounds. The various phenomena, such as the weak adsorption interactions, chemisorption phenomena, binding of organic matter in inter-packet spaces of clay minerals, and formation of salts and complex compounds, including chelates occur in soils depending on the mineral composition. It is suggested that the complexes are formed by the silica hydroxyl groups, HA amide groups, and by chelating groups. Investigation of the mechanism of interaction of humic acids with mineral components is of interest not only to predict the environmental redistribution of humic acids, but also to develop ways of management of contaminant migration in the environment, to rehabilitate and remediate soil, and to create a new generation of adsorbents and biologically active materials. It is well known that HA form complex organic systems in caustobioliths, so they can not be completely separated without additional processing. Dispersion produces the changes in their porous supramolecular structure, physical condition, and properties and increase in extraction efficiency.

The purpose of the work was to investigate the effect of conditions for mechanical activation of brown coals on the composition and adsorption properties of HA.

The object of investigation was HA extracted from oxidized Shivee-Ovoo lignite (Mongolia). The mechanical activation (MA) of coal was carried out in a planetary activator mill in several operating modes: MA without reagent, MA in the presence of 5% NaOH (puriss. p.a.), MA in the presence of 5% NaOH (and 3% $2Na_2CO_3$ $3H_2O_2$, at the frequency of drum rotation of 1820 rpm^{-1} and processing time of 2 minutes. Physico-chemical characterization of HA is given on the basis of IR spectroscopy and NMR^{13}C spectroscopy. The HA adsorption was investigated on the quartz river sand. The ratio of silicon to aluminum impurity was 9:1 according to the results of the plasma mass-spectrometric analysis of tested adsorbent.

The maximum adsorption of HA modified from coal was observed on the river sand for their concentration in solution of 0.1 g/l. The degree of adsorption on the river sand decreased sharply as with increased HA concentration in solution up to 0.5-1 g/l. does not affect The degree of adsorption was practically unchanged during MA with alkali. The dependence of the HA adsorption capacity on the concentration was determined by the conformational state of macromolecules, their aggregation and availability of free functional groups.

Fragment analysis of the HA showed that MA of oxidized coal in alkaline hydrolysis resulted in a reduction of the number of functional groups in the molecular periphery. Under oxidizing conditions MA favoured the increases of carbon amount in functional groups and oxidized fragments of HA macromolecules and promoted its decrease in aromatic groups.

The carbon atom content in phenolic groups was calculated on the basis of the chemical composition analysis according to the differences in the integrated intensities within the ranges of $C_{ar}O$-and CH_3O- fragments in the NMR^{13}C spectra of HA. Adsorption activity of HA changes within the following series: MA+5% NaOH - MA - MA +5% NaOH +3% $2Na_2CO_3 \cdot 3H_2O_2$ – initial charcoal.

The work was supported by the integration project № 17 of the Siberian Branch of the Russian Academy of Sciences and the Mongolian Academy of Sciences.

Simple Technique for Modeling Transcuticular Transport of Liquid Humates in Leaves

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Simple laboratory technique was designed for preliminary studies on transcuticular movement of foliar humic preparations. The rate of transport of liquid potassium humate (Lignohumate A, Amagro, Czech Republic) through mechanically, chemically and enzymatically isolated leaf cuticles and through the respective original leaves of several higher plants (*Rhododendrone*, *Bryophyllus calcynium*, *Prunus laurocerasus, Epipremnum pinnatum*) was observed in straightforward diffusion couple apparatus, in which cuticle (or leaf) sample was sandwiched between two agarose hydrogels (1% wt.) with different concentration of dissolved humate (0% wt. and 1% wt., respectively). Concentration of the humate at different positions of the "receiving" hydrogel was determined photometrically at various times. From such concentration profiles, corresponding values of diffusion coefficients were estimated in order to compare the rate of transport of the humate for different plants and different cuticle isolation procedures.

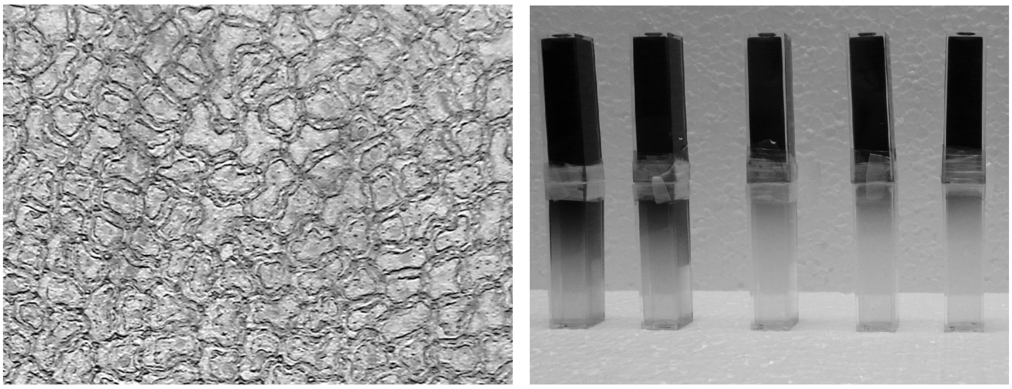

Figure 1: Microphotography of a leaf cuticle (*left*). Diffusion couples, in which potassium humate diffused through leaf cuticles into "receiving" agarose hydrogel (*right,* different penetration depths are obvious)

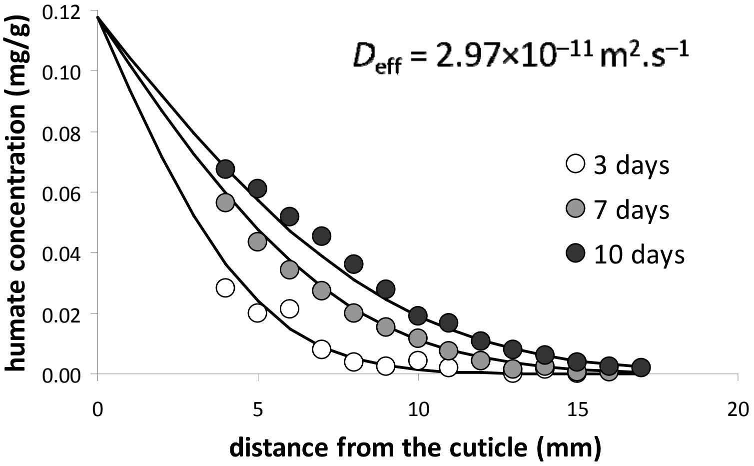

Figure 2: Example of concentration profiles in "receiving" hydrogels: experimentally determined (*circles*) and calculated using estimated diffusion coefficient D_{eff} (*solid curves*).

Determination of Low Molecular Weight Organic Acids in Water Extract from Soils by GLC-MS

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Dissolved low-molecular-weight (LMW) organic acids influence almost every process in soil and aquatic environmental. The determination of individual LMW organic acids remains a relatively difficult problem. Organic horizons of etalon plain loamy soils (taiga soils – Haplic Albeluvisols (HA) and Stagnic Albeluvisols (SA), tundra soils – Stagnic Cambisols (SC) developed on relief elevations have been studied. Qualitative analysis of water extracts for LMW organic acids was done using mass spectrometry by two methods converting organic acids into ethers and trimethylsilytion derivatives. Quantitative analysis of trimethylsilytion derivatives was fulfilled by the gas-liquid-chromatography method.

Two classes of acids were isolated, aliphatic and aromatic acids. Each class is divided into two groups, non-substituted (mono- or dibasic) and substituted (usually oxy-acids as mono-, di- and tribasic acids with one or several –OH-groups). The soils reveal common but due to different soil forming conditions also specific characteristics. The diversity of LMW organic acids is maximum in SA, less in HA and minimum in SC. SA and SC soils are characterized by the highest number of water-soluble oxyacids (both aliphatic and aromatic). This may be related to their low-speed transformation in SA in contrast to HA due to unfavorable hydrothermal conditions such as low temperature and excessive moisture. In better conditions (case with HA), the intensity of chemical reactions proceeding due to the presence of -OH-groups in acids (oxidation to aldehyde group and then more easily to carboxylic -COOH group with the increasing basicity of acids; dehydration with formation of unsaturated acids) is higher. The range of pK_a values of carboxylic groups of aliphatic oxyacids (or pK_{a1} for di- and tribasic oxyacids) lies mainly within 3.2-4.0. The decrease in diversity of LMW organic acids on transition from SA to SC soils is related to the strong decrease in species diversity and number of acid-forming microorganisms due to severe temperature conditions, and, possibly, to the change in quality and quantity of organic matter involved into mineralization and humus formation. The maximum of aliphatic non-substituted saturated and non-saturated mono- and dibasic acids is observed in HA soils where they are a dominating group of acids. The range of pK_a values in these acids lies within 4.5-6.0. Aromatic acids reach their greatest diversity in SA soils, the lowest diversity in SC and are moderate in HA. The carboxylic groups of non-substituted aromatic acids have the value of $pK_a>4.2$. The acidity of –COOH-groups of substituted acids substantially varies depending on substitute itself and its position in ring. For example, *para*-oxybenzoic acid has $pK_a=4.6$, its *meta*-isomer – $pK_a=4.1$, *ortho*-isomer (salicylic acid, identified only in SA) – $pK_a=3.0$. Aromatic oxyacids contain –OH-group with $pK_a\approx10$.

Concentration of LMW organic acids in soil water extracts is evaluated only for the acids that are identified as trimethylsilyl derivatives, and equals 1-14 mg dm^3 (1-5 % as converted to carbon of water-soluble organic compounds. All soil types largely contain 2-oxypropanoic (lactic, 20-35 %), 2-oxyethanoic (glycolic, up to 12 %), dioxypropionic (glyceric, up to 10 %), oxybutanoic (3-oxybutyric), and oxybutanedionic (malic) acids.

The study is supported by Program of UD RAS, project № 12-T-4-1006 “Ecological property of etalon soils of European North-East of Russia, it bioorganic potential as criterion productivity and guarding in the time of prepare Red Book of soils in Komi Republic”.

Clay-Organic Interactions in Soils as One of Previous Stages at Formation of Clay Deposits

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It is known, that result of smectites intercalation by simple organic molecules is formation of regular tactoids and appearance of an integer spectrum 00L reflections from distance d001, strongly displaced in the small-angle region. Polymerization of monomers in interlayer space can change a dispersive state of smectite from intercalated to exfoliated and result or in essential decrease, or to full disappearance of basal reflections from smectites on diffraction spectra. However, these results of most cannot be extended to soils, because the interaction of the organic and mineral substances in nature always involves living organisms performing bio-abiotic interactions. The aim of this work was to show interrelation between actual structure of the clay phases with labile interlayer spaces and binding of organic matter into an oxidation resistant form on an example of a complex variant of biogenic transformation of sediments.

We studied virgin forest-steppe soils derived from a uniform parent material. By complex of modern methods it is shown, that fixation of organic substance in forms resistant to H_2O_2 treatment is related to change of actual structure of clay aggregates. At interaction of clay minerals with the products of transformation of plant residues in A horizon of forest-steppe soils such organic-mineral complexes as composites are formed. Penetrating into slits between thin particles of layer silicates and between smectite layers, organic molecules output from X-ray-diffraction a considerable part of crystalline substance, breaking a constancy and (or) plane-parallel arrangement of its interlayer distances. Remaining principally crystal phases, these original organic-silicate compositions can not bring the contribution to X-ray-diffraction of the oriented preparations. Formation organic-smectite complexes with hybrid structure, disorder on c* axis, is the usual and universal mechanism of clay transformation at soil formation in forest-steppe conditions. It limits possibilities of X-ray-diffraction for smectite quantification in natural organo-clays. Therefore, the labile interlayer spaces should be studied using the independent methods.

The main source of smectites are beds of the transformed volcanic ashes, however deposits of similar type practically are not present within the Central Russia region. As alternative sources, bentonites of fresh-water and sea basins are used. These bentonites were accumulated in the continental basins as the products of secondary micas biogenic degradation on the paleo catchments areas. Here zones with the most intensive interactions between clay minerals and organic matter are soils. Since Devonian the formation, degradation, transport and redeposition of a soil material is constant stages of sedimentary process. Most of the sediment carried in rivers is likely to have been part of a soil profile at some stage. Continental depositional environments are also sites of soil formation. Therefore actual structure of clay minerals in specific deposit may be has a soil history.

If we wish to produce nanocomposite materials and geosorbents from clay sedimentary rocks they should meet to strict technical conditions. Therefore presence of natural organo-smectite nanostructures in clay sedimentary rocks should be considered at creation of organo-clay production technologies.

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Molecular Weight of Humic Substances: Correlation with Fluorescence Quenching of Pyrene

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Fundamental properties of humic substances (HS) – polydispersity and heterogeneity – make the determination of its molecular weight complicated. Numerous approaches, based on size-exclusion chromatography, mass spectroscopy, NMR etc, provide varying results. Hence, novel approaches in HS molecular weight analysis are required. In the present work, the possibility of HS molecular weight characterization with the use of the fluorescence quenching (FQ) technique is discussed.

Binding of pyrene by HS is extensively studied over several decades. The basic approach includes the use of the Stern-Volmer plot for FQ of pyrene, assuming the excess of HS binding centers in solution and thus regarding the binding process as sorption. In this case, the binding constant K_B is determined with the equation (1):

$$K_B = \frac{[PyHS]}{[Py][HS]_{tot}}, \qquad (1)$$

where $[PyHS]$, $[Py]$ and $[HS]_{tot}$ are the concentrations of bound and free pyrene and the total concentration of humic substances, respectively. This gives a classical sorption equation for the fraction of the bound pyrene molecules (2):

$$\frac{[PyHS]}{[Py]_{tot}} = \frac{1}{1 + K_B[HS]}. \qquad (2)$$

In our experiments, connected with the investigation of the role of vibronic coupling in FQ of pyrene, experimental data couldn't be fitted with the Stern-Volmer equation. Moreover, the difference between FQ curves upon excitation into different electronic states of pyrene (excitation wavelengths 334 and 360 nm) showed significant dependence on the total pyrene concentration. In order to fit the experimental data, the following modification of the basic assumption (1) was tested (3):

$$K_B = \frac{[PyHS]}{[Py][HS]} = \frac{[PyHS]}{[Py]([HS]_{tot}/\mu - [PyHS])} = \frac{[Py]_{tot} - [Py]}{[Py]([HS]_{tot}/\mu - [Py]_{tot} + [Py])}, \qquad (3)$$

where μ is the average molar weight of HS molecule and $[Py]_{\mathrm{tot}}$ is the total pyrene concentration in the solution. The equation (3) describes the binding process as an intermolecular interaction, taking into account the decrease of binding centers in the system. Here, the concentration of HS must be in $M \cdot l^{-1}$, leading to the appearance of μ in the denumerator. As the result, the average molar weight of HS becomes the parameter of FQ curves fitting. It is worth mentioning that the possibility to obtain μ is based on the nonlinear character of the dependence $[Py]([HS])$ in (3) compared to (1).

The first experiments performed with leonardite HS resulted in determination of μ = 4 kDa, that is in agreement with our expectations. Possible applications of the suggested approach are presented in the current work.

The Study of Dissolved Organic Matter of the Northern Dvina River in the Different Hydrological Seasons by IR Spectroscopy and Elemental Analysis

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An important feature of the boreal (circumpolar) water objects is the presence of high concentrations of dissolved organic matter significantly allochthonous nature and, accordingly, colloidal most trace elements and heavy metals that form stable organic-mineral and organic (fulvic and humic) complexes. The rivers of the Russian Arctic, which include the Northern Dvina, viewed as important sources of continental origin matter in the seas of the Arctic. Despite the importance of the study of dissolved organic matter in the global natural processes, this issue is devoted not so much work. The aim is to study the structure and composition of DOM of the Northern Dvina River during winter and low water spring tide, 2012, to determine the origin and transformation mechanisms of organic matter.

Concentration of the filtrate was carried out on a rotary evaporator at 40°C and then using the lyophilizer. The preparation of the unfractionated mixture of fulvic and humic acids were analyzed by IR spectroscopy, providing valuable information about the chemical nature of DOM in natural waters. In parallel, to determine such parameters as COD, BOD_5, color, pH, O_2, etc.

Spectra selected samples were recorded on Vertex 70 IR spectrometer (Bruker, USA), the accessory FTIR GladiATR (Pike Tech., USA), with a range of recording the spectra from 4000 to 400 cm^{-1}, a resolution of 4 cm^{-1} and 128 parallel scans. For all spectra are characteristic absorption in the region from 3400 cm^{-1} to 3200 cm^{-1}, due to the presence of OH groups, for example, contained in the COOH radical, and a group of N-H. In the range of 2930-2880 cm^{-1} are observed peaks corresponding to aliphatic C-H groups. Two samples show absorption peaks around 1640 cm^{-1}, corresponding to the aldehyde or ketone C=O bond after the partial decarboxylation. All samples are characterized by the presence in the IR spectra bands of 1410-1400 cm^{-1} (vibrations of the dissociated carboxyl groups, vibrations of OH groups and C-CH_3). A small peak at 1210 cm^{-1} is associated with the rotational vibrations of C-O bond and vibrations of O-H bond in the group-COOH. Directly identifies the band of symmetric stretching vibrations of C-O-C bond, or variations of C-O bond in the carbohydrate fragments at 1100-1030 cm^{-1} in both submitted samples.

Based on data from the infrared spectroscopy, it should be noted that the sample number 2 (spring tide) is characterized by a strongly expressed aliphatic structure. The winter pattern prevails sulphate ion, while in the spring increases the content of carbonyls.

Information obtained by the infrared spectroscopic study, rather good agreement with the elemental analysis. On elemental analyzer EvroEA 3000 (configuration [CNHS]) by standard methods was defined cell (C, H, S, N) composition of selected samples of DOM of Northern Dvina. Found that the total carbon content in the sample number 1 (winter low water) is 10.81±0.54%, hydrogen – 2.42±0.12%, nitrogen – 0.450±0,045, sulfur 6.69±0.34. The sample number 2 (spring tide) recorded the following values of the carbon – 33.71±1.35, hydrogen 6.59±0.33, N – 0.62±0.03; sulfur 1.79±0.09. We also observed a clear increase in the color values of the indicators and COD in the spring sample.

This work was supported by RFBR grant 12-05-91055-NCNI_a, and the program of the Presidium of RAS № 12-P-5-1021and UB RAS № 12-U-5-1034, on the devices of joint use centre of scientific equipment "Arctic" NArFU.

Earthworms: the Great Soil Managers on Earth: Protective & Productive

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Earthworms derive their name from ‘earth’ meaning ‘soil’. Sir Charles Darwin believed that soil could not be present on earth until earthworms evolved and flourished. They are great ‘soil managers & protectors of earth’ adapted to live in different soil types from high organic carbon content to mineral soils (very low carbon content) and also sodic soils. Earthworms act as an aerator, grinder, crusher, chemical degrader and a biological stimulator in soil. They inevitably work as ‘soil conditioner’ & this they do by soil fragmentation and aeration, breakdown of organic matter in soil & release of nutrients, secretion of plant growth hormones & proliferation of beneficial soil microbes (e.g. nitrogen fixing & phosphate solubilising bacteria & actinomycetes) in billions & trillions in short time. Earthworms also act as ‘vector’ for dispersal of ‘disease-suppressive’ & ‘pest repellant’ microbes in soils like ‘chitin & cellulose degraders’. Microbes are also essential for converting soil nutrients into their ‘plant available forms’ and also for ‘facilitating nutrients uptake’ by plants. Soil microbes also create the ‘glue’ that sticks soil particles together, creating soil crumbs and pore spaces that make good soil structure decreasing ‘soil hardness’.

Worms swallow large amount of soil with organics everyday and digest them excreting out in the form of fine mucus coated granular aggregates (vermicast) containing ‘humus’ which are rich in NKP, micronutrients & useful microbes. Humus’ in vermicompost excreted by worms is of great agronomic value for the soils. It takes several years for soil organic matter (SOM) or ordinary composts to decompose to form humus while earthworms secrete humus in its excreta (vermicasts). Without humus plants cannot grow and survive. The ‘humic acids’, ‘fulvic acids’ & ‘humins’ in humus are essential to soil and plants in several ways. They hold ‘clay and sand’ together to form what we call ‘soil’. Billions of tons of humic substances are disappearing from soil worldwide every year due to floods, fires, and poor agricultural practices.

Addition of vermicompost to soils increases water holding capacity and works as a ‘good absorbent’ of atmospheric moisture due to the presence of colloidal materials – the ‘earthworm mucus’. The worm vermicast works as ‘micro-dams’ storing hygroscopic and gravitational water. The water stable aggregates of ‘polysaccharide gums’ produced by the bacteria inhabiting the intestine of earthworm increases the general entry of water into the soil and infiltration due to construction of cemented ‘macro-pores’. Increasing water holding capacity of soils prevents ‘soil erosion’ and improves productivity.

Earthworms & vermicompost plays an important role in managing ‘sodic’ and ‘saline’ soils. A soil is regarded as sodic where exchangeable sodium (Na) is higher than 6 % and the pH is greater than 8.5.

Sodicity is generally fought with application of ‘gypsum’ which increases the amount of ‘exchangeable calcium’ in the soil. Earthworms can help in spread of gypsum much faster in the soil by stimulating microbes and creating ‘channels & pores’ for movement of air and water & gypsum. Worms ingest soil & gypsum, mixing them together, resulting in fast & thorough spread of gypsum deep into the soil profile. Earthworms can also combat soil salinity. Farmers in India applied live earthworms to their sugarcane crop grown on saline soils irrigated by saline ground water. The yield was 125 tonnes/hectare of sugarcane and there was marked improvement in soil chemistry. Within a year there was 37% more nitrogen, 66% more phosphates and 10% more potash. The chloride content was less by 46%.

Vermicompost application also increases the cation exchange capacity (CEC) of soil. An increase in soil CEC leads to higher ‘soil adsorption’ of positively charged cations such as ‘calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na)’. The increase in cations translates into nutrients being held in the soil and made progressively available for plants uptake. This also leads to ‘reduced acidity’ and ‘higher soil pH’.

Much of the world’s carbon is held in the soils, as ‘soil organic carbon’ (SOC). Loss of SOC as CO_2 due to aggressive ‘ploughing and tillage’ has augmented the atmospheric carbon pool inducing global warming and climate change. Of the increase of atmospheric carbon over the last 150 years, about a third (33.3 %) is thought to have come from agriculture. All over the world agricultural & environmental scientists are trying to reverse the trend by putting more carbon back into the soil – a process called ‘carbon sequestration’ through use of composts. Vermicompost contains more ‘stable forms of carbon’ as ‘humus’ which remains in the soil for long periods of time and are not degraded and emitted as CO_2.

Practical Experiences in Ecotoxicity Bioassay Methods for Engineered Nanomaterials

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Engineered nanomaterials (ENMs) are currently used in many different areas such as electronics, pharmacology, cosmetics, energy devices, biotechnology. Nanoparticles have significant technological advantages in soil and wastewater treatment. The growing application of ENMs in every sector of society has resulted in uncertainties regarding their impacts on human health and environment. Most toxicological research performed to date has focused on effects of nanoscale particles on human health and mainly on respiratory systems, oxidative stress, inflammatory and fibrotic reactions. Comparatively little work has been done to study the impact of nanoparticles on ecological systems. But the release of ENMs into the environment carries potential ecotoxicological risks. While the medical effects of such particles are being investigated with clearly determined regulatory criteria for damage on human organisms, no special standards exist for ecotoxicity tests with nanoparticles.

The standardized methods for the regulatory ecotoxicity testing of chemical substances have aspects of international harmonization (the OECD tests, ISO, *Daphnia* immobilization test), and many countries also have established their own protocols. For example, the American Society of Testing and Materials Committee on Biological Effects and Environmental Fate have approved protocols for testing substances on a range of aquatic invertebrates and fish, the U.S. EPA has protocols for testing aquatic, terrestrial, and microbial organisms. Similar list with about ten protocols for ecotoxicological assessment exists in the Russian Federal Agency for Technical Regulation and Metrology. All of those tests, however, were established for testing traditional chemicals, not ENMs.

Methodical instructions on sampling procedures recently established by the Russian Federal Center of Hygiene and Epidemiology for characterization of the nanomaterials in laboratory animals (MU 1.2.2745-10), fish (MU 1.2.2744-10), and in the water bodies (MU 1.2. 2743-10) were designed for unification of sampling methods. The requirements set out in these guidelines are applied in the course of the toxicological and biomedical safety assessments of nanomaterials in order to take decisions on the nanomaterials risks assessment first of all on the human body - biosystem with more or less stabile physical and chemical parameters.

In the Certified Laboratory for Soils Ecotoxicological Analysis of MSU (RU.0001.513050, www.letap.ru) we conducted ecotoxicity assessments of two widely used types of carbon– and metal-containing ENMs. This was done on standardized cultures of living organisms – representing all main trophic ecosystem's levels – producers, consumers, reducers, e.g. bacteria, microalgae, crustacean, protozoan, higher plants and *in vitro* cell culture of warm-blooded animals as well as on nonstandard cultures of micromycetes. It was identified that existing endpoints with bacteria and plants tests are enough sensitive to ENMs in aqueous media. It was confirmed that some environmental factors like pH, salinity, divalent ions, and the presence of natural organic matter may alter the toxicity of ENMs as it is established for the traditional pollutants. Some evidence of ecotoxicity depending on size of ENMs was obtained by testing of nanodiamonds (NDs 15, 30, 100 nm) using algae, fungi and higher plant tests. But this effect was determined only under lower NDs concentrations. High-dose agglomeration of ENMs modified the toxicity of small size NDs nanoparticles. Strong evidence of humus substances (HS) influence was demonstrated by bioactivity of nanoparticles estimation for TiO_2 and Fe_3O_4 and NDs. HS has modified remarkably the ecotoxicity in standard biotest-systems (up to 100-200 times, depending on origin and HS structure). That means that soil matrix plays a crucial role in the hazard ENMs assessment strategy in terrestrial ecosystems, and the standardization of soil samples is required to investigate the damage caused by ENMs.

We do agree with the opinion (Handy et al., 2011; Tourinho et al., 2012) that although all existing biotests require modifications to work optimally with ENMs, the concern that we would have to start over with completely new tests is not supported by experiences.

Sorption of Humic Substances by Bacteria and Related Biological Effects

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Sorption of humic acids (HA) on bacteria was mainly investigated for the case of *Bacillus subtilis* and *Escherichia coli* species (Fein et al., 1999; Frost et al., 2003; Moura et al., 2007). The research was focused on the applied aspects of the heavy metals' response on the presence of microorganisms.in sediments and soils. It is assumed, that the sorption of HA on the cell surface should play a specific role in the interaction of living cells with other xenobiotics.

The capability of bacteria from different ecological groups to adsorb HA from aqueous solutions was demonstrated for 38 strains. We found, that the sorption parameters k and Qmax in Langmuir equation, which characterize the bonding strength of HA with bacteria and the maximum amount of adsorbed HA, correspondingly, differed significantly for Gram-positive and Gram-negative bacteria. At that Gram-positive bacteria sorbed higher amount of HA, but the bonding strength was less than for Gram-negative ones (Fig. 1).

The difference in sorption of HA can be explained with the distinction in the structure of the cell wall of Gram-positive and Gram-negative bacteria. Probably, the external lipopolysaccharide layer of the cell wall of Gram-negative bacteria prevents HA molecules from penetrating in the underlying layer of peptidoglycan. Gram-positive bacteria lack the external membrane, and thus HA can penetrate the peptidoglycan layer, which in order surpasses this layer in Gram-negative bacteria in mass and volume. (Dobrovolskaya, 2002).

HA sorbed on bacteria protected the cells from the adverse effects of sodium dodecyl sulfate, and didn't protect against sodium azide. HA sorption by bacterial cells can be used in non-waste technology of dark-colored natural waters' treatment for water supply or for the protection of bacteria when introduced in adverse conditions.

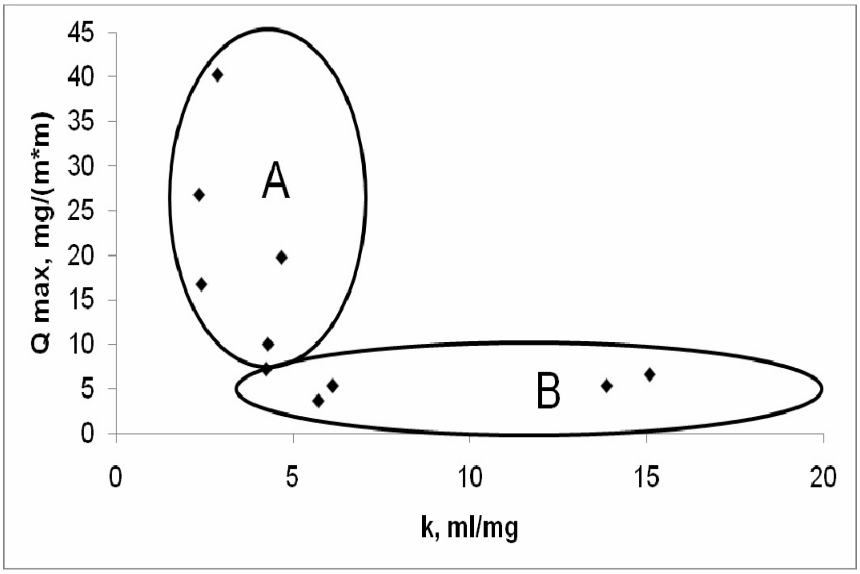

Figure 1. The maximum sorption (Qmax) and the coefficient of affinity (k) for Gram-positive (A) and Gram-negative (B) bacteria.

This work was supported by grants RFBR № 11-04-00580-a, 12-04-01652-a, №12-04-31720 mol_a.

Mechanochemical Modification of Humic Acids to Create Microreator Particles Absorbing Inorganic Pollution

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Artificially synthesized "core-shell" particles, in which the shell is composed of humic acids(HA) are efficient absorbents of heavy-metal (HM) pollutants. In the case of a lignocellulosic material as the core, we can ensure the floatability of the particle. In the case of a sorbent as the core, for example, a nanoporous carbon sorbent, humic acids (HA) will act as an intermediary between the HM dissolved in water and HM adsorbed on the surface of the core.

At present, several mechanochemical processing methods of humic materials are known that can effectively increase the yield of HA in a water-soluble form [1].

The aim of this work was to determine the relationship between the structure of HA and their sorption properties and to modify the HA structure by mechanochemical method in order to obtain of soluble salts and insert additional functional groups to improve sorbtion properties.

In the experiments, the brown coal containing 26% HA, soluble in alkaline solutions, was used. Among the “model’’ fractions of HA, which were extracted from coal with solvents of different basicity (Fig. 1), HA containing the largest number of phenolic (10 mmol/g) and carboxylic (7 mmol/g) groups showed the maximum capacity (210 mg Cd^{2+} per 1 g HA).

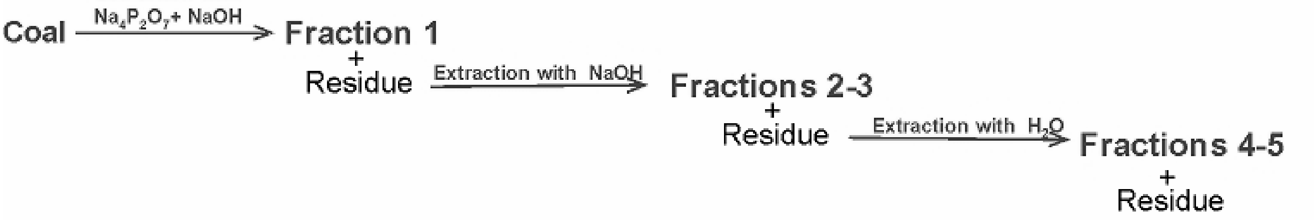

Figure 1. Scheme of extraction of the “model” fractions.

Using mechanochemical treatment of brown coal with an alkaline (NaOH) and an alkaline-oxidizing (sodium percarbonate) reagents, we have obtained sorbents showing high yields of HA (75%). The details of mechanochemical treatment were presented elsewhere [2]. The content of functional groups in the products shows that the only result of mechanochemical treatment with an alkaline reagent is the formation of salts of HA. The treatment of coal with an alkaline-oxidizing agent leads to the formation of new phenolic groups which, in turn, results in an increased sorption capacity.

The obtained sorbents were tested for multi-element (Cd, Pb, Cr, Co) pollution. It was found that they remove heavy metals from model solutions, and the best results was in the case of the sorbent obtained by mechanical treatment with alkaline-oxidizing agent, which correlates with its chemical structure.

We have conducted experiments, in which the contaminated medium was water in natural conditions of Ob reservoir. The salts of copper, zinc and cadmium were added into a confined volume of water. We have shown that the sorbents can successfully bind HM in natural conditions. This allows us to recommend these sorbents for removal of heavy metals from polluted water.

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Self-Assembly of Silanol Derivatives of Humic Substances into Nanocoatings and Its Remedial Applications

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Good quality of soil and groundwater is one of the most important assets throughout world. There are various methods for their remediation, among which one of the most promising is installation of permeable reactive barriers (PRBs), as it allows increasing efficiency and reducing the cost of technology. An interesting possibility is the use of natural humic substances (HS) in these technologies for *in situ* installation of the reactive organic layer by adhesion to aquifer mineral materials. However, to do this, HS need to be modified. The goals of this study were twofold: first, humic materials were modified to acquire mineral-adhesive properties not inherent within natural HS; and, second, humic derivatives were immobilized onto mineral support to obtain humic nanocoating for remediation technologies. To introduce new function into natural humic materials, alkoxysilylation was used.

Leonardite humic acid (CHS) and peat humic acid (PHA) were used for the experiments. 3-aminopropyltriethoxy-silane (APTES) was used for treatment of humics. The APTES was chosen due to the presence of reactive amino groups which can yield amide bonds upon reaction with carboxyl and carbonyl groups. The reaction was run at two different APTES-to-humics ratios, nominally: 0.5 and 1 g of APTES per g of CHS and 1 g of APTES per g of PHA. These ratios corresponded to different extents of modification associated with carboxyl groups available within the humic backbone. Depending on modification degree, the corresponding samples were designated CHS-APTES-50, CHS-APTES-100 and PHA-APTES-100. Sorption of the modified HA was carried out on 100 mg of silica gel. The total volume of experimental solution was 10 mL, concentration of humic samples was 4 g/L. All sorption experiments were conducted in phosphate buffer (0.03 M, pH 6.0). Equilibrium time was 24 hours. As a result, the amount of sorbed humic substances were 194, 221, 223 mg of humic per g of silica gel for CHS-APTES-50, CHS-APTES-100, PHA-APTES-100 respectively.

To prove the feasibility of silanol derivatives of HS as agents for remediation technologies for the installation PRB, studies were performed to evaluate their sorption capacity with respect to the azo dye Direct Brown, used for dyeing fabrics in the textile industry. Sorption of azo dye on pure silica gel and on silica gel modified by silanol derivatives of HS were studied by sorption isotherm technique. To 50 mg of pure silica or modified silica gel was added 10 ml of azo dye in the range of 5-200 mg/L and stirred on a rotary mixer for 24 hours. As a result, it was shown that the modified silica gels had much higher affinity for the azo dye as compared to the not-modified one. For the bare silica gel, maximum sorption was 1.1 mg per 1 g of silica gel, while for silica gel modified with PHA-APTES-100, CHS-APTES-100, and CHS-APTES-50 the maximum sorption was 2.5, 2.7, and 5.9 mg of azo dye per 1 g of silica gel respectively.

The obtained results show the capability of humic coatings for sequestering waterborne organic toxicants which indicates their suitability to *in situ* installation of humic PRBs in the contaminated aquifers. At the same time, we believe that immobilization of reactive engineered nanoparticles (e.g., nanosized zero-valent iron, nZVI) onto the humic nanocoatings would allow for a substantial increase in performance of humic PRBs. In this case, humic coating would enable fixation and stabilization of NZVI and thereby increase the efficiency of contaminant degradation by the combined nZVI-humic PRB.

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Total Technogenic Organic Carbon in Water

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Traditionally for the evaluation of the water organic matter the integral parameters of the quality such oxidability by permanganate or bichromate, dissolved organic carbon (DOC) are applied. These parameters do not reflect the variety of possible water contaminants; the methods of their definition are insensitive. At the same time, waste water, industrial emissions, agricultural wipes, falling into water sources, contain organic compounds of technogenic nature, which are highly toxic, mutagenic and carcinogenic activity and have low values of maximum contaminant levels. Therefore it is necessary to use a high sensitive integral parameter for estimate the water contamination by technogenic nature organic compounds differentiated from organic compounds of natural origin during the optimization of water treatment technologies. Such indicator has not been available to date. Widespread high sensitivity index of Total Organic Carbon (TOC) evaluates the total carbon content of organic water pollutants, both natural and technogenic origin, and is not suitable for the task.

We found that assess of the total carbon content in technogenic organic compounds differentiated from natural ones is possible by using gas chromatography with atomic emission detector (GC-AED), with its unique combination of properties such as a wide range of linear response, high sensitivity to carbon content (at a carbon emissions wavelength of 193 nm) in the components of the sample and the possibility of a component-independent calibration. The index is named as a technogenic organic carbon (TgOC).

TgOC index assesses the total carbon content in the organic compounds extracted from the water sample and eluted from the chromatographic column. It allows to evaluate the substances with Kovach retention index from 900 to 3200 on nonpolar phases, boiling in the range 150-500°C, that are called semi-volatile organic compounds (SVOS). Pesticides, hydrocarbons of different nature, fatty acids, esters, phenols, polycyclic aromatic hydrocarbons and other ecotoxicants and their derivatives enter in this range. The TgOC is a highly sensitive integral Index ($1\text{x}10^{-5}$ mg/dm^3, 193 nm).

The analysis of river water samples spiked by technogenic substances (pesticides, chlorophenols and hydrocarbons) has shown that the contaminants in the concentrations close to their MCLs did not reflect in the results of the oxidability by permanganate and DOC determination. But the TgOC content in samples appeared to be close to the spiked amount of the carbon, in contrast to the flame-ionization and mass-spectrometry detectors are commonly used for a review analyses. TgOC definition in the samples does not always require a clear separation of the components, but during the work with capillary column type HP-1, HP-5 and others GC-AED method allows to determine the nature of the pollutant by the elements content in the molecule of analytes and thus to determine the qualitative composition of the sample. The new integral index of water quality is well established in the optimization of water treatment processes (coagulation, flocculation, filtration, adsorption, disinfection).

Influence of Natural Water Dissolved Organic Matter on the Quality of Drinking Water of Ufa

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Dissolved organic matter (DOM) of natural waters is formed with the participation of the soil and peat humus, plankton, higher aquatic vegetation, animal organisms, as well as organic substances of anthropogenic origin. The composition and quantity of humus compounds have a significant impact on the water quality.

It is known that in the preparation of drinking water with the use of the stages of coagulation, flocculation, sedimentation and filtration normally removed from 20% to 50% of the dissolved organic matter. Analysis of data on effectiveness of the removal of the DOM in the water treatment process on the river water intake supply system of Ufa showed that the value of the DOM falls on 21-32%. It points to the effective operation of the water treatment facilities even with low content of DOM in the water of the Ufa river (from 1.4 mg/dm^3 up to 6.4 mg/dm^3). Note that levels of DOM for drinking water of infiltration water intake supply system is 2-3 times lower, which is achieved due to the natural water filtration.

Evaluation of qualitative composition of the DOM (the aromatic fragments content, C_{Ar}) of the natural and drinking water samples of Ufa was carried out with the help of the well-known equation ($C_{Ar} = 2 \times C/PO + 14.44$, where C is the chromaticity, PO – permanganate oxidability). For the period of investigations from 2006 to 2010, in the natural and drinking water samples of the river water intake supply system of Ufa quantity of C_{Ar} in the DOM was within the range from 22.3% to 28.4% from 17.8% to 19.9%, respectively. On the water treatment stages the C_{Ar} content is reduced, which testifies to delete structures enriched with aromatic fragments in the water filtration and chlorination process. The minimum values of the C_{Ar} were recorded in the natural water samples, collected in the winter period, when a flow and the humus formation speed decrease is obtained.

Polyhydroxiaromatic fragments of DOM in the water source are the main precursors of water chlorine disinfection by-products, most of whom are trihalogenmethanes (THMs) and haloacetic acids (HAAs). According to the World Health Organization THMs and HAAs possess carcinogenic properties, show toxic, mutagenic effects.

Study of the content of HAAs in the drinking water of Ufa carried out by the reaction gas chromatography method with electron capture detection. The obtained data allowed to build a correlation-regression dependence of the total concentration of the HAAs in drinking water of the river water intake supply system of Ufa from doses of chlorine and content of the C_{Ar}, which is included in the DOM content of water source:

$C_{HAAs} = 0.019 \times D_{CL1} + 0.009 \times D_{CL2} + 0.011 \times C_{Ar}$ (R = 0.96), where

C_{HAAs} – the total concentration of nine HAAs, mg/dm^3, D_{CL1} – the dose of chlorine at the stage of primary chlorination, mg/dm^3, D_{CL2} – the dose of chlorine at the stage of secondary chlorination, mg/dm^3.

This dependence allows to express evaluate the content of the HAAs on the water treatment stages without conducting of complex analytical measurements. It is important for the water supply enterprises in the optimization of technological measures in the processes of natural water purification.

Commercial Humic Products: the Role of Organic Matter Genesis for Application in Environmental Technologies

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Humic substances are being increasingly used in remediation technologies. Industrial companies manufacture humic products (HPs) using different industrial processes and a big variety of raw source materials, mostly lignite, peat and organic waste materials. Since the mechanism of HPs-action is apparently correlated to their certain chemical parameters, the effect of HS will depend on organic matter genesis. In this study a number of commercial HPs produced from coalified materials (brown coal BC, leonardite Le, lignite Li and humalite Hu), plant-originated resources peat (Pe), sapropel (Sa) and organic waste material (OW) were examined in respect to their chemical composition and structure. Five selected HPs (two from BC, two from Pe and one from lignosulphonate) were then tested for their detoxication ability in sets of incubation experiments with soils, polluted with lead (320 mg kg^{-1}), copper (660 mg kg^{-1}), and phosphogypsum (3.3 and 7.5 w%). Toxicants were applied to model soil mixture (20% of kaolin, 10% of peat and 70% of sand; ISO 11268-1) together with suspensions of HPs at rates giving 0.0025, 0.005, 0.010 and 0.020 w%. Content of extractable Pb, Cu, as well as Sr, Ca, F^- and NO_3^- prevailing in phosphogypsum, were determined by AAS.

Patterns of C and N distribution in HPs show that the ones from coalified materials contain higher amount of C and minor amount of N, whereas products from Pe, Sa and OW are significantly higher in N and lower in C. Some individual samples contain up to 4-7% of S. Amount of humic and fulvic acid fractions in individual samples varies greatly, although there is a trend that BC-products are rich in humic, products from Pe and Sa contain both, and in OW-product fulvics prevail. Advanced investigations of molecular structure of humic acids extracted from selected HPs were performed; results are discussed in presentation. In brief, molecular structure HPs from plant originated material (Pe, Sa and OW) were enriched in O-containing functional groups, whereas HUM from coalified materials in aromatic moieties.

Under conditions of pollution all HPs modified availability of toxicants in soils. For Pb content of water extractable species decreased in treatments with HPs up to 57-77% to polluted control. For Cu a smaller decrease was observed for all the HPs (70-94%) except the one from lignosulphonate which increased mobility of Cu (129%).

In contrast, in experiments with phosphogypsum mobilization of available Sr and Ca was observed. All the HPs increased content of AAB-extractable Sr on 8-24% and Ca on 24-32%, in both cases being the highest for the Pe-product.

Changes in availability were also observed for anions. Content of nitrates drastically increased, for florid-ions increase was recorded at the highest rate of phosphogypsum.

The results show that detoxication ability of humic products towards heavy metals is unequal and depends both on organic matter origin and properties of HPs and the chemical nature of a toxicant.

This work was supported by Russian Foundation for Basic Research, project 10-04-01681.

Self-organized Nanoparticles in Ruff and Fenton Systems

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Oxidative degradation of organic pollutants gave rise to Advanced Oxidative Processes (AOPs), which are considered as very promising area of green chemistry. The most popular advanced oxidants are Fenton system (hydrogen peroxide and Fe^{2+}) and Ruff system (hydrogen peroxide and Fe^{3+}).Decomposition of hydrogen peroxide induced by ferric or ferrous ions leads to a generation of very reactive radicals $HO_2\cdot$or$\cdot OH$. Initial value of pH is known to be the crucial parameter, which determines the state of iron in the solutions. It is generally accepted that optimal range of pH for oxidative destruction of organic pollutants is 2.5-3.5 since above 3.5 hydroxocomplexes are formed and their polymerization takes place. In the optimal pH range the systems are considered as true solutions.

However our resultson oxidation of indigo carmine by Fenton and Ruff systems indicate that the solutions contain nanoparticles even at low values of pH. The particles consist of iron compounds. The size and ζ-potential of particles were determined by dynamic light scattering (Table 1). In spite of widespread opinion concerning negative effect of the presence of hydrolyzed and polymerized iron compounds at oxidation efficiency it appears that nanoparticles promote the oxidation process.

Table 1. Characterization of nanoparticles found in the solutions after indigocarmine oxidation

pH	Ruff system		Fenton system	
	Average diameter, nm	ζ, mV	Average diameter, nm	ζ, mV
4.5	118.8	-17	59.7	-20
3.5	58.6	-14	74.9	-14
2.5	68.7	-3	47.7	-3
1.5	83.7	-2	88.6	~0
1	-	-	70.3	~0

Effect of Humic Substances Concentration on Properties of Magnetic Nanoparticles

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This study is aimed to estimate dose-dependent effect of humic substances (HS) on growth and properties of nanoparticles of magnetite (Fe_3O_4). Humics-conjugated magnetite can be served as detoxifying agent for the removal of almost any kind of pollutants from contaminated water and soil systems using magnetic separation technique.

The nanoparticles of magnetite were synthesized in situ by oxidative alkaline hydrolysis of the iron (II, III) powder precursors into humics medium. The synthesized particles prepared at different humics concentration (20, 50, 80 wt%) were characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Mössbauer and ultrasound spectroscopy.

The results showed that the size of nanoparticles depended upon the humics concentration. XRD results (Fig. 1) indicate that the addition of HS into Fe_3O_4 nanoparticles media have not changed the crystal structure of nanoparticles, but the intensity of the peaks is reduced with using of HS. The average crystal size of the nanoparticles calculated from the diffraction peak half-widths according to Scherrer's equation for the Fe_3O_4 nanoparticles stabilized by humics in concentrations of 20-80 wt.% decreased from ~30 nm to ~17 nm, respectively. Moreover, increasing of humics concentration leads to decrease of particle size distribution.

For characterization of magnetic properties of sorbents they were examined using a vibrating sample magnetometer Lake Shore. The maximum grain size, magnetic susceptibility and magnetic hysteresis properties were obtained from the magnetite synthesized at a concentration of 20 wt% Fe in composite.

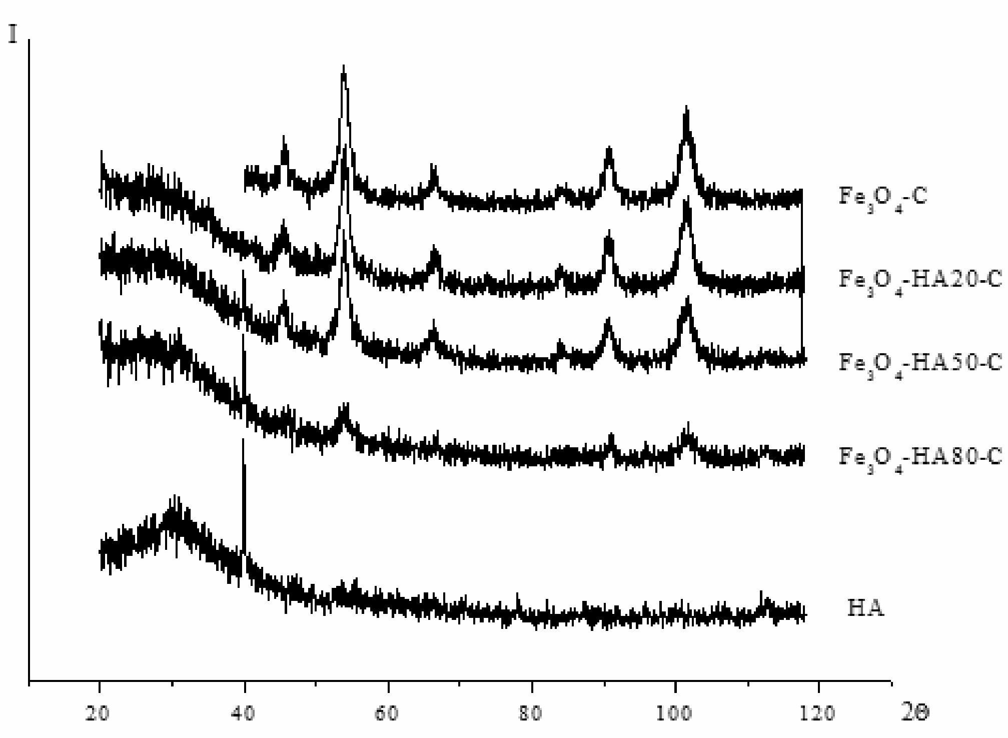

Figure 1. XRD patterns of bare and conjugated Fe_3O_4 particles (Philips X-pert, Cu-Kα).

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Synthesis of Humic-Clay Nanoparticles By Laccase-Catalyzed Heterophase Polymerization of Soluble Precursors

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Humic substances are ubiquitous natural macromolecules which are formed during partial oxidative transformation of plant and microbial tissues or during condensation of soluble precursor material. HS formation steps include catalytic oxidation of phenolics into reactive species (phenoxy-radicals, quinones and semiqionones) and their subsequent spontaneous coupling with nitrogenous and other compounds. In well-aerated soils most of humic material is stabilizied within organo-mineral complexes and occurs as organic films on the surface of mineral grains. These surface coatings are represented not only by low molecular weight and thus soluble humic fractions, which can easily be adsorbed on the minerals. Part of the mineral-associated humic matter is highly polymeric (MW > 75 kDa). We have demonstrated in the laboratory experiments that this polymeric material can originate from polymerization of soluble precursors on/near the mineral surfaces in presence of immobilized phenoloxidase (Zavarzina 2006, 2011). Apart from the long-time stabilization of organic carbon, this heterophase polymerization results in transformation of potentially toxic soluble phenolics into non-harmful natural polymers, strongly associated with the mineral phase.

In this work we are summarizing the results from the laboratory experiments on heterophase condensation of phenolic acids and nitrogenous compounds near mineral surfaces with formation of humic-clay nanoparticles. Kaolinite and kaolinite-aluminum hydroxide complex were used as mineral supports. Purified laccases from basidiomycete Panus tigrinus (PtL) and peltigerous lichen Solorina crocea (ScL) were used as biocatalysts. Laccases were immobilized on 5 mg of the minerals and then 1 ml precursor solution (gallic, caffeic, ferulic, vanilllic, hydroxybenzoic acids, tyrosine, tryptophane; total concentration 1 mg ml^{-1}, pH 4.5) was added. After 72 h incubation at 30ºC reaction products were extracted from the minerals and analyzed by gel-filtration (Fig 1 AB) or HPLC (Fig 1C).

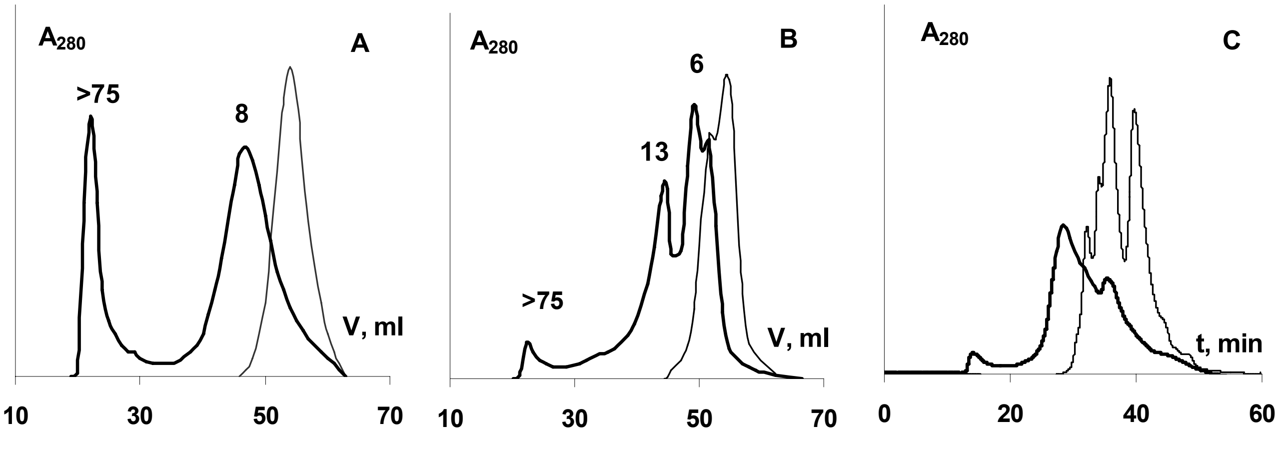

Fig.1 Molecular weight distributions of humic-like polymers synthesized on the mineral supports. A: kaolinite-Al(OH)x – PtL, B: kaolinite – PtL , C: kaolinite-Al(OH)x – ScL. Thin line – supernatant after 72h of incubation, solid line – extracts from the mineral surfaces.

As is shown on the Fig.1, products with highest molecular weight were formed in presence of basidiomycetous laccase on kaolinite, modified by positively charged amorphous aluminum hydroxide (A). Much less amount of polymeric fraction with MW of >75kDa was formed on pure kaolinite in presence of the same enzyme (B) or on kaolinite-Al(OH)x in presence of lichen laccase, characterized by lower oxidation potential (C). Effect of aluminum hydroxide can be explained by the increased mineral surface area and by the increased electrostatic attraction of negatively charged phenolics, resulting in higher monomer concentration near mineral surface.

Synthesis of Model Humic Substances and Their Analysis Using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Humic substances (HS) represent a complex mixture of oxypolycarboxylic aromatic acids which possess biological activity. However, they are still very scarcely used in practice due to irregular structure and unknown mechanism of their action. The synthesis of structural analogues of HS with might solve this problem.

The goals of this study were twofold: first, the structural analogues of aromatic backbone of HS were synthesized using different reaction pathways, and, second, the chemical space of the synthesized analogues was characterized using high resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT ICR MS) and compared to the humic acid and fulvic acid fractions of natural peat HS.

The structural fragment of soft lignin: 3-(4-hydroxy-3-methoxyphenyl)-3-oxopropionic acid (M) was chosen as a monomer for obtaining model HS. This was done due to substantial role of lignin in HS genesis. It was further polymerized with hydroquinone and gallic acid to obtain high molecular weight models of synthetic HS,

At the first stage, 3-(4-hydroxy-3-methoxyphenyl)-3-oxopropionic acid was obtained from vanillic acid using synthetic scheme shown in Figure 1.

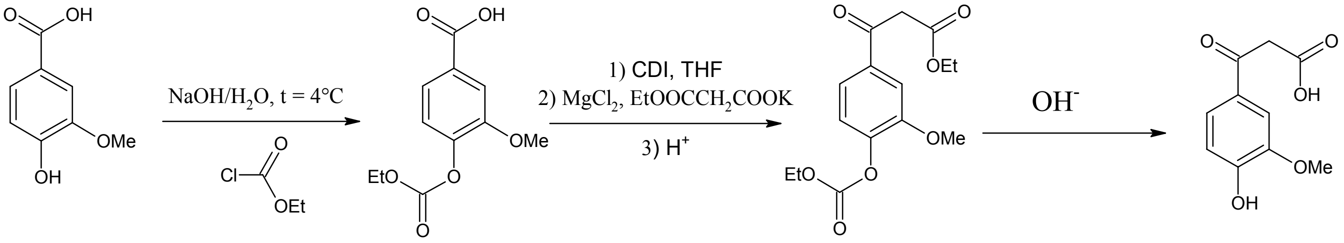

Figure 1. Synthetic pathway of 3-(4-hydroxy-3-methoxyphenyl)-3-oxopropionic acid.

Compositions and structures of the synthesized compounds were confirmed using elemental analysis and NMR spectroscopy. At the second stage, the synthesized monomer M was copolymerized with hydroquinone under oxidative conditions using reagent ratio of 3 mmol of M and 6 mmol of hydroquinone. Hydroquinone was selected because of its presence in humic structures. Potassium persulfate was used as an oxidizing agent. All experiments were conducted in 1 M NaOH. Reaction time was 2 hours. Then, the reaction mixture was acidified to pH 2 to isolate humic acid-like fraction (MHQ). The formed precipitate was centrifuged and the acidic supernatant was discharged through the Amberlite XAD-8 column to isolate fulvic acid-like fraction (MHQ-XAD). The reaction of M with gallic acid was carried out under similar conditions. However, no precipitate was formed after acidification. So, only fulvic-acid like product was isolated using XAD-8 resin. The isolated samples were investigated using FT ICR MS. The determined molecular compositions were represented using Van Krevelen diagrams. The synthetic HS turned out to be similar to aromatic constituents of peat HS. Furthermore, the compositions of MHQ and MHQ-XAD occupied a large area on the Van Krevelen diagrams for peat humic and fulvic acids, respectively. The conclusion was made that the synthetic HS derived from 3-(4-hydroxy-3-methoxyphenyl)-3-oxopropionic acid and hydroquinone could serve as models of natural HS and have a great potential for biological activity studies.

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Biological Activity of Different Fractions of Humic Substances from Peloids

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The use of humic substances (HS) is very important for the modern medicine, in particular, this concerns HS from freshwater sediments - peloids. They represent supramolecular assembly which is confirmed by the data of Fourier Transform Ion Cyclotron Resonance Mass Spectroscopy (FT ICR MS) on a compositional space of HS. The structure of HS contains of highly functionalized aromatic backbone and carbohydrate-protein periphery. HS of peloids have profound catalytic activity and demonstrate high biological activity.

HS from peloids influence the cell metabolism. This was confirmed in the model experiments *in vitro.* The protective action of HS was demonstrated for the cellular plasma membrane against toxic agents.

HS from peloids demonstrated *in vivo* metabolic activity, which manifested itself as detoxifying effect with respect to polychlorinated biphenyls, hydrazines, alloxan and streptozotocin. This had benevolent effects on the conditions of oxidative stress, hemolytic anemia, and diabetes in the study groups of animals.

Studies on the effect of HS on the metabolic processes *in vivo* showed that the most active fraction of the HS are hymatomelanic acid. This fraction is characterized by high metabolic activity manifested in the ability to maintain activities of catalase, superoxide dismutase, and glutathione peroxidase as well as to bring to normal levels an index of total bilirubin and plasma glucose of the groups of animals.

Оценка химического состава и сравнительной биологической эффективности сухих и жидких марок препарата «Лигногумат»

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ООО «НПО «РЭТ» является единственной в мире компанией, которая освоила крупнотоннажное производство промышленных гуминовых препаратов – Лигногуматов, используя в качестве сырья лигносульфонаты. Лигногумат получают методом направленной окислительно-гидролитической деструкции лигносульфонатов в щелочной среде, где основное сырье смешивается в указанной пропорции с гидроокисью калия и подвергается гидролизу в условиях высокого давления и определенных температур. В результате процесса получается концентрированный жидкий продукт, который имеет физико-химические показатели и биоактивные свойства, схожие с природными гуминовыми веществами (ГВ). Таким образом, ГВ из материала, который изначально не содержит эти вещества. Фактически, происходит моделирование и ускорение процесса, который в природе протекает в течение долгих лет.

В настоящем докладе приводятся результаты физико-химических, биологических и полевых исследований промышленных и модифицированных Лигногуматов в различной препаративной форме.

Исследования химических свойств Лигногумата в сравнении с гуминовыми препаратами (ГП) из различных источников: углефицированных материалов (бурого угля, лигнита, леонардита, гумалита), торфа, и сапропеля показали, что по базовым показателям – величинам pH, зольности и составу золы – Лигногумат находится в ряду прочих ГП. По данным элементного состава Лигногумат наследует от сырья низкое содержание азота и довольно высокое содержание серы – от 4% до 7%. По содержанию гуминовых кислот Лигногумат занимает промежуточное положение по сравнению с ГП из угля и сапропеля, а по содержанию веществ кислоторастворимых фракций - лидирует. По данным ИК-спектроскопии в Лигногумате наблюдаются интенсивные пики поглощения алифатических структур, наряду с ароматическими структурами [2, 4]. Еще одной особенностью является наличие третичных спиртов, карбоксилов и спиртовых групп в полисахаридах. По данным ^{13}С-ЯМР в спектре Лигногумата присутствует много линий, не характерных для ГВ из угля, торфа, сапропелей и почв. Эти результаты согласуются с данными Ertani с соавторами, где показано наличие в его составе сахаров и низкомолекулярных органических кислот [3].

Поскольку Лигногумат выпускается как в виде сухих, так и жидких марок, был подробно рассмотрен вопрос о возможном изменении физико-химических показателей, биологической активности и молекулярно-массового распределения в процессе сушки продукции. Для этого проведены сравнительные физико-химические анализы, серия лабораторных биотестов и полевых испытаний с использованием различных с/х культур. Для корректности тестирования выбирались образцы сухих модификаций полученных при сушке тех же жидких партий в условиях, предусмотренных технологическим регламентом. Такая схема приготовления образцов гарантировала идентичность состава образцов, что позволяло выявить возможные изменения, происходящие в продукте при сушке.

Результаты исследований показали, что в молекулярно-массовом распределении органических веществ в жидком Лигногумате (марка Б) около 70% от суммы фракций составляет среднемолекулярная фракция (СМФ) с молекулярной массой 34 кД, 6% низкомолекулярная (НМФ, 19 кД) и 23% – высокомолекулярная фракция (ВМФ, 50 кД). В сухом образце Лигногумата (Марки «А) доля НМФ снижается до 10%, а ВМФ несколько повышается. Это является подтверждением того, что высушивание жидкого препарата приводит к частичной полимеризации низкомолекулярных структур. Тем не менее, по сравнению с промышленными ГП из углей, для которых характерно наличие одной фракции с гораздо большими значениями молекулярной массы - порядка 60-70 кД, сухой Лигногумат также является относительно низкомолекулярным препаратом. Сравнительное биотестирование препаратов показало, что образцы сухих и жидких Лигногуматов одной партии имеют идентичную биологическую активность.

Полевые (деляночные) испытания проводились на опытных полях Краснодарского ГАУ [1]. В качестве тест-культур использовали: сою сорта Виллана, сахарную свеклу сорта Орикс, рис сорта Флагман. Некоторые результаты полевых испытаний стандартных сухих и жидких марок Лигногумата (К-ЛГ «А» и К-ЛГ «Б»), а также новых модификаций (партии Супер), на 3-х культурах приведены в таблице 1.

Таблица 1. Эффективность применения Лигногумата разных марок на с/х культурах

Показатели	Контроль	Марка «А»	Марка «А Супер»	Марка «Б»	Марка «Б Супер»
Соя					
Урожайность, ц/га	26,4^{a}	28,3^{c}	30,0^{b}	28,6^{c}	30,4^{b}
Прибавка урожайности к контролю, %	–	7,2	13,6	8,3	15,2
Содержание белка, %	39,0	39,9	43,1	41,6	43,7
Содержание жира, %	21,2	22,1	23,2	22,2	23,5
Сахарная свекла					
Урожайность, ц/га	417,2^{a}	454,4^{c}	499,8^{c}	458,9^{c}	501^{c}
Прибавка урожайности к контролю, %	–	8,9	19,8	10,0	20,1
Сбор сахара, т/га	7,843	8,724	9,848	8,857	9,92
Рис					
Урожайность, ц/га	66,1^{a}	73,8^{c}	76,8^{b}	73,7^{c}	76,9^{b}
Прибавка урожайности к контролю, %	–	11,6	16,2	11,5	16,3
Масса 1000 зерен, г	28,4	29,5	30,3	29,4	30,4
Стекловидность, %	90	95	97	94	97

^{a}без обработки; ^{b}обработка семян + 1 обработка растений; ^{c}2-кратная обработка растений

В целом проведенные исследования показали, что модифицированные образцы Лигногумата независимо от препаративной формы при воздействии на растение имеют заметно более высокую эффективность, чем базовые модификации, причем в результате термической сушки жидких марок Лигногумата не меняется их эффективность и биологическая активность.

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Author's index

Авторский указатель

Natural macroligands and magnetic nanoparticles: spontaneous processes and rational design

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In most environments, dissolved organic compounds among them natural macroligands (humic substances - HS) can be found besides the tremendous variety of natural and engineered nanoparticles. The amount and diversity of the latter have increased recently due to their expanding use. Magnetic nanoparticles (MNPs) may be natural soil constituents (magnetic iron oxides), but remediation processes have applied the MNPs such as magnetite nanoparticles or the even more favored nano-sized metal iron (ZVI) particles corroding to magnetite and iron oxyhydroxides. Reactivity of particles in the nanoscale (<100 nm) or colloidal range (<1000 nm) is enhanced, because of their high specific surface area and active site density. MNPs especially the naked and ZVI nanoparticles react immediately as get contact with a partner such as pollutant or HS. Spontaneous processes can take place, resulting in inherent surface modification of MNPs besides designed adsorption of pollutants, which either enhance (synergic effect) or spoil (antagonistic effect) the effectiveness of pollutant removal. The solution composition influenced surface properties of MNPs play the governing role in the colloidal particle-particle interactions resulting in either dispersing or aggregation of particles; therefore determine the transport in porous matrices, sedimentation in aquatic systems or the efficiency of magnetic separation.

In aquatic and soil systems, a polyanionic organic coating can spontaneously form on MNPs. In the presence of indifferent cations (typically Na+), the bound natural ligands smear out the differences between the surface properties of natural and engineered NPs. Above an appropriate adsorption loading, the humic coating hinders the particle aggregation, therefore enhances colloidal stability of MNPs. This protective effect of HS promotes the dispersing of particles and enhances their colloidal transport in the most aquatic environments except those with low pHs and high ionic strength. However, if specific cations in the sense of chemical affinity for functional groups (natural or designed) of HS are also present, their accumulation in the solid phase is mutually enhanced. A natural example is the chemical affinity between carboxylic groups of HS and Ca2+ ions, when humate coated MNPs may be bound through Ca bridges to the mineral surfaces and pores may entrap them.

In this presentation some spontaneous processes which are worth considering in rational design of MNPs are discussed, and examples of the authors' own experience of working with MNPs under environmental relevant conditions are presented.

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Мы – группа российских компаний, которые являются разработчиками, производителями и продавцами натриевых и калийных гуматов, выпускаемых на нашем предприятии в Санкт-Петербурге. Наш продукт – Лигногумат – производится из возобновляемого растительного сырья с использованием уникальных инновационных технологий, не имеющих аналогов в мире. Конкурентным преимуществом Лигногумата, выгодно отличающим его от традиционных гуматов, является высокая стабильность водных растворов. Это обеспечивает возможность компаундирования и получения широкого спектра высокотехнологичных продуктов на основе Лигногумата. Так, наша компания обладает технологиями изготовления гуматизированных минеральных удобрений как путем получения гуминовых пленок на гранулах, так и введения гумата в состав минеральных удобрений. Многочисленные исследования показали, что применение наших гуматизированных удобрений позволяет добиваться такой же урожайности при снижении дозы по NPK на 20-30%.

Экологическая безопасность и высокая физиологическая активность Лигногумата подтверждена сертифицированными лабораториями. Поэтому наш продукт уже нашел устойчивый спрос в передовых технологиях растениеводства, где он применяется в качестве стимулятора роста растений и адаптогена, снижающего стрессовые нагрузки на растения. Высокие адаптогенные свойства Лигногумата обеспечивают хорошую результативность его применения в качестве кормовой добавки в птицеводстве и животноводстве. Лигногумат способствует и активизации почвенных микробиологических сообществ, что приводит к усилению процессов очищения почвы от антропогенных загрязнений. При этом максимальной эффективностью обладает применение Лигногумата в сочетании с биопрепаратами. Лигногумат увеличивает сроки хранения биопрепаратов и приводит к синергизму эффективности их применения. Это обеспечивает хорошие перспективы применения Лигногумата в быстро растущей биотехнологической индустрии.

Наша продукция сертифицирована в России в 1999 году и на сегодняшний день мы являемся одним из крупнейших в России производителей и поставщиков гуматов. Мы занимаемся продвижением наших продуктов как в России, так и за рубежом. У нас есть надежные партнеры в странах СНГ, Евросоюза, в Китае, США, Канаде и др. Мы развиваем совместные исследования с более чем 20 научными институтами в России и в ряде зарубежных стран и всегда открыты для научного и коммерческого сотрудничества.

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Environmental safety and high physiological activity of Lignohumate is confirmed by certified laboratories. Therefore, our product has already found strong demand in advanced plant technology, where it is used as a plant growth promoter and adaptogen, which reduces stress on the plants. High adaptogenic properties of Lignohumate provide good results of its use as a feed additive for poultry and animal breeding. Lignohumate promotes the intensification of soil microbial communities, which leads to increased soil purification processes from human contamination. In this case, Lignohumate has the maximum efficiency in combination with biological products. Lignohumate increases the storage life of biologics and leads to synergism of their efficiency. This provides good prospects of Lignohumate in the rapidly growing biotechnology industry.

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General Director of "LIGNOHUMATE, LTD"

Oleg Gladkov
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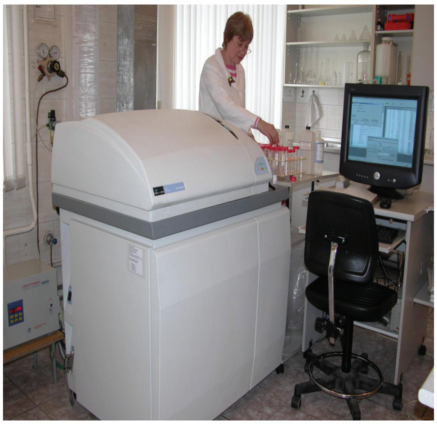
Обеспечение качества питьевой воды



Задача обеспечения качества питьевой воды решается:

- совершенствованием системы контроля качества воды водоисточников и питьевой воды;
- внедрением высокоэффективных технологий водоподготовки и обеззараживания;
- повышением технологической и санитарной надежности системы водоснабжения.

В Центре аналитического контроля качества воды предприятия используются современные достижения и методы в области контроля качества воды: высокоэффективная жидкостная хроматография, масс-спектрометрия с индуктивно-связанной плазмой, хроматомасс-спектрометрия, газовая хроматография с атомно-эмиссионным детектированием, атомно-абсорбционная спектрометрия, метод иммуноферментного анализа, метод полимеразной цепной реакции и др.

Повышение экологической безопасности и охраны окружающей среды

Стратегия повышения экологической безопасности и охраны окружающей среды направлена на:

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- повышение надежности системы канализации города.

Технологии денитрификации и реагентного удаления фосфора, механического обезвоживания с низкотемпературной сушкой осадка и технология сгущения избыточного ила включены в Единый реестр инновационных проектов Республики Башкортостан.

Энергоресурсосбережение и развитие информационных систем

Осуществляется комплекс работ, направленных на снижение потерь воды при транспорте до потребителей. Ведутся работы по оптимизации гидравлического режима работы сети и водоводов. Проводится модернизация трубопроводной системы города. Внедрены в производство современные высокоэффективные энергосберегающие технологии и оборудование.

За эффективную финансовую деятельность и высокую деловую активность МУП «Уфаводоканал» получил Диплом Международной премии «Лидер экономического развития России» (2006 г.), Диплом I степени за эффективную инвестиционную деятельность (2007 г.), Диплом городского конкурса «Лучшее промышленное предприятие г. Уфы» (2009 г.), Диплом и медаль победителя X Всероссийского конкурса «1000 лучших предприятий и организаций России-2009».

Профессиональная организация работы предприятия с опорой на научные исследования, новейшие технологии и методики, передовую технику позволили МУП «Уфаводоканал» войти в ряд лучших предприятий отрасли.

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система менеджмента качества
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по ГОСТ Р ИСО 9001-2008

Non-Commercial Partnership “Center for Biogenic Resources “Humus Sapiens”

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Non-commercial Partnership “Center for Biogenic Resources “Humus Sapiens” (NCP CBR “Humus Sapiens” was founded in 2007 by three leading Russian institutions in the field of chemistry, petroleum chemistry and chemical engineering: Lomonosov Moscow State University, Mendeleev Russian Chemical Technology University, and Gubkin Russian State University of Oil and Gas. The goal of NCP CBR “Humus Sapiens” is to provide research and development support to the “green chemistry” industry in Russia which implies a use of plant and humic materials as feedstock and plasticizes environmentally friendly technologies. The products of “green chemistry” include biofuel, biofertilizers, food additives, bioplastics, nanomaterials, composites and other

To reach these goals the NCP CBR “Humus Sapiens” concentrate its efforts on the following activities:

gives expert-analytical conclusions on innovative potential of “green chemistry” products and technologies;

launches and performs research and development projects in the field of “green chemistry”;

creates data bases on humic and plant raw materials and feedstock for “green chemistry”, on commercial products, producers and scientific centers active in this field;

develop and realizes standardization systems for humic-based and other bioproducts including development of reference materials and standard protocols;

organizes conferences for discussion of theoretic and applied problems in humic science and technology;

performs editorial and publishing activities for publishing scientific materials, conference papers and others;

forms the positive image of “green chemistry” products from humic and plant raw materials.

The portfolio of “Humus Sapiens” includes “know-how” for estimating quality and origin of commercial humic preparations by means of classification analysis based on date base containing data on more than 300 humic preparations. We also have two patented technologies for producing labeled humic preparation and for synthesis of silicon-containing self-adhesive preparations. Many more technologies are under development.

Некоммерческое партнерство «Экспертно-аналитический центр по проблемам органогенного сырья «Гумус Сапиенс»

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Некоммерческое партнерство «Экспертно-аналитический центр по проблемам органогенного сырья «Гумус Сапиенс» (НП ЭАЦПОС «Гумус Сапиенс») создано в 2007 г. Его учредителями стали лидирующие научно-образовательные учреждения России в области химии, нефтехимии и химической технологии: МГУ имени М.В. Ломоносова, РХТУ имени Д.И. Менделеева и РГУ нефти и газа имени И.М. Губкина. Цель партнерства – содействие становлению индустрии «зеленой химии» в России, которая предусматривает преимущественное использование в качестве сырья растительных и гуминовых ресурсов и реализует безотходные и экологически безопасные технологии. Продукты «зеленой химии» на основе растительного и гуминового сырья включают в себя биоэнергоносители, биоудобрения, наноматериалы, композиты, биопластики и другие инновационные продукты.

Для достижения поставленных целей НП ЭАЦПОС «Гумус Сапиенс» концентрирует свои усилия на следующих направлениях:

дает экспертно-аналитические заключения по оценке инновационного потенциала продуктов «зеленой химии» и соответствующих технологий;

выполняет научно-исследовательские и конструкторские разработки по приоритетным направлениям НП ЭАЦПОС «Гумус Сапиенс», формирует инновационные бизнес-проекты;

формирует базы данных по сырьевым ресурсам, коммерческим продуктам, поставщикам научных услуг, работающим в области органогенного сырья; организует информационно-консультационную деятельность;

разрабатывает и внедряет системы стандартизации продуктов на основе гуминового и растительного сырья, включая разработку стандартных образцов и стандартных методик;

созывает научные конференции и совещания для обсуждения теоретических и прикладных проблем гуминовой отрасли;

осуществляет издательскую деятельность, издает труды ученых, научных организаций, конференций и др.;

формирует позитивный имидж продуктов на основе органогенного сырья путем просветительской деятельности, в том числе с применением интернет-технологий.

На настоящий момент в портфеле инновационных разработок НП ЭАЦПОС «Гумус Сапиенс» способ оценки качества коммерческих гуматов и гуминоподобных соединений путем классификационного анализа, основанного на обширной базе данных (более трехсот препаратов) по структуре и свойствам природных и модифицированных гуминовых веществ, а также две патентованные технологии: получение меченых гуминовых препаратов и синтез кремнийсодержащих гуминовых веществ. Большое количество разработок завершено на лабораторном уровне и готово к масштабированию.

Regional Chapter of the Commonwealth of Independent States of the International Humic Substances Society

We are the Regional Chapter of the Commonwealth of Independent States of the International Humic Substances Society (CIS IHSS). The chapter was founded in Zvenigorod, Moscow Region, Russia at the Open Meeting of the Russian IHSS - Chapter held on September 25, 2002. As such, CIS-IHSS is a successor of the Russian IHSS Chapter founded in 1994. The main goal of the CIS IHSS is consolidation of the efforts of the CIS scientists in the field of basic and applied humic research. At present, the CIS IHSS has 110 members and is the largest chapter of the IHSS. The membership includes scientists, students, engineers, practitioners, and business representatives from Belarus, Kazakhstan, Kyrgyzstan, Russia, Ukraine, and Uzbekistan. The scientists and engineers are both from research institutes and industrial firms. The scope of scientific interests includes structure, molecular properties, genesis of humic substances, interactions of humics with heavy metals and organic ecotoxicants, application of humics for remediation technologies, biological activity of humics; technologies of manufacturing and agricultural applications of humics, and others. We are glad to be a part of the world-wide humic research community. We are open for cooperation and any kind of HUMIC activities.

For more information about the CIS IHSS visit our website at http://www.humus.ru/ihss/.

You are very welcome to join us!

Irina Perminova
Regional Coordinator of the CIS IHSS

Olga Yakimenko
Secretary of the CIS IHSS