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# **1. Humic systems: structure, evolution, analysis, properties**

## **The soil humeome and the significance of humification**

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The novel awareness of humic matter as supramolecular associations of relatively small heterogeneous molecules has gained a consensus following the progressively larger number of experimental evidence present in the literature. This new understanding has implied that the humic molecules may be separated from each other by a sequential fractionation and be analytically identified one by one, thereby increasing our knowledge on their molecular structure. A method called Humeomics was thus conceived to solubilize not only unbound small molecules but also those bound in ester and ether linkages and allow to separate less chemically complex fractions easier to characterize. Humeomics was first successfully applied to humic extracts from soil, and then, directly to cropped and uncropped soils to reach a more detailed understanding of the soil Humeome, that is the molecular composition of the totality of soil humic molecules.

Based on the increasing knowledge of the soil Humeome and on the general literature findings, a new perception was developed for the significance of Humification. A body of experimental evidence reveals, in accordance with the supramolecular nature of humus, that humification, rather than being the progressive increase of molecular mass of humic substances via a presumed but highly unlikely energy-intense formation of new covalent bonds, is nothing else than the selective accumulation in soil of hydrophobic molecular materials. In fact, the biotic transformation of fresh organic matter in soil progressively consumes the easily accessible hydrophilic biomolecules, whereas the hydrophobic components are firstly associated to each other and then squeezed out of the soil solution, thus being separated from the degrading biota by a spontaneous physical-chemical drive. This primary mechanism of chemical hydrophobic protection justifies the accumulation and persistent stabilization of natural organic matter in the environment and well integrates the process of secondary physical protection, the only one called so far to account for the stability of humus in soil.

## Evaluation of the accuracy of assignment of molecular formulas of humic substances in UHRMS performance by an external calibration with a flavonoid reference material

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Keywords: ultra-high-resolution mass-spectrometry, Fourier transform mass spectrometry, natural organic matter, untargeted analysis

Ultra-high-resolution mass spectrometry (UHR-MS) is widely used for analyzing natural organic matter including humic substances (HS). However, the problem of quality control of UHR-MS results is topical [1] especially considering the absence of HS reference materials (RM) with a known composition. Therefore, to confirm the trueness of the molecular-formula assignment in UHR-MS, RM of known compounds that are as close as possible in nature to HS are needed.

Towards this aim, commercially available RMs of natural compounds for chromatography and mass spectrometry were used as an external standard added to Suwannee River fulvic acid (SRFA) solutions prior to UHR-MS analysis. RM include 40 flavonols, flavonones, and chalcones that are commonly found in plants, foods, and health supplements and are similar in structure and identical in molecular formulas to ions found in HS and belong to the mass range of 200-600 Da (Figure 1, A). The matched concentrations of RM did not affect the intensity of HS mass spectra.

As a result, we confirmed the trueness of the molecular-formula assignment based on all measured UHR-MS signals of the RM. The signals of individual RM compounds are completely identical in  $m/z$  with SRFA signals with an error of  $m/z$  of 1 than 0.5 ppm (Figure 1, B), what indicates the identity of molecular formulas. We believe that the proposed approach significantly improves the precision and trueness of the results obtained both within the same laboratory and between separate scientific groups.

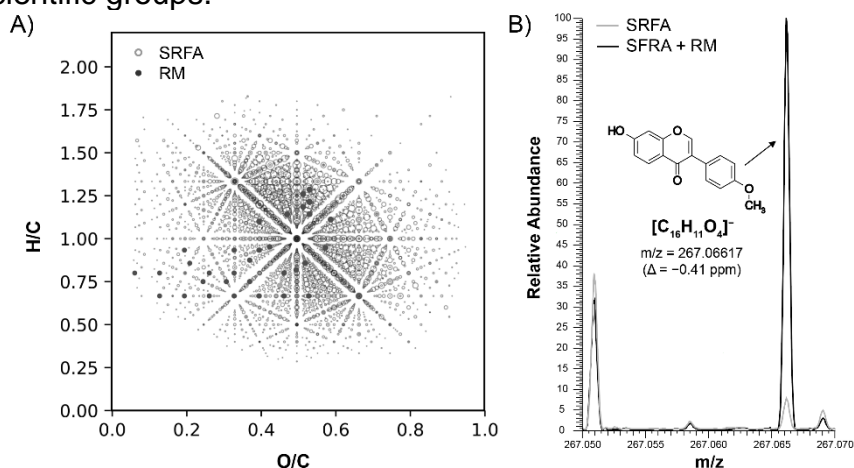


Figure 1. A, H/C vs. O/C ratios for RM compounds and each formula assigned in SRFA; B, mass-spectra of SRFA solutions without and with the RM added.

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## **Humic substances as a form of carbon stabilization in the bio- and lithosphere**

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Keywords: climatic trends, age of HS, climatically active gases, coal and oil formation

Humic substances (HS) were defined by V.I.Vernadsky as a universal product of transformation of plant residues not only in the soil, but also in other natural areas. Moreover, the transformation processes of these residues go in the direction of the relative accumulation of the most biothermodynamically stable products (according to D.S.Orlov), which in itself determines their stability.

The process of humification itself leads to the formation of specific large macromolecules, which already have significantly higher biothermodynamic structural stability, which significantly increases the age of preservation in conditions of an active biological cycle in the soil (1-3 thousand years). And in conditions of its slowdown and inhibition of microbial transformation in buried or paleosols, the age of HS can reach 5-6 thousand years. and more.

At the same time, concepts of the so-called non-humic stabilization of soil organic matter are currently being actively developed, which are based mainly on the process of occluding organic residues with highly dispersed mineral particles. However, according to various researchers, the age of these occluded non-humic fractions of organic matter usually does not exceed tens, at most hundreds of years.

This leads to an important conclusion that the stabilization and stability of soil organic carbon compounds depends mainly on the presence of HS in the soil. Therefore, in balance calculations and especially in modeling the processes of carbon runoff into soils, it is necessary to take into account not only the amount, but also the molecular structure and biothermodynamic stability (Chukov, 2001) of the soil HS.

Of course, the levels of stabilization of soil organic matter, including HS, depend on biological productivity and hydrothermal conditions in soils of different natural zones. However, the prospect of climatic trends in recent years can have a very significant impact on the levels of stabilization of organic carbon compounds and mineralization stability of soils in the taiga and Arctic zones of Russia. All this is important for the correct prediction of the processes of emission or runoff of climatically active gases in the soil cover.

Unfortunately, to date, another direction of emission of organic carbon compounds directed from the soil into the lithosphere remains poorly studied. Since the biogenic hypothesis of the origin of combustible minerals (coal, oil and gas) is one of the main ones in modern geology, it can be argued that the plant residues from which they were formed, to some extent at the initial stage, underwent a process of humification.

It is not surprising that the process of replenishing oil and gas from already pumped reservoirs and wells continues at the present time. The process of modern oil and gas formation (Zelenskaya, 2013) took place in ancient geological epochs and continues continuously to this day.

This is evidenced by the oil wells that have been completely pumped out 100 years ago in recent years. In some cases, they turned out to be 100% filled with fresh oil. Tatarstan and the Chechen Republic are among such regions. A pulsating oil production regime in wells has also been recorded in a number of fields in Western Siberia. Thus, HS serve as a reservoir for carbon stabilization in almost all spheres of the Earth.

## **Migration of carbon and substances: humic substances and their evolution**

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Keywords: organic carbon, humic substances, anthropogenic influence, evolution of protective properties

Organic substances in the environment perform important protective properties: from removing pollutants from the system to improving the quality of the ecological state. In addition, over time, under the influence of anthropogenic pollutants, the qualitative and quantitative composition of organic substances changes.

In the north of European Russia (ER), two large copper-nickel smelters are located in the western part of the Kola Peninsula - "Pechenganikel" and "Severonikel" and the emission of sulphur dioxide and metals continues more than 50 years. However, sulfur emissions have decreased substantially due to the modernization of production and purification of emissions in the ER over the last 25 years. The enrichment of surface water by metals is a result of both natural processes and human activities.

The aim of the work was to study the change (evolution) of the qualitative composition of natural aquatic organic substances and their protective properties in the waters of lakes at different distances from the pollutant; this was a model of the evolution of organic substances.

We used the following lake gradation: lakes without a direct pollution source (background lakes more than 200 km from the pollution source or isolated within Khibiny Mountains), lakes near the pollution source (up to 20–30 km from NPPs or smelters), lakes successively removed from the pollution source (to assess changes in the protection provided by humic substances against pollution as the lake water progresses from polluted to conditionally background quality); and lakes with a clear marine influence (for the balance of Na and Cl relative to other ions. Also, lakes by transect (every 20-30 km) from smelters to background site were considered.

Organic substances were isolated from the waters during freezing (or lyophilic drying) and were also investigated «in situ» in the sample. Dynamic light scattering technology was used to determine the zeta potential (colloid stability), molecular weight (MM), and size of the organic complexes (Malvern ZetasizerNano equipment). Additionally, IR spectrometry was used to confirm the functional groups, and chromatographic methods were used to assess the molecular weight distribution. The isotopic composition (C and N) of the samples was determined using an isotope mass spectrometer isoprime precisionION with a headspace gas analyzer module isoFLOW, Elementar, UK.

Based on data on the qualitative composition (IR spectra and molecular weight distribution), isotopic composition and size estimates of the colloid, it is possible to assess differences in the qualitative composition of organic matter, the influence of anthropogenic factors and changes in protective properties in relation to nickel and cobalt ions.

Acknowledgements. The work was carried out with funding from the Russian Science Foundation grant 24-27-00144

## Enhanced Antioxidant Activity of Fulvic Acid Fractions Correlates with Reduced Polarity in RP-HPLC Separation

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Keywords: antioxidant activity, fulvic acids, high-resolution mass spectrometry

Fulvic acids (FA) represent a class of humic substances (HS), which are complex organic macroligands capable of selectively binding various biological macromolecules. Fractionation is a key method developed to isolate components with enhanced antioxidant, antibacterial, and other biological activities. In this study, fractions were separated from the commercial available FA sample Fulvagra provided by Humintech Ltd (Grevenbroich, Germany) using reverse-phase high-performance liquid chromatography (RP-HPLC) with 0.01% formic acid in water and isopropyl alcohol as eluents. The method enabled complete desorption of FA from the column (ReproSil Pur C18-Aq). The 21 fractions obtained were subsequently characterized by Fourier transform infrared (FTIR) spectroscopy, UV-vis, and fluorescence spectroscopy. High-resolution mass spectrometry (HRMS) was employed to analyze the molecular composition of the organic substances in the fractions. Additionally, the average molecular weight of each fraction was determined using size exclusion chromatography (SEC).

Based on the kinetic curves, total antioxidant efficacy (AOE) values were determined for all extracted FA fractions. A clear trend emerged, with AOE values increasing systematically from 0.3  $\mu\text{M ABTS}\cdot\text{+}/\text{mg FA}$  for the polar fractions to a maximum of 0.9  $\mu\text{M ABTS}\cdot\text{+}/\text{mg FA}$  for the nonpolar fractions. The initial FA sample had an AOE value of 0.65  $\mu\text{M ABTS}\cdot\text{+}/\text{mg FA}$ . The decrease in fraction polarity significantly enhanced antioxidant activity, as the nonpolar fractions demonstrated a threefold increase in AOE compared to the polar ones. Additionally, the nonpolar fractions exhibited substantial antioxidant activity relative to the initial FA sample, suggesting the successful isolation of compounds with superior antioxidant properties. The Pearson correlation coefficient was calculated for antioxidant activity, molecular chemotypes, and isopropyl concentration. The heatmap shows strong positive correlations between antioxidant activity and isopropyl concentration ( $R > 0.8$ ), linking antioxidant potential to hydrophobic and aromatic structures in the fractions. Antioxidant activity also correlated positively with condensed, less oxidized tannin and lignin-like compounds ( $R > 0.8$ ) and inversely with oxidized hydrolyzable tannins ( $R < -0.8$ ).

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## Determination of urea and humic components in humate fertilizers by ATR-FTIR spectroscopy

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Keywords: urea, humate fertilizer, ATR-FTIR-spectroscopy

Urea is the predominant species in many nitrogen fertilizers. The blend of urea with humic substances reduces nitrogen losses, thereby increasing the efficiency of nitrogen uptake by plants [1]. There are no standardized methods of control of the composition of fertilizers based on humic substances (HS). Their analysis is complicated due to many components, as well as due to the non-stoichiometric composition of HS.

IR spectroscopy is widely used to determine the composition of organic substances, inorganic, coordination, and highly molecular compounds, as well as for qualitative and quantitative analysis of samples of various origins, in particular for humic substances [2, 3].

Therefore, this study aimed to develop a FTIR method for directly determining urea and HS in aqueous solutions of HS-based fertilizer preparations by ATR-FTIR spectroscopy with minimum sample preparation. Several commercial fertilizers, potassium humate (Powhumus), and urea were investigated. A Bruker Vertex 70 spectrometer with a diamond-crystal ATR attachment was used.

For the determination of urea and HS in their mutual presence, the error in the determination of urea is minimal at 1628 and 1598  $\text{cm}^{-1}$  (vibrations of  $\text{NH}_2$  and  $\text{C}=\text{O}$ , respectively) in the concentration range of 10–200 g/L; potassium humate, at 1380  $\text{cm}^{-1}$  ( $\text{C}-\text{H}$  bending vibrations in  $\text{CH}_2$  and  $\text{CH}_3$  groups and symmetric  $-\text{COO}^-$  stretching vibrations) in the concentration range of 10–100 g/L. When calculating the contents of HS and urea in their mixtures using the Vierordt's method, the error in assessing each component is no higher than 3%.

The proposed determination conditions have been tested on model fertilizers and commercial humate fertilizers. The found component contents in model fertilizers are in good agreement with the added quantities. In fertilizer A, the calculated values are higher than those declared by the manufacturer, but with a rough estimate, it can be assumed that the ratio of components is also consistent. This may indicate the correct technological process of mixing. According to the analysis, fertilizer A is a concentrated solution of humate with urea, which is claimed by the manufacturer. In contrast, fertilizer B is a solution of urea with a small addition of HS, although the manufacturer stated that this fertilizer is a concentrated solution of humate without urea, i.e. fertilizer B is a falsification.

The proposed conditions for the simultaneous determination of HS and urea are applicable for the analysis of fertilizers of relatively simple composition. To build calibration graphs, it is important to use HS of the same brand as in the fertilizer. Otherwise, the calculation error may be high due to the different functional-group composition of HS of different origins.

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## Analysis of the composition of fulvic acid isolated from oxidized brown coal

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Keywords: fulvic acid, dialysis, adsorbent, oxidized carbon.

Fulvic acid (FA) is a high-molecular nitrogen-containing organic acid containing various functional groups (aromatic ring, phenolic, hydroxyl, ketocarbonyl, quinonecarbonyl, carboxyl and alkyl groups) [1]. The method of obtaining Ammonium humate from oxidized weathered coals by electrophysical process consisted of several stages. Namely, crushed oxidized coal "Sarykol" was subjected to intensive oxidation and dispersion of coal particles with atmospheric oxygen in the RPA at 50°C, and the particles were reduced to an ultrafine state and a homogenized in the presence of a 3% aqueous ammonia solution for 20 minutes. After RPA, the final mass was transferred to the extraction tanks to hold the solution for an hour. Subsequently, the aged solution was subjected to an ultrasonic dispersion at a specific frequency for 25 minute. to obtain concentrated FA a solution of potassium humate is mixed with an aqueous acid solution (5%), acidified to pH = 1-2, stirred for 30 minutes, then transferred to a centrifuge to separate fulvic acid from humic acids, centrifuged at 3000 rpm for 30 minutes, resulting in humic the acid settles to the bottom, and fulvic acid is released in the form of a solution, the resulting solution of fulvic acid enters the purification stage. After isolated the fulvic acid it was purified by the Forsyth method. Its composition was analyzed using an ATR-FTIR spectrophotometer. It is based on direct measurements of samples, which provide valuable information on the composition and structure of various materials. The results of the study are presented in Table 1.

Table 1. Name and quantity of substances, components in the composition of fulvic acid

Name	Name and quantity of substances, components %						
Initial FA before purification	Glutaraldehyde (25% in water)-33.7 %	Polyvinyl alcohol-28.3%	Magenesium chloride hexahydrate-10.7%	Choline chloride-9.6%	Xylyl bromide-7.5%	Calcium chloride crystalline-6.3%	Magnesium bromide diethyl etherate-3.9%
FA after «Shubarkol» sorbent, cation exchanger KU-2-8 and membrane treatment	Glutaraldehyde (25% in water)-33.4 %	Polyvinyl alcohol-27.9%	Magenesium chloride hexahydrate-11.2%	Choline chloride-9.9%	Xylyl bromide-7.1%	Calcium chloride crystalline-6.5%	Magnesium bromide diethyl etherate-4.0%
FA after «Shoptykol» sorbent, cation exchanger KU-2-8 and membrane treatment	Glutaraldehyde (25% in water)-41.9 %	Polyvinyl alcohol-32.3%	Magenesium chloride hexahydrate-15.9%	Choline chloride-9.9%	-	-	-
FA after «Coconut» sorbent, cation exchanger KU-2-8 and membrane treatment	Glutaraldehyde (25% in water)-30.5 %	Polyvinyl alcohol-28.2%	Magenesium chloride hexahydrate-12.8%	Choline chloride-9.9%	Xylyl bromide-6.6%	Calcium chloride crystalline-5.9%	Sodium iodide-3.6%

The results of the ATR-FTIR analysis showed some components that are vital for the human body. Fulvic acid improves metabolic processes, restores cellular energy reserves, has antioxidant properties, neutralizes heavy and toxic metals, and helps remove toxins from a living organism. Therefore, the future goal is to study the biological activity of the obtained products.

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## **The organic matter and biological activity of sod-podzolic soils in the north-western part of the Moscow region under different types of phytocenoses.**

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Keywords: labile organic matter, enzymatic activity

A large area of the Moscow region is covered with forests, under which sod-podzolic soils of different thickness, degree of podzolization and thickness of the humus horizon are formed. A large number of works are devoted to the study of their agrochemical properties, changes in properties during various successions, after fires, as well as the influence of the ornithological factor on soil properties (Bogatyrev, 2022). However, less attention is paid to soils under natural vegetation.

At the same time, forests are a carbon sink, and the study of various issues related to the processes of humification and mineralization of organic matter entering the natural soil is very important. In the 20th century, there were many works dedicated to the humus state of sod-podzolic soils. However, there is not much researches on the content of labile organic matter in the area of natural sod-podzolic soil.

The purpose of the study is to characterize the composition and properties of labile organic matter and the biological activity of sod-podzolic soils of the north-west of the Moscow region, formed under different phytocenoses.

The objectives of the study were to evaluate:

1. The stocks of litter and elements in soils under different plant associations
2. The absolute and relative content of various labile carbon fractions in the soil.
3. The biological activity of soils in terms of respiration and the content of enzymes (catalase, invertase, dehydrogenase and urease)
4. The relationship between the content of individual enzymes (catalase, dehydrogenase, invertase, urease) and the content of labile organic matter in the soil based on data on the content and composition of labile organic matter in the soil

The objects of the study were samples of sod-podzolic typical soil selected under two different phytocenoses: spruce with an admixture of birch and spruce-birch fern-sedge.

The following results were obtained during the research:

1. The difference in litter stocks under spruce with an admixture of birch and under spruce-birch fern-sedge is due to the intensity of decomposition of plant residues: under spruce-birch, the intensity of decomposition of litter is higher.
2. Compared with the spruce forest, the relative content of labile fractions of organic matter of sod-podzolic soil is higher under the spruce-birch forest.
3. The biological activity of sod-podzolic soils under spruce and spruce-birch forest also differs. Compared with the spruce forest, the catalase activity is higher under the spruce-birch forest, as well as the potential respiration of microorganisms.

## **Structural biochemistry of humus acids of polygenetic soils of forest-steppe, according to $^{13}\text{C}$ -NMR spectroscopy**

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Keywords: forest-steppe,  $^{13}\text{C}$ -NMR spectroscopy

The aim of this study was a comparative study of the structure of humic acid molecules of polygenetic Holocene soils of the Central forest-steppe, as well as ferruginous-manganese nodules from them, by  $^{13}\text{C}$ -NMR spectroscopy. The objects of the study were grey forest soils forming typical geochemical catenae in the Moscow and Bryansk regions. The studied soil series are represented by agro-grey soils of watershed micro-uplands, their podzol varieties - in the upper parts of slopes and in saucer-shaped depressions on watersheds, gleyed soils - in the middle parts of slopes, and gley soils - at the foot of slopes and in depressions.

Humic acid preparations were isolated from the studied soils by triple extraction with 0.1 n NaOH/ 0.4 M NaF from samples decalcified with 0.05 n  $\text{H}_2\text{SO}_4$ . After separation of colloids by centrifugation (2500 g, 15 min; (Beckman, Model J - 6)), purification of humic acid preparations from mineral salts was carried out by electrodialysis (MWCO 12,000 - 14,000). The dialysed and freeze-dried humic acid preparations (50 mg) were dissolved in 0.6 ml of 0.3 M NaOD/ $\text{D}_2\text{O}$ . Spectra were acquired in a 5 mm sample tube (ampoule) on a Bruker Avance DRX 500 NMR spectrometer at 290 K at 25.18 MHz. The relative content of individual forms of compounds in humic acids was estimated by integrating the intensity of the signals obtained on the spectra. The age of soils was determined by radiocarbon dating of humic acid preparations.

The  $^{13}\text{C}$ -NMR spectroscopy data obtained for 10 preparations of humic acids from grey forest soils of different degrees of waterlogging and four preparations - from ferruginous-manganese nodules from soils, indicate a significant transformation of the carbon skeleton of macromolecules during increasing overwatering and nodule formation. More than 20 peaks were identified on NMR spectra extracted from humic acid soils. In hydromorphic soils all shifts are more contrasting, aliphatic fragments of molecules have the greatest branching and longer hydrocarbon chains in comparison with automorphic soils. In general, the molecular structures of humic acids from day humus horizons of grey forest soils of microhills have very low aromaticity - 21-24 %, close to sod-podzolic soils of the boreal zone. The age of these horizons is 1650+60 years. A significant increase (up to 75 %) in aromaticity is demonstrated by humic acids from the second humus horizons of the soils of micro-declines (6990+110 years), which is typical for humus of chernozems. Consequently, in the Middle Holocene, the studied areas of the forest-steppe were occupied by herbaceous vegetation on chernozem soils (which is confirmed by the results of isotopic analysis, analysis of the pool of n-alkanes and lignin phenols, and phytolith analysis), and at the turn of historical time, apparently, there was a large-scale climate change and forest encroachment on steppe areas. Under reducing conditions, the carbon skeleton of humus macromolecules is transformed: their aromaticity decreases, and the degree of oxidation, branching and stretching of aliphatic structures in length increases. The bands of the aliphatic part of the spectrum in the nodules lose their intensity compared to humic acids of the host horizons. The ratio of peak areas of the aromatic part of molecules to the aliphatic part was 0.70-1.04 for nodules, and 0.32 for soils. The amount of carboxylic structures in humus acids of nodules is two times higher than in humus of soils. At the same time, the radiocarbon age of nodules is 1600-1990 years, i.e. the beginning of the epoch with variable redox regime coincides with the beginning of historical time and the spread of forest vegetation.

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## A study of the conditions of the recording of CP/MAS $^{13}\text{C}$ NMR spectra of humic acids

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Keywords: solid-state NMR spectroscopy, contact time

The use of modern, high-precision physico-chemical analytical methods allows researchers to obtain comprehensive information on the molecular composition of humic acids (HAs). HAs have a heterogeneous and polydisperse molecular composition, challenging numerous attempts to describe their chemical structure quantitatively. The application of chemical and various spectroscopic methods often gives conflicting results. NMR spectroscopy is the only physical method that promises to provide a reliable characterisation of HAs. However, analysis of literature data shows a wide variation in the parameters used by researchers to record solid-state  $^{13}\text{C}$  NMR spectra, making it impossible to further compare the results obtained. Therefore, the aim of our work was to comparatively study the influence of CP/MAS  $^{13}\text{C}$  NMR spectra recording parameters on the information obtained about the molecular structure of HAs.

The object of study was a HA preparation isolated from the T1 horizon (0-10 cm) of Hemic Folic Cryic Histosol according to the method recommended by IHSS. CP/MAS  $^{13}\text{C}$  NMR spectra of HAs were recorded on a Bruker Avance III WB 400 NMR spectrometer with an operating frequency of 100.6 MHz. The sample rotation frequency was 12.5 kHz, the contact time varied from 0.02 to 3.5 ms, the relaxation time was 2 s and the number of scans was up to 8000.

Figure 1 shows the intensity dependence of the CP/MAS  $^{13}\text{C}$  NMR spectra observed for the peaks of the six regions most commonly used by HA researchers.

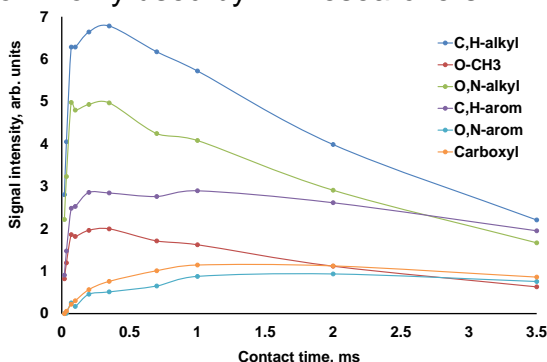


Figure 1. Signal intensity of the CP/MAS  $^{13}\text{C}$  NMR spectrum of the HAs as function of contact time.

Although different groups of  $^{13}\text{C}$  atoms show significant differences in intensity increase ( $I_t$ ), all signals satisfy the conditions – the cross-polarisation time ( $T_{\text{CH}}$ ) is much shorter than the proton spin lattice relaxation time ( $T_{1\rho\text{H}}$ ). The decrease in  $\log I_t$  at  $t > 1$  ms is linear in the plot of  $\log I_t$  versus  $t$ . The  $T_{1\rho\text{H}}$  of different  $^{13}\text{C}$  groups were calculated from the slope of this line, which ranged from 2.86 ms for C,H-alkyl to 11.03 ms for O,N-arom groups. These carbon atoms can become invisible in the spectra and frustrate attempts to extract quantitative information from the spectra. The difficulty of the CP/MAS method arises in the determination of  $^{13}\text{C}$  atoms in large condensed aromatic structures, which do not have protons in close proximity and do not undergo polarisation transfer in a cross-polarisation experiment. As a result, the aromatic region is often severely underrepresented in solid-state spectra.

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## Development of a methodology for the $C_{HA}/C_{FA}$ determination in humic substances of various genesis

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Keywords: humic acids, fulvic acids, total organic carbon analysis, dichromate oxidation

The ratio of  $C_{HA}/C_{FA}$ , representing the content of humic acids (alkaline-soluble fractions) to fulvic acids (acid-soluble fractions of humic substances (HS)), serves as an index for assessing the degree of humification—a process that transforms organic matter in natural environments. The classical method for determining carbon in HS involves oxidizing organic materials with an excess of potassium dichromate in an acidic medium, followed by spectrophotometric analysis at 590 nm using glucose standards. However, this method has limitations, including significant measurement errors, lengthy procedures, and the use of toxic reagents. To reduce environmental risks and chemical waste, newer methodologies are needed that minimize the use of hazardous substances. Notably, the optimal pH for acidification remains uncertain in the literature, with a general recommended range of 1–2. Advanced instrumental techniques, such as Total Organic Carbon (TOC) analysis using high-temperature combustion of organic matter offer more refined approaches.

The objective of this study is to propose a quantification method for HS utilizing instrumental techniques, using Total Organic Carbon (TOC) analyser, and to compare these results with the traditional method of oxidizing organic materials using an excess of potassium dichromate. The study further investigates the kinetics of HA precipitation over a 24-hour period at pH levels of 1.0, 1.5, and 2.0, aiming to identify the optimal pH conditions for the effective separation of FA and HA fractions. The study analyzed unfractionated samples of chernozem soil (SHF) from the Kursk region, coal (CHF) from Gusinozersk, and commercially available humic substances (HS) extracted from peat (KG-HS) provided by Ecobiosphere Ltd. (Kaluga, Russia), as well as HS extracted from Leonardite (CHS), distributed by Sakhalin Humates GC, Russia.

The kinetics of HAs separation from HS solution at pH levels of 1.0, 1.5, and 2.0 were analyzed for all samples, and the  $CHA/CFA$  ratio was calculated using both instrumental TOC analysis and the traditional potassium dichromate oxidation method. The highest  $CHA/CFA$  values were recorded in the CHF and CHS samples, reaching  $7.39 \pm 0.37$  and  $7.59 \pm 0.23$ , respectively, at pH 1 after 1 hour of acidification using the TOC analyzer method. The  $CHA/CFA$  ratio remained stable across all samples throughout the 24-hour observation period (with measurements taken at 1, 2, 3, 4, 12, and 24 hours after acidification). The elevated  $CHA/CFA$  ratios in these samples are likely due to the significant contribution of humic acids, reflecting the humified and highly transformed nature of their source materials. A similar trend was observed in the SHF and KG-HS samples, which exhibited lower  $CHA/CFA$  ratios of  $1.73 \pm 0.02$  and  $1.79 \pm 0.06$ , respectively, at pH 1 after 1 hour of acidification, attributed to the greater FA content in these samples. Comparing the results of the instrumental TOC-analysis measurements with the traditional dichromate oxidation method revealed a significant underestimation of organic matter in the latter method. The highest  $CHA/CFA$  values in the CHF and CHS samples using the dichromate method were  $6.79 \pm 0.58$  and  $6.68 \pm 0.31$ , respectively, while the SHF and KG-HS samples showed ratios of  $1.06 \pm 0.23$  and  $1.24 \pm 0.37$ . The lower values in the dichromate method likely result from the prolonged procedure and incomplete oxidation of organic matter.

In conclusion, the direct comparison of the  $CHA/CFA$  ratios from the TOC analyzer and the traditional dichromate method highlights the superiority of the instrumental method, offering greater accuracy and faster results. It was also demonstrated that reducing the HA fractionation time to 1 hour with acidification at pH 1 provides reliable results, significantly accelerating the analysis process for HS samples.

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## Determination of the stability constants of humic substances with zinc by the Schubert method

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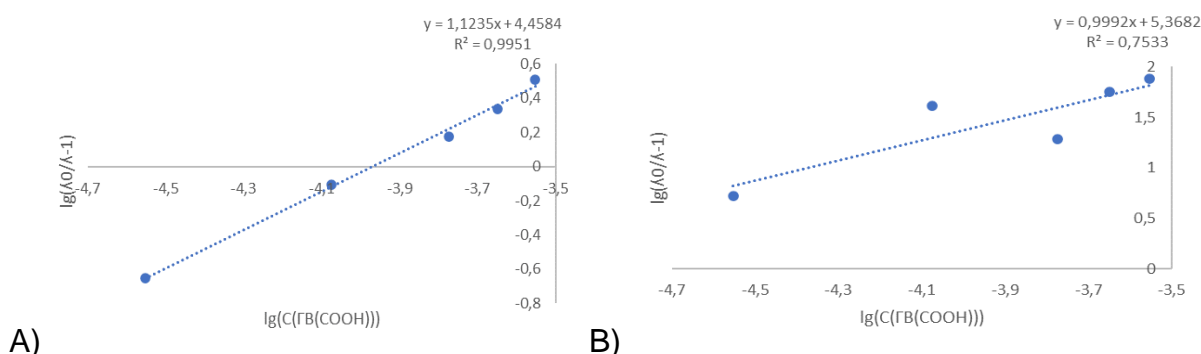
Keywords: Humic substances, zinc, stability constant

Humic substances (HS) represent a broad class of natural organic compounds and are found in soil, natural waters, and solid fossil fuels. They possess the ability to form complexes with heavy metals due to the presence of various functional groups in their structure such as carboxyl, hydroxyl, carbonyl, nitrogen- and sulfur-containing groups as well as aromatic fragments. By forming chelate complexes with heavy metals HS retain them in soil preventing their migration to plants and groundwater. Therefore, understanding the interaction between HS and heavy metals plays a key role in describing and creating models of biogeochemical cycles. This highlights the importance and relevance of studying the reactivity of HS concerning heavy metals quantitatively characterized by the stability constants of the complexes [1].

The aim of this study was to determine and compare the stability constants of zinc complexes with humic and fulvic acids using the Schubert method.

For the experiment a strong acid cation exchange resin KU-2-8 was used along with a series of HS concentrations: 0.4, 0.32, 0.24, 0.12, and 0.04 g/L. Humic acids (HA) from coal and fulvic acids (FA) from peat were used as the humic substances. The concentration of zinc ions was kept constant at  $Zn^{2+} = 100 \mu\text{g/L}$ , with an ionic strength of 0.01 M. The determination was conducted at pH 9 for FA and HA. Based on the results of the experiment straight lines were constructed to

determine the binding constants in the coordinates.  $\log\left(\frac{\lambda_0}{\lambda} - 1\right) - \log([HS])$  figure 1.



A) B)  
Figure 1. Determination of the stability constants at pH = 9 for A) FA and B) HA complexes as a free term in the equation of the straight line.

From the data dependencies the binding constant can be determined as an intersection of the constructed line with the Y-axis. The calculated constants were  $5.75 \times 10^3$ ,  $4.17 \times 10^4$  and  $3.24 \times 10^5$  L/mol of carboxyl groups for FA (pH = 5), FA (pH = 9) and HA (pH = 9) respectively. The obtained values of the constants indicate that zinc complexes with HA are more stable than those with FA according to a greater affinity of zinc for the functional groups of HS, specifically phenols, compared to the carboxyl groups of FA.

Acknowledgements. The work was supported by the Ministry of Science and Higher Education of the Russian Federation, the grant No. 075-15-2024-533

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## **Humic substances and green technologies**

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## Internal calibration of high-resolution mass spectra of humic substances with information from isotopic patterns

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Keywords: humic substances, high resolution mass spectrometry, internal calibration

Non-target analysis of humic substances (HS) consists in assigning molecular formulas of probably present compounds to peaks in high-resolution mass spectra and thus represents a qualitative analysis of HS. Most often, such assignments of elemental composition are based only on the distance between  $m/z$  values of peaks and molecular masses of formulas. Therefore, the accuracy of measurements of  $m/z$  values is one of the factors that affects the validity of non-target analysis results. However, the measured  $m/z$  values contain a systematic error. A number of internal calibration algorithms have been proposed in the literature to correct this error type [1-3]. Nevertheless, none of the proposed methods uses the confirmation of the assigned formulas. Incorrectly assigned calibrant formulas can distort the approximated calibration function, which will reduce the validity of the results. Therefore, the aim of this work is to develop a method for the internal calibration of high-resolution mass spectra of humic substances that relies only on calibrant formulas that are confirmed using information extracted from isotopic patterns.

The algorithm proposed in this work includes searching for isotopic patterns, assigning formulas to monoisotopic peaks with 5 ppm  $m/z$  radius, selecting validated formulas, and approximating the calibration function using a quadratic polynomial. Unfortunately, we observed that high-resolution mass spectra have low accuracy in measuring the relative intensities of peaks in isotopic patterns (it is consistent with the data presented in the literature). Therefore, the algorithm only confirms the set of elements (C, N, O, S), not their exact numbers.

The new internal calibration method was tested on segmented mass spectra of humic substances obtained with an Orbitrap Elite and a resolution of 480,000 ( $m/z$  400). Also, the results of the algorithm were compared with other previously published methods [2, 3] by 4 metrics: increase in the number of assignments, RMSE of assigned formulas, average assignment error, and standard deviation of assignment error. The results show that an algorithm using confirmation by isotopic patterns is able to correct the systematic  $m/z$  error. However, its effectiveness dramatically depends on the averaging of which number of microscans the mass spectrum under consideration was obtained. At the values considered so far (128 and 256 microscans), the new algorithm is on average worse than the algorithm from [2] but can outperform it for individual spectra.

Acknowledgements. This work was supported by the Russian Science Foundation, project number 21-73-20202.

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## Photodegradation of aqueous solution of some phenol derivatives in the presence of humic acids

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Keywords: humic acids, peat, photodegradation, excilamps, phenolic compounds, UV irradiation

Phenols are one of the most common pollutants in industrial wastewater, chemical, petrochemical, paint, textile, pesticide plants, etc. They serve as intermediate links in the industrial synthesis of products, such as a variety of adhesives and antiseptics [1]. Alkylphenols are released into aquatic environment as major metabolites of non-ionic surfactants widely used in a variety of industrial, household and commercial application [2]. Cyanophenols also attract attention because the nitrile group acts as an electron accepting group, whereas the hydroxyl group is a weak electron donor.

The potential of photoprocesses to remove organic compounds from water or air is currently being intensively studied. These processes include direct ultraviolet (UV) photolysis, which are promising methods for the production of drinking water or ultrapure water without the addition of other reagents. These methods can be successfully applied to remove aromatic pollutants such as phenols. In recent years, mercury-free excimer and exciplex lamps (excilamps) emitting in a narrow band have been increasingly used as sources of UV radiation. For studies, excilamps on working molecules KrCl (222 nm), XeBr (282 nm) and XeCl (308 nm) developed at the Institute of High Current Electronics of the SB RAS, were used as a sources of UV radiation. The quantum yields of phototransformation of phenol derivatives using various UV radiation sources were estimated. It was shown that in order to obtain efficient photodegradation direct photolysis must be supplemented with a KrCl excilamp with the addition of hydrogen peroxide to an aqueous solution of *p*-cyanophenol in order to start the mechanism involving hydroxyl radicals.

To study the effect of humic acids (HAs) on the processes of photodegradation of phenolic compounds, the HAs were added to aqueous solutions of 2,6-bis(hydroxymethyl)-4-methylphenol ( $5 \times 10^{-6}$  M) and *p*-cyanophenol ( $2,5 \times 10^{-6}$  M). Samples of HAs were obtained Aldrich Chemical Co and prepared from peat in the Arhangelsk region.

The results allow us to conclude that the addition of Aldrich humic acid significantly increases the photodegradation of the compounds under study. The addition of peat humic acid leads to much weaker changes in the absorption and fluorescence spectra of the mixtures, though in the same direction as the addition of the Aldrich humic acid. As the concentration of *p*-cyanophenol decreases, these changes become more obvious and occur faster. The irradiation time is halved, and after 80 minutes complete decomposition is observed.

Depending on their origin and structure, humic substances have a remarkable ability to absorb light and transfer this energy to other substrates. Excited singlet and triplet states of dissolved humic acids, the major component of humic substances, are important players for the transformation of organic chemical contaminants in water. The presence of HAs could either enhance or inhibit the photolysis of organic pollutants.

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## **Separation of humic substances into individual compounds: possibilities and limitations of multidimensional chromatography**

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Keywords: preparative chromatography, separations methods, natural organic matter, untargeted analysis

Humic substances (HS) are a very complex mixture of organic compounds of relatively similar nature. In the literature, there are various estimates of the number of compounds that make up HS, but the estimate from below based on ultra-high-resolution mass-spectrometry data is tens of thousands. The problem is that the solution of fundamental issues of HS chemistry, namely the determination of the structure of the constituent compounds, the quantitative analysis of their content, the establishment of the mechanism of formation, as well as several issues of practical application of HS, such as the isolation of biological activity, require the separation of HS into components up to individual compounds.

At present, the most effective and widely used method for separating complex mixtures of organic compounds is high-performance liquid chromatography (HPLC). However, even a single application in this case does not lead to the separation into individual HS components. This is due to both the limitations of HPLC itself and the specific features of HS. We propose using two-dimensional and even three-dimensional HPLC to overcome his limitation. This approach is applied to mixtures of organic substances that are similar in nature, such as protein metabolites, environmental and natural products and provides the separation of mixtures consisting of thousands of compounds [1, 2].

The application of multidimensional HPLC for HS has great potential, which will be discussed in the report. We will demonstrate some of the examples we have gained of application to HS and discuss the theoretical and practical limitations of this approach.

Acknowledgements. The work was supported by the Russian Science Foundation, project number 21-73-20202.

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## **Separation of asphaltene fractions of natural non-living organic matter of sedimentary rocks using preparative column chromatography**

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Keywords: normal phase preparative chromatography, separations methods, non-living natural organic matter, untargeted analysis, ICP-AES, FTIR

Most of the natural non-living organic matter (NOM) on the planet is dispersed organic matter or kerogen. The Glossary of Geological Terms of the American Geological Institute defines kerogen as the solid bituminous mineraloid substance in oil shales which yields oil when the shales undergo destructive distillation [1]. At present, kerogen is more often defined as a solid-phase macromolecular organic matter found in sedimentary rocks and insoluble in conventional organic solvents [2]. In the process of oil and gas formation, high-molecular compounds soluble in organic solvents — asphaltenes — are initially separated from kerogen. The amounts of hydrocarbons obtained depend mainly on the concentration and initial composition of kerogen. Asphaltenes are defined as the heaviest component of petroleum fluids that is insoluble in light n-alkanes such as n-pentane or n-heptane, but soluble in aromatic hydrocarbons such as toluene [3]. Due to the physico-geochemical similarity of asphaltenes to kerogen, the study of asphaltenes also provides important information for understanding the transformation processes of NOM.

Despite the significant development of fractionation methods, the separation of asphaltenes using normal-phase liquid chromatography (NP-LC) methods is rarely studied and used, despite the simplicity, low cost, and efficiency of this method. In addition, the effect of the separation technique on the content of microcomponents in different fractions has not been studied in practice. Thus, the aim of the study was to develop the conditions for preparative NP-LC of asphaltenes.

As a result, the conditions for the preparative separation of asphaltene fractions using preparative NP-LC are proposed, which ensure the separation of asphaltenes into 10 fractions. After separation, there is a mass loss of 5.3%, which is due to the presence of irreversibly sorbed substances. For the isolated fractions, data of elemental and structural-group composition were obtained, which show that, under the proposed conditions, asphaltenes are separated into fractions enriched with saturated functional groups of molecules, enriched with polyaromatic molecules, as well as heterocyclic molecules. Significantly different contents of organometallic compounds between the fractions were revealed.

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## Alkali extraction under air significantly enhances antioxidant and biological activities of humic acids

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Keywords: humic acids, priming, DPPH•, antiradical activity, antioxidant activity, biological effect

Humic substances are polydisperse and heterogeneous compounds formed during decay and transformation of organic residues in the diversity of the environments (IHSS 2022). Based on solubility in alkali they are divided into humic acids (HA), fulvic acids (FA) and insoluble humin. Alkaline extraction is criticized for the possibility of creating artifacts, such as oxidation of phenolic constituents, hydrolysis of ester groups, etc. To avoid these, International Humic Substances Society has recommended alkaline extraction under the atmosphere of inert gas (e.g. nitrogen). However, extraction under N<sub>2</sub> is ignored when HA are obtained for commercial or medical purposes. Here we studied the effects of extraction (under air or nitrogen) on physico-chemical properties, antioxidant and biological activities of HA of different origin. We hypothesize that extraction under air might be beneficial to obtain biologically active HA preparations for commercial use.

HA from 5-year old static pile compost (HAC), and from Ah horizons of sod-podzolic soil (HAS) and chernozem (HACH) were used. Extraction was performed by three consecutive treatments with 0.1 M NaOH (1 hour each) under nitrogen (HA-N<sub>2</sub>) or under air (HA-O<sub>2</sub>). The pH of each extract was adjusted to 7.0, extracts were purified by membrane filtration (0.22 μm). HA were obtained by acidification to pH 2 and washing from Cl ions by distilled water. The ash content of the preparations was 2-5%.

Some properties of HA are shown in Table 1. Aromaticity of humic acids (E<sub>4</sub>/E<sub>6</sub>, Car) and free radical content increased in the order HAS~HAC<HACH, and HA-O<sub>2</sub> were generally more oxidized than HA-N<sub>2</sub> (O:C, CH-ON, CH-O, free radical content).

Table 1. Physico-chemical and antioxidant properties of humic acids

HA	Elemental omp.		E <sub>4</sub> /E <sub>6</sub>	Solution-state <sup>13</sup> C-NMR			Free radical content	
	H:C	O:C		CH <sub>n</sub>	CH-ON	CH-O	Car	EPR
HAS-N <sub>2</sub>	1.1	0.4	5.0	20	21	24	6.9×10 <sup>16</sup>	4.65
HAS-O <sub>2</sub>	1.2	0.6	5.0	13	23	21	8.1×10 <sup>16</sup>	7.33
HAC-N <sub>2</sub>	0.7	0.5	4.7	23	17	23	7.1×10 <sup>16</sup>	3.05
HAC-O <sub>2</sub>	0.8	0.6	5.5	17	20	24	9.1×10 <sup>16</sup>	4.55
HACH-N <sub>2</sub>	0.6	0.6	3.1	-	-	-	1.3×10 <sup>18</sup>	3.42
HACH-O <sub>2</sub>	0.7	0.5	3.1	15	22	31	1.5×10 <sup>18</sup>	2.73

We have tested biological activities of HAs by seed priming which is cost-effective and a quick way to stimulate growth of various crop plants. Application antioxidants as priming agents has been shown to be effective in increasing seedlings vigorosity. In our work, primed seeds produced more vigorous seedlings than unprimed seeds in case of radishes, but not in case of wheat. Radish seed priming with HAs-O<sub>2</sub> resulted in an increase in vigour index (VI) of 1.1-2.1-fold. The VI of radish seeds primed with HAs-O<sub>2</sub> exceeded that after treatment with HAs-N<sub>2</sub> by 1.3, 1.1 and 1.8 times for HAS, HACH and HAC respectively. Thus, alkaline treatment under air enhances antiradical and biological activities of HA, making such preparations more attractive for use as natural antioxidants and priming agents.

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## Composition of humic substances fractions of brown coals.

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Keywords: brown coals, humic substances

Samples of humic substances (HS) were isolated from brown coals of the Kansk-Achinsk and South Ural basins. The following fractions were obtained: humic (HA), fulvic acids (FA), hylatomelanic (HmA), and humus (HuA) acids [1]. The fractions were studied using IR-Fourier and <sup>13</sup>C-NMR (CPMAS) spectroscopy, technical and elemental analysis.

The highest quantitative yield of HS is observed in weathered (naturally oxidized) brown coal of the Tisulskoye deposit of the Kansk-Achinsk basin: HA - 60.9% (of which HmA - 11.3%, HuA - 49.6%) and FA - 9.6% on daf of coal.

Based on the results of <sup>13</sup>C NMR spectroscopy, the features of the structural-group composition of the HS fractions were established (Fig. 1). It is shown that the HA fraction is characterized by the highest content of carbon of aromatic fragments ( $C_{ar}$  and  $C_{ar-O}$ ), with the lowest content of carbon of aliphatic ( $C_{O-Alk-O}$ ,  $C_{Alk-O}$  and  $C_{Alk}$ ), carboxyl and carbonyl groups ( $C=O$  and  $COOH(R)$ ) in the studied series of HS. In turn, in the FA fraction, the carbon of aliphatic ( $C_{O-Alk-O}$ ,  $C_{Alk-O}$  and  $C_{Alk}$ ), carboxyl and carbonyl groups ( $C=O$  and  $COOH(R)$ ) dominates. The content of aromatic carbon ( $C_{ar}$  and  $C_{ar-O}$ ) is the lowest. The carbon content of the HmA and HuA fractions is characterized by intermediate values between HA and FA (Fig. 1).

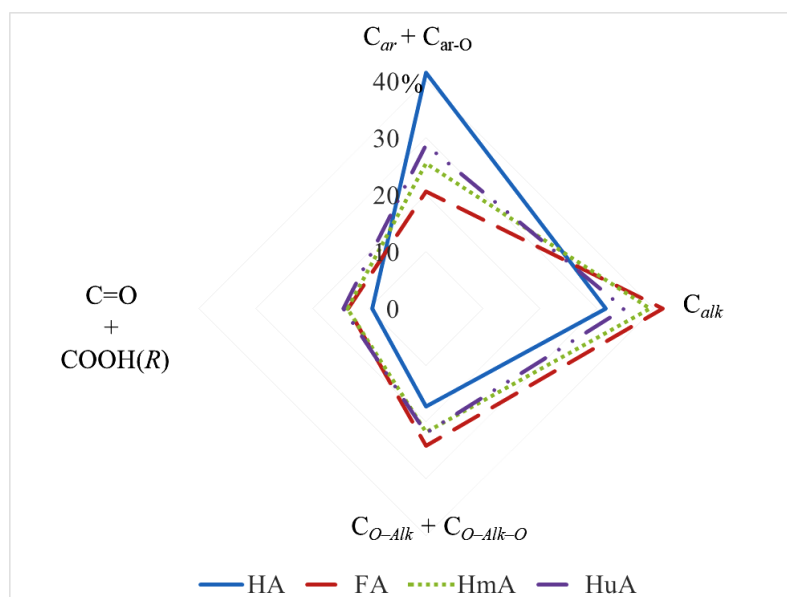


Figure 1. Carbon distribution in HA, FA, HmA and HuA samples from brown coals according to <sup>13</sup>C NMR spectroscopy data.

This work was carried out within the framework of a state contract of the FRC CCC SB RAS (project no. 124041100050-4) using the equipment of the Center for Collective Use of the FRC CCC SB RAS.

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## **2. Humic systems as markers of the climate, soils and aquatic ecosystems and their application to minimize anthropogenic impact**

## Changes in rhizosphere dissolved organic matter under influence of pharmaceutical contaminants

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Keywords: soil, root, rhizosphere, dissolved organic matter (DOM), pharmaceuticals and personal care products (PPCPs), mass-spectrometry

By interacting with the soil-microorganisms-plant system, the PPCPs presumably influences the biochemical processes occurring in soils and changes the characteristics of the labile pool of organic matter. To test the working hypothesis, changes in soil organic matter (SOM) at different concentrations of pollutant contamination were investigated.

The studies were conducted on samples of the humus horizon of loamy-micellar chernozem on loess-like carbonate loam. Lettuce (*Lactuca sativa*) served as the model plant. Drugs from different therapeutic groups with different physicochemical properties were selected as pollutants: ketoprofen (analgesic), ciprofloxacin (antibiotic), clotrimazole (antifungal) and atenolol ( $\beta$ 1-adrenoblocker). The samples were small containers of soil contaminated with drugs at different concentrations (1, 10, 100 and 1000 multiples of the average contamination rates found in soils, table 1).

Table 1. PPCP concentration (mg/kg of soil)

Drug	X1	X10	X100	X1000
Ketoprofen	0.005	0.05	0.5	5
Ciprofloxacin	0.01	0.1	1	10
Clotrimazole	0.001	0.01	0.1	1
Atenolol	0.01	0.1	1	10

After the lettuce had reached maturity, plants were removed from the container, and then soil was carefully collected from the roots for DOM analysis. DOM characteristics were analyzed by ESI- FT-ICR mass spectrometry. Changes in relative content of different classes of DOM compounds were accounted: Lipid, N-saturated, Aliphatic, Unsaturated with low O/C (U-LOC) and high O/C (U-HOC), Aromatic with low O/C (A-LOC) and high O/C (A-HOC), Condensed with low O/C (C-LOC) and high O/C (C-HOC).

In all samples most prominent changes were observed in relative content of Lipid, N-saturated, aliphatic and unsaturated compounds. With addition of ketoprofen growth of N-saturated and decrease of aliphatic compounds correlated with higher concentration of the drug. With addition of lower dose (0.01 mg/kg of soil) of ciprofloxacin relative content of lipids grows notably (+30%), but with higher doses of the drug it drops to the same level as in control sample. All other fractions relative content is decreasing with low dosage and grows with higher dosage of the drug. With addition of atenolol lipid fraction relative content grows, especially in samples with higher concentrations (1 and 10 mg/kg of soil) of the drug.

Most notable, in variants with the addition of clotrimazole with increasing concentration (0.1 and 1 mg/kg of soil) of the drug, a decrease in the content of aliphatic and N-saturated compounds in soil DOM was observed. This is possibly the result of its antifungal action, since fungal microbiota plays an important role in the decomposition of nitrogen-rich plant residues and their conversion into soluble forms.

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## Characterization of humic substances isolated from Cryosols of Schirmacher oasis and Bunger Hills, East Antarctica

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Keywords: humic acids, soil organic matter, Cryosols, Antarctica

Despite of harsh environmental conditions, ice-free areas of East Antarctica provide various soil forming conditions as well as considerable diversity of soil types. Our study is aimed at the detailed investigation of molecular composition of humic substances isolated from remote areas of East Antarctica - Schirmacher oasis and Bunger Hills.

Soils investigated were predominantly with coarse structure and low organic carbon content (from 0.52% to 6.40%), which is connected with harsh climatic conditions and absence of vascular plants. Soil pH in studied soils varied from slightly acidic and acidic in topsoils horizons with Histic features and from almost neutral to alkaline in places of active salt accumulation (in both oases).

<sup>13</sup>C-NMR spectra of humic acids (HA) isolated from soils investigated in East Antarctica varied significantly from those from Maritime Antarctica (King George Island). We have observed differences in elemental composition and atomic ratios of O/C, H/C, and C/N as well as the dominance of the peripheral part over aromatic fragments. The C/N ratio in humic acids from Bunger Hills was quite low, which is explained by low carbon content in molecules of peripheral compounds with a significant proportion of nitrogen. Very weak aromatic part in HA in studied Antarctic soils was also observed, which was caused by extremely low content of phenylpropane structural fragments.

All studied soils in Schirmacher oasis and Bunger Hills are characterized by predominance of aliphatic structures. In addition, HAs contains significant amounts of carbohydrates, polysaccharides, esters and amino acids as well as predominance hydrophilic fragments (Fig. 1).

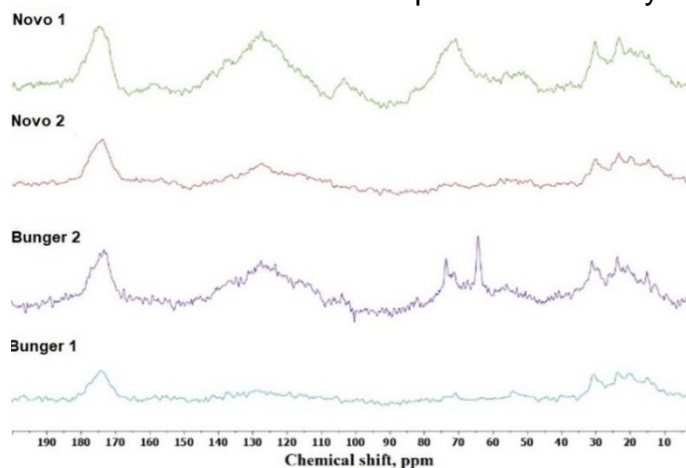


Figure 1. <sup>13</sup>C-NMR spectra of humic acids isolated from studied soils in Bunger Hills (Bunger) and Schirmacher oasis (Novo).

In principle, our work shows that humification process occurs in soils and soil-like bodies of East Antarctica even in conditions of lack of aromatic phenylpropane precursors. It was also shown that in harsh climatic conditions of Antarctica the formation of humic acids with a pronounced aromatic and peripheral part is possible.

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## Study of optical and hydrochemistry properties of water bodies on Kunashir Island

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Keywords: dissolved organic matter, total carbon content, fluorescence spectroscopy, Kunashir Island

The study of Kunashir Island is of significant importance due to its unique ecological and geological characteristics, particularly its proximity to active volcanoes and diverse water bodies. By examining the hydrochemistry parameters and optical properties of dissolved organic matter (DOM) in these reservoirs using UV-vis analysis, fluorescence spectroscopy, and organic carbon measurements, this research seeks to uncover volcanic influences on DOM composition of water samples obtained in the Kunashir Island. The primary aim is to compare the optical and hydrochemistry characteristics of DOM from volcanic sources with those of other water bodies on Kunashir Island.

The objective of this study was comparison of water properties of rivers and lakes of Kunashir Island and volcanic influence on them. Samples were collected in the summer of 2024 from Rubezhny Creek (N 44.32138°, E 146.28416°), Goryachee and Kipyashchee Lakes (N 43.86349°, E 145.50617° and N 43.86349°, E 145.49891°, respectively), and from the Lesnaya (N 44.00112°, E 145.70699°) and Filatovka (N 44.19108°, E 146.01891°) Rivers. The water reservoirs are situated in proximity to the Golovnin, Mendeleev, and Tyatya volcanoes. Specifically, Kipyashchee and Goryachee lakes are located near the Golovnin volcano, while the Lesnaya and Filatovka rivers and the Rubezhny stream is less influenced by volcano activity. Thus, the study encompasses reservoirs located near the active volcanoes of the Greater Kuril Ridge.

The optical properties of the natural water samples were investigated after filtration through a GFF filter with a pore size of 0.7 µm. Fluorescence spectroscopy and UV-Vis spectrometry were utilized to analyze the samples providing insights into the optical characteristics of DOM present in various water sources. Additionally, the total organic carbon (TOC) content of the samples was measured using a TOC-L analyzer. The analysis revealed a broad range of TOC concentrations:  $4.99 \pm 0.01$  mg/L in the Lesnaya River,  $1.95 \pm 0.33$  mg/L in Rubezhny Creek,  $0.95 \pm 0.025$  mg/L in Lake Goryachee,  $3.26 \pm 0.03$  mg/L in Lake Kipyashchee, and  $1.02 \pm 0.99$  mg/L in the Filatovka River. Furthermore, key hydrochemistry parameters including pH and oxidation-reduction potential (Eh) values were measured to assess the geochemical conditions of these water bodies. The pH values exhibited notable variation across the different sites ranging from neutral to slightly alkaline in the Lesnaya (8.15) and Filatovka (7.03) rivers, mildly acidic in Rubezhny Creek (6.03), to highly acidic conditions in Lake Goryachee (2.79) and Lake Kipyashchee (2.29), likely as a result of volcanic activity in the region.

Since the water bodies of Kipyachiye and Goryachee lakes are stagnant in volcanos mouths, the large amount of sulphur, in form of sulphates, bisulphates, thiosulphates, polythionates and sulphuric acid can be released into the water and further influence the optical and hydrochemistry parameter, which leads to decrease of the pH values.

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## Humic substances interfere with the determination of ciprofloxacin in soil

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Keywords: soil extracts, antibiotic, ecotoxicity, fluorescence

Ciprofloxacin has been designated by the World Health Organization as a critically important antibiotic in fresh surface water, groundwater, saltwater, treated municipal wastewater, untreated municipal wastewater, treated hospital wastewater, and untreated hospital wastewater worldwide. Rapid urbanization leads to the fact that not only the wastewater treatment from drugs is not being resolved promptly, but also soils become polluted as a result. In addition, the spread of antibiotics used in animal husbandry and crop production is a real ecological disaster for soils. The danger of this phenomenon lies not only in the increase in antibiotic resistance of pathogenic bacteria, but also in the disruption of the functioning of all links of the trophic chain in natural ecosystems [1]. The relevance of the studying the ecotoxicological characteristics of soils exposed to pharmaceuticals is beyond doubt.

In this work, we found different degrees of impact of the same doses of ciprofloxacin on living organisms when added to soil samples with different humic status. To explain the obtained data on the effect of aqueous extracts of soils on the survival of aquatic organisms, we need to measure the actual concentrations of the antibiotic in the samples of aqueous extracts of soils studied in biotests. However, the qualitative measurements of low doses of ciprofloxacin in presence of high concentrations of soil humic substances is very sophisticated task. The resolution of high-performance liquid chromatography is not always adequate. Spectrophotometric measurement of ciprofloxacin in soil extracts is complicated by the presence of humic substances in concentrations several orders of magnitude higher than the concentration of the antibiotic.

To determine ciprofloxacin in aqueous soil extracts in small quantities, a new approach was developed using synchronous fluorescence spectra with a difference in excitation and recording wavelengths of 160 nm. This corresponds to the shift in the maximum of the ciprofloxacin emission spectrum (435 nm) relative to the maximum in the fluorescence excitation spectrum (275 nm). To determine the concentration of the antibiotic, synchronous fluorescence spectra were measured in a sample without the antibiotic and with an antibiotic of unknown concentration, the difference spectrum was calculated, and the antibiotic content in the sample was determined from its integral intensity using a calibration dependence. Despite the fact that the fluorescence spectra of humic substances and ciprofloxacin in water are close in the position of the maximum and bandwidth, the measurement of synchronous fluorescence spectra made it possible to identify the presence of the antibiotic in fairly low concentrations, about 5 µg/l, by routine screening without preliminary sample preparation.

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## Effect of humic substances on synthetic polymers degradation

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Keywords: humic substances, plastics, microorganisms, biodegradation

With rapidly increased production of synthetic polymers (SPs), plastic wastes appeared in the environment. Decomposition of plastics under environmental conditions is low and leads to accumulation of hazardous microplastics (MPs). MPs can disturb the cell membrane structure, damaging the intracellular molecules and generating oxidative stress. It was shown that MPs can change the biophysical properties and the bulk density of soil resulting in enhanced water evaporation and soil drying [1]. Today for deep degradation of plastic wastes used various biocatalytic systems, including consortia of microorganisms and their enzymes [2]. Biodegradation of various SPs has been shown with varying efficiency under the influence of bacteria, fungi, yeast, phototrophic MOs. At the same time, under natural conditions, the process of biodegradation of SPs is strongly influenced by abiotic factors, including the presence of humic substances (HSs). HSs can have both a positive and inhibitory effect on MOs, which ultimately can affect the biodegradation of SPs in in vitro and in situ experiments. For example, some bacteria can use HSs as the main carbon source, and could be involved in extracellular electron transfer [3]. On the other hand, suppression of the metabolic activity of fungi and yeasts in the presence of HSs has been demonstrated [4].

The positive effect of HSs on biodegradation was shown in aqueous environments. HSs bind to MPs particles due to the formation of multiple hydrogen bonds and hydrophobic interactions, thus promoting their sedimentation on the bottom and stimulation of the metabolic activity of MOs. The rate of biodegradation of polyethylene in the waters of the lake containing HSs was 22 times higher than in clean lake waters [5]. In soil a stimulating effect of HSs (50–250 mg/L.) on the growth of bacterial biofilms on the surface of polyethylene was achieved within 14 days with HS concentrations in the range of established (increasing roughness of the polymer surface in 2.0–3.5 - times) [6]. The positive effect of HSs was associated with increased bacterial adhesion to the polymer surface and with the induction of the synthesis of bacterial enzymes.

HSs also can sorption on the SPs surface and change their properties which contribute to an increase in the bioavailability of SPs for cells and promote the photooxidative degradation [7]. In general, positive effect of HSs on biodegradation on SPs was observed but it should be noted that there is still very little data.

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## Effect of water-soluble organic matter on phenanthrene desorption from Tidalic Fluvisols

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Keywords: PAHs, coastal areas, leaching, pollution, organic matter, Fluvisols

Phenanthrene is one of the most common polycyclic aromatic hydrocarbon that poses a significant threat as an environmental pollutant. Its accumulation in the components of aquatic landscapes affects the growth and development of living organisms, as well as their biodiversity in general. The most significant parameter contributing to the stability of the aquatic ecosystem is the ability of the soil to deposit the environment, sorbing and retaining chemical pollutants, causing their interaction between the different components of the landscape. The presence of water-soluble organic matter in soil contributes to increased lability of lipophilic compounds, such as phenanthrene. In this regard, the goal of this work was to ensure the desorption of phenanthrene by any water-soluble organic substance in Tidalic Fluvisols. The object of this study was Tidalic Fluvisol, located on the southern coast of the Taganrog Bay far from man-made sources. Soil properties: organic matter – 2.1%, clay visibility – 46.3%, silt – 27.5%, pH – 7.8. To conduct the desorption experiment, a fraction of water-soluble organic matter was preliminarily isolated from the soil solution by shaking 20 g of soil in 100 ml of deionized water for 24 hours. At the first stage of the experiment, the soil was saturated with pollutant. For this purpose, a working solution with a phenanthrene concentration of 3 mg/ml was prepared. The mass ratio of liquid and solid phases was 1:40. Soil weighing 0.25 g was placed in 50 ml falcons of the solution. Later, a solution of phenanthrene in acetonitrile was added to the soil samples to achieve concentrations of 0.1, 0.3, 0.6, 1.2, and 2.4 mg/ml or 0.6, 1.7, 3.4, 6.7, and 13.5 mM l<sup>-1</sup>. The total volume was adjusted to 10 ml and shaken for 24 hours, followed by centrifugation of the sample for 15 minutes. The supernatant was drained and the sediment was air dried. All procedures were carried out at a temperature of 295±1 K. Under the influence of air in a dry state, 10 ml of the isolated water-soluble organic substance was added to the soil samples and shaken for 24 hours. Centrifugation was carried out and the content of the pollutant in the sediment liquid was reduced. The coli content of phenanthrene was determined using high-performance liquid chromatography. As a result of the study, it was established that at a phenanthrene concentration in the initial solution of 0.6, 1.7, 3.4, 6.7, and 13.5 mM l<sup>-1</sup>, the equilibrium concentration of the pollutant was 0.2, 0.4, 1.2, 3.7, and 10.1 mM l<sup>-1</sup>, and the corporate one is 0.4, 1.3, 2.2, 3.1, and 3.4 mm kg<sup>-1</sup>, which is equivalent to 71.0%, 78.0%, 65.1%, 45.6%, and 25.2%, respectively. Under the influence of water-soluble soluble organic matter, the desorption of iron phenanthrene was 0.01, 0.02, 0.05, 0.08, and 0.12 mM l<sup>-1</sup>, which amounted to 2.1%, 2.0%, 2.4%, 2.7 and 3.6% of the amount of absorbed pollutant, respectively.

Thus, the degree of phenanthrene sorption from tidal fluvisols decreased significantly from 71.0% to 25.2% with an increase in the initial liquid of the pollutant in the solution from 0.6 mM l<sup>-1</sup> to 13.5 mM l<sup>-1</sup>, thereby leading to an increase in the desorption of the pollutant under the influence of water-soluble organic matter.

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## Fenton-like systems in combination with nature-like polymers as inactivators of organic dyes in aqueous media

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Keywords: fenton-like systems, inactivators of organic dyes, ferric (II) humate.

Various industries produce wastewater containing organic pollutants in dissolved, suspended and emulsified states [1]. Currently, a large number of physicochemical methods have been developed for the treatment of wastewater of this category. By using Fenton's reagent, as a strong oxidizing agent, it is possible to achieve almost complete mineralization of organic pollutants. One of the ways to increase the rate of degradation of organic compounds by Fenton's reagent is the use of complexes with organic ligands instead of soluble iron (II) salts. Humic acids can serve as such organic ligands.

The aim of the work was to evaluate the applicability of iron (II) humate for the degradation of organic dyes in the Fenton reaction.

All reagents used in the work were qualified not lower than b.w.a. Spectrophotometric measurements were carried out on spectrophotometer SF-2000 ("OKB Spektr", Russia). Mordant Blue 13 was used as a model dye. The working wavelength was determined experimentally ( $\lambda = 530$  nm). To study the degradation of Mordant Blue 13, 0.2 cm<sup>3</sup> 0.1 g/dm<sup>3</sup> of dye solution, 0.5 cm<sup>3</sup> 0.4 g/dm<sup>3</sup> of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution, 1.3 cm<sup>3</sup> of distilled water, and 10 mg of iron (II) humate were added to a glass cuvette (l = 10 mm).

Kinetic parameters and degree of degradation obtained during the decomposition of Mordant Blue 13 in the presence of heterogeneous iron (II) humate catalyst and homogeneous FeSO<sub>4</sub> catalyst were compared. To evaluate the maximum number of cycles of continuous operation of the iron (II) humate catalyst, a new portion of dye was introduced into the system every 15 min. Table 1 shows the results of the degree of degradation of Mordant Blue 13 in different systems.

Table 1 - Degree of degradation of Mordant Blue 13 in the Fenton system with homogeneous and heterogeneous catalysis

Catalyst	Q, %	Number of cycles
FeSO <sub>4</sub>	92±1	1
Iron (II) humate	84±1	1
Iron (II) humate	81±1	10

The degree of dye degradation is 8% higher in homogeneous catalysis (in the presence of FeSO<sub>4</sub>). The differences in the performance of the catalysts are due to different iron content in them. The content of iron (II) and (III) in iron (II) humate was determined by the method of wave dispersive X-ray fluorescence spectrometry. In 10 mg of catalyst, the amount of total iron was 7.2 µg. The amount of Fe<sup>2+</sup> ions in the homogeneously catalyzed system was 74 µg.

The Fenton-like system of iron (II)/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> humate allows to oxidize dyes with degradation degree higher than 80% in 10 minutes and is superior to analogues using Electro-Fenton, hydrogen peroxide and heterogeneous catalysts.

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## **Purification of water contaminated with copper and nickel ions by humate-saturated magnetic peat**

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Keywords: copper, nickel, sorption, magnetite, humic substances.

Heavy metals are very dangerous because they pollute the environment and, when they enter the human body, accumulate and affect the nervous and cardiovascular systems. The sources of such pollution are often metallurgical plants and engineering enterprises that dump waste into the nearest water bodies. Since the aquatic environment promotes active migration of ions, including heavy metals, an important solution is to prevent their further movement at this stage. The aim of the work was to obtain magnetic peat modified by humic acids of coal for water purification from Cu<sup>2+</sup> and Ni<sup>2+</sup> ions.

A series of experiments on the sorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> ions were conducted. It was found that when using a mixture of peat with highly aromatic humic substances (in particular, coal of the Sakhalinskiy humate brand) as a sorption center, the binding to Cu<sup>2+</sup> ions increase.

Two sorbents were obtained, one is magnetite particles immobilized on neutralized lowland peat, the second is the same product modified with a solution of coal humic substances. Both sorbents were characterized by XRD and SEM. In addition, a series of experiments on the purification of model solutions of copper and nickel of different concentrations was carried out. The sorption capacity of magnetite on lowland peat was

15 mg/g for copper and 12 mg/g for nickel. Modification with humic substances increased the sorption capacity from 15 mg/g to 30 mg/g when sorption of a solution containing Cu<sup>2+</sup> ions, and from 12 mg/g to 16 mg/g when sorption of a solution containing Ni<sup>2+</sup> ions.

Magnetite particles themselves, on the basis of which the sorbents were obtained, were synthesized according to the method given in [1]. The presence of the product is confirmed by the data of X-ray phase analysis, and the sorption experiments were controlled by the ICP-AES method.

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## Efficiency of using potassium humates in the remediation of oil-contaminated soils

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Keywords: humic acid, potassium humate, petroleum product

As a result of oil displacement in the soil under the influence of the chromatographic effect, fractional separation of oil occurs. In the upper humus layer, sorption of high-molecular oil components takes place, including many resinous-asphaltene substances and cyclic compounds.

Humic acids and humates are the chemical foundation of soil humus, which serves as the concentrate. Humus is also essential for the activity and stability of most soil biochemical processes [1].

Table 1. The amount of petroleum products in the soil (basic humate) depending on the number of days at different concentrations.

Model name	Mass fraction of petroleum products in soil sample, mg / kg, 5 days	Mass fraction of petroleum products in soil sample, mg / kg, 30 days	Mass fraction of petroleum products in soil sample, mg / kg, 60 days	Mass fraction of petroleum products in soil sample, mg / kg, 90 days	Content of petroleum products , %	Cleaning degree,%
Initial sample	72.000	72.000	72.000	72.000	100	0
1% Basic potassium Humate	76.200	52.700	34.600	2.000	2.62	97.38
10% basic potassium Humate	65.800	48.200	21.600	2.600	3.96	96.04
30% basic potassium Humate	73.000	45.400	32.800	3.800	5.21	94.79
50% basic potassium Humate	69.200	47.600	28.400	2.800	4.05	95.95

In the experiment, vertical concentrations of potassium humate at 1%, 10%, 30%, and 50% were used. As a result, we observed that the samples treated with 1% and 10% vertical potassium humate achieved better cleaning results than the other samples.

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## Optical properties of waste water at the Baikalsk pulp and paper mill lignin dumpsite as compared to solutions of natural humic substances

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**Keywords:** sludge lignin, Baikalsk pulp and paper mill, fluorescence, UV-absorbance, humic substances

Pulp and paper mills (PPMs) contribute significantly to pollution of the adjacent ecosystems. This results from accumulation of sludge lignin in the dump sites. At the Baikalsk Pulp and Paper Mill (BPPM), the sludge lignin is stored in ten concrete cells yielding a total area of 105 hectares and a volume of 4 million m<sup>3</sup> [1]. Flooding risks threaten the integrity of the dams, potentially leading to the discharge of pollutants into the Lake Baikal. Monitoring the composition of above-sludge water is crucial for identifying the potential contamination of the Baikal Lake. Absorption and fluorescence characteristics of dissolved organic matter (DOM) suit very well for the purpose of rapid environmental monitoring and water quality assessment. However, identification of sludge lignin optical footprint could be complicated by the overlap with the fluorescence and absorbance of natural DOM and humic substances (HS). The aim of this study was to determine optical characteristics of water contacting with the sludge lignin deposits at the Solzan landfill of the Baikalsk Pulp and Paper Mill (BPPM) and to compare it with optical properties of the solutions of natural humic substances (HS).

To reach this goal, the extensive sample set of humic materials was assembled of seventy samples of humic acids and fulvic acids from peat, soil, and coal, the samples of humic-like materials of lignohumates as well as lignosulphonates were also included. All samples were dissolved at the concentration of 10 mg/L at pH 6,8 in 0,028 M phosphate buffer. Along with natural HS, a set of 80 samples of the sludge lignin water was collected during the 2024 summer expedition to the Solzan landfill. The water samples were filtered through a GFF filter (0.7 μm). Optical properties were analyzed using fluorescence spectroscopy and UV-Vis spectrometry. Absorption and excitation-emission matrix (EEM) spectra were used to calculate optical descriptors. Fluorescence emission band asymmetry was calculated as a ratio of integrated intensities at 350 nm excitation in the blue (420-460 nm) and red (550-600 nm) spectral regions.

Fluorescence EEM spectra revealed characteristic fluorescence maxima typical of humic substances, with excitation peaks ranging from 250 to 280 nm and emission maxima between 340 and 470 nm. UV-Vis spectra, normalized to DOM concentration (mg/L), demonstrated typical DOM absorbance profiles. The fluorescence spectra of waste water and humic substances were characterized by key parameters such as maximum intensity wavelengths, spectral asymmetry, and SUVA<sub>254</sub>. The highest asymmetry coefficient values were observed in samples from sludge cells 6 and 7 (4.85 and 4.87 respectively), suggesting a significant contribution of protein-like fluorescence. In contrast, the lowest asymmetry coefficient was found in accumulation cell 3 (4.45), where waterlogging processes dominate. The SUVA<sub>254</sub> value reflecting the ratio of absorption at 254 nm to organic carbon content was the lowest for cells 5, 6, and 7 (1.1-1.6 L/mg·m<sup>-1</sup>), indicating a lower content of aromatic structures compared to cells 2, 3, and 4 (2.0-3.0 L/mg·m<sup>-1</sup>).

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## Fluorescence-based insights into dissolved organic matter dynamics in Siberian shelf seas

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Key words: dissolved organic matter, excitation-emission matrices, parallel factor analysis, humic-like fluorescence, protein-like fluorescence,

The Arctic Shelf receives substantial inputs of dissolved organic matter (DOM) from major Siberian rivers, including the Ob, Lena, and Indigirka, influenced by permafrost thaw. These inputs have the potential to significantly alter the optical properties of DOM in coastal waters. This study aimed to identify key optical trends in DOM characteristics across three Siberian river-to-ocean systems: the Ob River–Kara Sea, Lena River–Laptev Sea, and Indigirka River–East Siberian Sea. UV-VIS spectrometry and fluorescence spectroscopy were employed to analyze 264 marine water samples collected during an expedition aboard the vessel Ac. Mstislav Keldysh in October 2020. Fluorescence excitation-emission matrices (EEM) and UV-visible absorption spectra were analyzed using Parallel Factor Analysis (PARAFAC), a method widely employed for decomposing multilinear data arrays to identify independent fluorescent components.

The selection of the optimal model, comprising 5 components, was determined through split-half analysis and validated by Tucker's congruence coefficient (TCC), set at 95%. This model demonstrated the highest stability and capacity to describe the fluorescence signatures of CDOM in arctic marine waters. All fluorescent components showed single emission maxima with one or more excitation peaks. The obtained DOM fluorescence components in the shelf seas were compared to the OpenFluor spectral database and revealed high similarity to those previously identified by PARAFAC in the region. The identified components can be classified into terrigenous-origin components with humic-like fluorescence (C1, C3, and C4), marine organic matter characterized by humic-like fluorescence (C2), and a bio-labile component exhibiting protein-like fluorescence (C5). The humic-like component (C1) was the dominant fluorescent component of DOM in all marine water samples, regardless of the region or sampling depth. Its presence was significantly higher in the Kara Sea (63.4%,  $n = 27$ ) compared to the Laptev Sea (59.0%,  $n = 162$ ) and the East Siberian Sea (54.2%,  $n = 75$ ) ( $P < 0.05$ ). The marine organic matter component (C2) was significantly lower in the Kara Sea (23.1%) ( $P < 0.05$ ) compared to the eastern Arctic seas, namely the Laptev and East Siberian Seas, where it accounted for 24.9%. The relative contribution of the protein-like component (C5) was significantly higher in the East Siberian Sea, at 8.5%, decreasing in the Laptev Sea (4.7%) and reaching its lowest value in the Kara Sea (1.7%).

The distribution of fluorescent components along the salinity gradient (16.8–34.8 psu) was calculated for the Kara, Laptev, and East Siberian Seas. For the Ob–Kara and Lena–Laptev systems, the correlation coefficient between component C1 and salinity was 0.91 and 0.85, with similar intercept values (1.45 and 1.20), indicating river runoff as the source. In contrast, the Indigirka–East Siberian system had a lower correlation (0.74) due to reduced freshwater inflow and a narrower salinity gradient (22–30 psu). Component C1 also correlated strongly with the optical absorption parameter obtained at wavelength of 254 nm ( $a_{254}$ ) ( $R^2 = 0.75$ ,  $n = 264$ ), which is linked to the contribution of terrigenous organic matter. This suggests less vascular plant input and more intense microbial degradation in the Indigirka basin compared to the Ob and Lena rivers.

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## Investigation of palladium sorption by humic substances in the context of application for selective extraction of PGM from sulfuric and hydrochloric acid solutions

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Keywords: Palladium, Humic substances, Platinum, Copper, Nickel, Sorption, Extraction

This paper presents the results of a study of the sorption of palladium by humic substances from sulfuric and hydrochloric acid solutions. Palladium is a platinum group metal (MPG), the most valuable metal used as catalysts in the chemical industry, in medicine and is an indicator of the country's wealth. Russia is home to one of the largest palladium producers in the world. [1-3] In connection with the above, studies aimed at assessing the sorption capacity of humic substances with PGM in hydrochloric and sulfuric acid solutions in the presence of metals - chalk and nickel are relevant.

It has been established that Pd is sorbed by humic substances (HC) in sulfuric acid solutions and is described by the Langmuir model, which indicates that the sorption centers are equivalent to each other and equal in energy. The maximum sorption capacity of GW to Pd is  $5.5 \pm 0.4$  mg/g  $R^2=0.999$ . It was found that the degree of palladium extraction is practically not affected by the presence of iron in molar excess: 40, 400 and 1000. It was found that the degree of palladium extraction is practically not affected by the presence of copper, nickel and iron in 40-fold excess, including the presence of platinum in an equivalent amount. It has been established that Pd, Cu, Ni, Fe and micro quantities of Pt pass into the sediment of HC, while the mass fraction of metals (counting only metals) in the sediment is 44% Fe, 22% Cu, 16% Ni, 15% Pd and 1% Pt; and the molar fraction of metals (counting only metals): 51.3% Fe, 21.9% Cu, 17.3% Ni, 9.1% Pd and 0.4% Pt

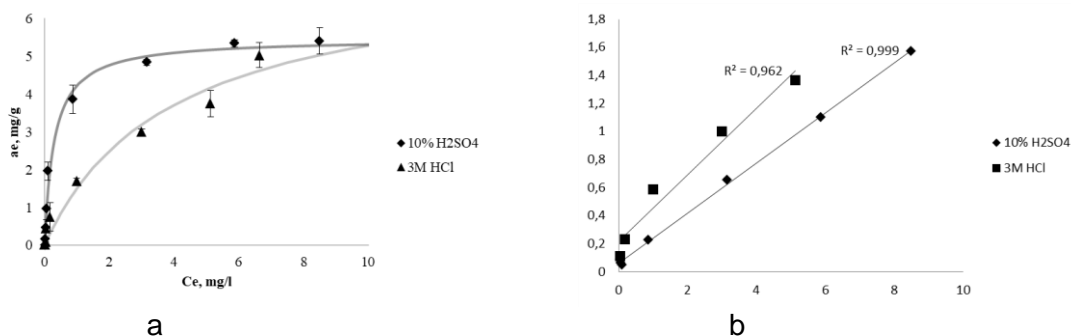


Figure 1 – Graphical dependencies based on the results of the study: a – The isotherm of the sorption of Pd 0.5g/l with humic substances, liquid volume 10 ml, T = 3980C; b – Langmuir's model.

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## Sorption of $\text{Cu}^{2+}$ and $\text{Pb}^{2+}$ on vermiculite of different densities

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Keywords: Vermiculite, sorption, heavy metals

The problem of pollution by heavy metal ions is widely presented on the Solzan waste deposits, due to accumulation of ash and slag from power stations. Nowadays many methods of wastewater treatment from heavy metal ions have been developed, but the most widespread and economically effective are sorption approaches. In recent years, interest in the use of natural sorbents for the removal of heavy metals from wastewater has increased. The group of aluminosilicates is an example of materials that are readily available in nature, inexpensive and environmentally friendly. The best known materials from this group are montmorillonite and bentonite. Vermiculite is also an aluminosilicate with the general formula  $(\text{Mg}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+})_3 [(\text{Al}, \text{Si})_4 \text{O}_{10}] \cdot (\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , but its sorption properties are not widely investigated. Therefore, the aim of this work is to compare the sorption properties of vermiculite with densities of  $167 \text{ kg/m}^3$  and  $107 \text{ kg/m}^3$ , towards  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  ions for their application on the Solzan waste deposits.

Before the sorption experiment, vermiculite was immersed in distilled water to fill the interlayer space and reach equilibrium pH for 10 hours. The pH was not further adjusted during the experiment because vermiculite has a high buffering capacity. The time to reach sorption equilibrium was 12 hours.

As a result, sorption isotherms for vermiculite with different densities were obtained. It was found that the obtained data are best described by the Langmuir model. The parameters of the Langmuir equation for  $\text{Cu}^{2+}$  sorption are  $q_m = 4.2 \pm 0.1 \text{ mg/g}$ ,  $KL = 0.14 \pm 0.2$  for vermiculite with bulk density  $167 \text{ kg/m}^3$ , and  $q_m = 2.8 \pm 0.6 \text{ mg/g}$ ,  $KL = 2.4 \pm 0.8$  for vermiculite with bulk density  $107 \text{ kg/m}^3$ . For  $\text{Pb}^{2+}$  sorption,  $q_m = 131 \pm 2 \text{ mg/g}$ ,  $KL = 0.019 \pm 0.002$  for vermiculite with bulk density of  $167 \text{ kg/m}^3$ , and  $q_m = 66 \pm 14 \text{ mg/g}$ ,  $KL = 0.07 \pm 0.01$  for vermiculite with bulk density of  $107 \text{ kg/m}^3$ . Comparing the obtained Langmuir constants we can talk about higher adsorbate-adsorbent affinity for vermiculite with density of  $107 \text{ kg/m}^3$ . But vermiculite with density of  $167 \text{ kg/m}^3$  is more promising as a sorbent for application on the Solzan waste deposits, as it has a higher sorption capacity with respect to the metals under study.

Acknowledgements. State budgetary contract Development of nature-like technology solutions aimed at enhanced humification and placement of a water-permeable sorbing cover on the Solzan waste deposits contributing to cleaning, intensification of overgrowth of vegetation on the cover surface.

## **Humics-aminosiloxane polyelectrolyte complexes for immobilization of technogenic hematite in contaminated soils**

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Keywords: soil contamination, interpolyelectrolyte complexes, humic substances, aminoorganosiloxanes, hematite

In the context of hydrometallurgy, the oxidative processing of non-ferrous metal ores results in the formation of a red by-product, predominantly composed of hematite, a natural red pigment and a ferric oxide. In contrast to the natural mineral, the red tailings contain hematite in a microdispersed state, which makes it mobile upon release into the environment. The same colour and contamination type is observed in acid mine drainage. In order to prevent the spread of pollution and neutralise its reddish colour, we proposed the use of natural black pigment, humic substances (HS), which mask the colour of natural hematite in soils, as mineral-adhesive compositions with aminoorganosiloxanes (AOS).

The objective of this research was to develop humics-based compositions that would reduce the migration of hematite in the environment and neutralise its red colour. For this purpose we used interpolyelectrolyte complexes (IPEC) based on coal humate and four different AOS. As previously demonstrated [1], the IPEC of HS and 3-aminopropylethoxysilane (APTES) has the capacity to restore soil structure by facilitating the formation of water-resistant soil aggregates. AOS-HS complexes of varying stoichiometry were prepared by the addition of AOS to a concentrated potassium humate solution (20% mass). The AOS-HS compositions were then applied to the surface of the tailings and thoroughly mixed. The red tailings, which were contaminated with hematite, were found to contain 36% Fe and a moisture content of about 29%. The efficiency of the aforementioned complexes was evaluated through an express test on the water stability of the produced aggregate.

The results demonstrated that APTES was the most effective AOS. Furthermore, the technique of wet sieving was employed for testing purposes. The application of IPECs to the red tailings resulted in an increase in water-resistant aggregates with a diameter greater than 0.2 mm. The observed increase in the average size of tailing aggregates indicated that IPECs had a binding effect on hematite and clay particles, thereby reducing their mobility and preventing the spread of pollution. Furthermore, the treated tailings acquired a dark brown hue.

During the course of the work, the stability of the IPECs in solution and their size were studied at different APTES:HS ratios using the dynamic light scattering technique.

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## **Synthesis and applications of composites based on carbon materials and natural polymers**

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Keywords: humic composites, carbon nanomaterials

Pollution of water and soil with pollutants of various chemical nature predetermines the search for environmentally friendly sorbents and technologies of their inactivation, where the priority is the use of natural raw materials. For these purposes natural polymers - humic acids (HA), isolated from different caustobiotites and capable of binding inorganic and organic ecotoxicants into non-toxic complexes, are increasingly used.

To improve the sorption characteristics of HAs, additional functional groups are introduced into their structure and composites based on them are synthesised. Graphene oxide (GO) has recently been widely used due to its high electrochemical activity and sorption capacity. Structurally, OH and HA have a similar structure: central aromatic core and peripheral functional groups, so it is of interest to obtain supramolecular nanostructured composites based on them.

In this work humic acids were subjected to functionalisation by elemental sulphur thiolation, oxidative thiolation with sodium sulphide, and aminomethylation according to Mannich. Functionalisation was proved by vibrational and electronic spectroscopy and energy dispersive X-ray fluorescence analysis. Graphene oxide covalently modified with humic acids was obtained by electrochemical graphite exfoliation method in one stage, the obtained composite was characterised by IR, XR and UV spectroscopy, spectrofluorimetry and cyclic voltammetry. The reducing capacity and limiting sorption towards heavy metal ions were determined for all samples.

It was shown that thiolation and oxidative thiolation of humic acids leads to an increase in their sulphur content by 15-20%. Sorption capacity of thiolated HAs towards zinc ions is 3-5 times and 2-3 times higher than that of the original HAs towards lead ions. Aminomethylation of HA with iminodiacetic acid leads to a 2-fold increase in sorption capacity towards manganese ions. It is shown that graphene oxide modified by humic acids is able to transfer electrons more efficiently in the standard ferrocene/ferrocenium cation system. Thus, the application of composites based on humic acids and carbon nanomaterials in the creation of sorbents and electrochemical systems is promising.

## **The effect of magnesium and calcium cations on the aggregative stability of colloidal bentonite in the presence of humic acid**

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Keywords: colloidal bentonite, humic acid, magnesium ion, calcium ion, aggregative stability

Dissolved organic matter of natural waters, as well as ions present in water, is crucial in the processes of interaction of clay particles in their suspensions and colloidal solutions. The study of these processes is important for understanding soil formation, water treatment and assessment of the formation of suspended matter in the river-sea barrier zone [1]. Previously, we showed the stabilizing effect of humic acids on the stability of a colloidal solution of bentonite clay in the presence of sodium chloride [2].

The aim of this work was to study the effect of divalent magnesium and calcium cations on the aggregative stability of a colloidal solution of bentonite clay in the presence of humic substances.

This work was carried out on a model system in which a solution of magnesium or calcium chlorides was added to colloidal bentonite (pure or modified with humic acid). The turbidity of the samples, as a measure of the stability of colloidal system, was studied on a HI 98713-02 turbidimeter (Hanna, Romania). The kinetics of the process was studied in a wide range of salt concentrations. The bentonite clay sample (Jembel deposit) is more than 50% represented by a fraction of less than 1 microns. Colloidal bentonite (0.3 g/l) was prepared by decanting the filler liquid of bentonite suspension (2 g/l) after settling for 10 days at room temperature. Clay modification with humic acid, separated from coal (leonardite) (Humintech, Germany), was carried out by its solution, so that the final concentration was 10 mg/l. MgCl<sub>2</sub> and CaCl<sub>2</sub> salts AR reagent grade was used without purification.

The presence of humic acid has been shown to stabilize the colloidal solution of bentonite clay in the presence of added salts, which is manifested in the absence of coagulation under conditions when the untreated suspension coagulates. It was shown that, contrary to the Hofmeister series, the coagulating ability of magnesium ions in relation to a colloidal solution of bentonite clay was higher than for calcium ions. Thus, it has been shown that at some concentrations of calcium salt, coagulation is not observed, whereas even at lower concentrations of magnesium salt, coagulation occurs. An explanation of this «non-standard» behaviour of salts in the process of colloidal bentonite coagulation is proposed. Further study of the co-action of cations of seawater is of interest for the assessment of mass transfer by river suspension into the marine environment.

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## Linking Optical Properties and Molecular Size of Dissolved Organic Matter in Arctic Shelf

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Keywords: dissolved organic matter, fluorescence, high-performance liquid chromatography, Arctic seas

More than half of the global organic matter reserves are stored in the permafrost sediments of the Arctic region. As permafrost thaws, dissolved organic matter (DOM) is released and transported into Arctic seas via the Great Siberian Rivers, altering the molecular composition and optical properties of DOM. The molecular size distribution of DOM is a critical trait linked to its susceptibility to degradation. DOM absorption and fluorescence characteristics are known to correlate with bulk chemical properties, such as average molecular size, lignin content, and molecular composition. Despite significant research on DOM dynamics in aquatic environments, the connection between its optical properties and molecular size—an important factor influencing DOM degradation—remains insufficiently understood. This study aims to characterize the composition and optical properties of DOM in three Arctic seas and to examine the size-dependent optical properties of DOM extracts in shelf waters.

DOM extracts (10 in total) were isolated using solid-phase extraction (SPE) technique from marine water of the Arctic seas. The water samples were collected during the 82nd expedition of the R/V Akademik Mstislav Keldysh in 2020 from three shelf areas: the Kara Sea, Laptev Sea, and East Siberian Sea. The isolation of the samples was occurred on the lab onshore. The optical properties of these samples were analyzed using fluorescence spectroscopy and UV-vis spectrometry. Additionally, high-performance liquid chromatography (HPLC) with sequential UV and fluorescence detectors was employed to investigate DOM composition based on apparent molecular weight ( $M_w$ ) through rapid analysis techniques.

For DOM extracts,  $SUVA_{254}$  values ranged from 1.89 to 2.45 L/(mg·m<sup>-1</sup>) in the Kara Sea, 2.01 to 2.52 L/(mg·m<sup>-1</sup>) in the Laptev Sea, and 2.05 to 2.46 L/(mg·m<sup>-1</sup>) in the East Siberian Sea. Band asymmetry parameter ( $ASM_{350}$ ) values were 4.40 to 4.76 in the Kara Sea, 4.43 to 4.60 in the Laptev Sea, and 4.48 to 4.70 in the East Siberian Sea. The  $E_2/E_3$  ratios ranged from 6.02 to 6.61 in the Kara Sea, 6.58 to 6.76 in the Laptev Sea, and 7.58 to 7.82 in the East Siberian Sea. Molecular weight distribution curves for DOM extracts were also obtained, with  $M_w$  values of 1403 to 1450 Da in the Kara Sea, 1340 to 1368 Da in the Laptev Sea, and 1300 to 1307 Da in the East Siberian Sea.

Absorbance at the wavelength of 254 nm ( $R^2 = 0.72$ ) and the  $E_2/E_3$  ratio ( $R^2 = 0.71$ ) demonstrated strong inverse correlations with the molecular weight of the DOM samples. The results indicate that DOM samples from the East Siberian Sea, characterized by higher  $E_2/E_3$  ratios, exhibit lower molecular weights and a more aliphatic, less transformed nature compared to the more conjugated, higher molecular weight samples from the Kara Sea.

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## **In search of a footprint of sludge-lignin from the Baikalsk pulp and paper mill dumpsite with a use of optical descriptors**

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Keywords: lignin, Baikal Lake, fluorescence, modeling, clustering

The Baikal Natural Area, a UNESCO World Heritage Site, faces significant environmental problems as pollution from cities and industrial centers affects the lake ecosystem. The large volume (more than 1 million m<sup>3</sup>) of accumulated above-sludge water poses a threat of dam breakage in the region of Solzan dampsite. The development of integrated geo-ecological monitoring and predictive models is crucial for the preservation of Lake Baikal. Computational hydrodynamic models are needed to assess water pollution and accelerate research efforts. DOM absorption and fluorescence characteristics that correlate with molecular properties make fluorescence spectroscopy and UV-Vis spectrometry effective tools for rapid monitoring of environmental changes and water quality in Lake Baikal. The aim of the study is to develop clustering models for drainage water samples from lignin sludge storage ponds and background waters of Lake Baikal based on a set of optical data obtained from the sample set.

The dataset was derived from an extensive optical data set of over 80 drainage water samples from lignin sludge ponds and Lake Baikal background waters collected during an expedition in the summer of 2024. Samples were filtered through a GFF filter (pore size 0.7 μm) and their optical properties were analyzed using fluorescence spectroscopy and UV-Vis spectrometry. Absorption and excitation-emission matrix (EEM) spectra were obtained for further analysis. Total organic carbon (TOC) content was measured using a TOC-L analyzer, and key hydrochemistry parameters such as pH and redox potential (Eh) were recorded. The asymmetry of fluorescence emission bands, reflecting the contribution of protein fluorescence, was calculated as the ratio of integral intensities at 350 nm excitation in the blue (420-460 nm) and red (550-600 nm) spectral regions.

The EEMs and absorbance spectra were treated to calculate key parameters for clustering, including spectral band-shape asymmetry, blue-shift area, excitation wavelength values, E2/E3 and E4/E6 ratios (intensity ratios at 265 to 365 nm and 465 to 665 nm, respectively), specific ultraviolet absorbance (SUVA<sub>254</sub>), and the absorbance spectra slope ratio in the long-wavelength region (>500 nm) of the spectrum. Additionally, hydrochemistry parameters such as pH and Eh values of the wastewater samples were integrated into the clustering analysis. Datasets was clustered using various methods including KMeans, MeanShift, Affinity Propagation, Ward and DBSCAN, and classified using nearest neighbor, linear SVM, RBF SVM, Gaussian processes, neural networks, Naïve Bayes and QDA methods. Among them, Naïve Bayes classification method showed high accuracy (70%) in identifying the storage source from which the sample was taken. The clustering and classification processes contribute to the development of models for tracking lignin in dissolved organic matter. Optimization of methods for analyzing and identifying humic substances improves the accuracy of estimating their contribution to nutrient cycling and facilitates the development of more effective ecosystem management strategies. This study highlights the integration of fluorescence methods with other data to improve the classification and understanding of humic substance processes and presents the main results of our research.

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## **Molecular composition of humic acids of different aged soils of fallow lands in North-West of Russia**

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Keywords:  $^{13}\text{C}$  NMR spectroscopy; boreal zone; fallow agrosol; arable lands; Podzol

Worldwide, the problem of agricultural land conservation is a leading issue in the global fight against hunger. The area of agricultural land in Russia amounted around 318 million hectares. About 44 million hectares of agricultural land are not used, of which - about 20 million hectares of arable land. Fallow lands of Russia are quite diverse in terms of soil types, vegetation succession, and post-agricultural dynamics. As a result of large-scale transition of soils to fallow state in Russia accompanied by landscape transformation, self-overgrowing, waterlogging of territories, there was a significant accumulation of organic matter in soils, which is estimated in the range from 64 to 870 TgC [1]. Depending on soil type and natural zone, they are able to sequester different amounts of SOM. The highest sequestration rates are observed in the boreal belt, this is due to the formation of natural vegetation and an increasing the content of primary plant production. Postagrogenic transformation of fallow soils leads to changes in soil carbon content, molecular composition of humic substances as well as rates of organic matter stabilization, and can affect on climate change on the planet. In this regard, we analyzed the molecular composition of humic acids isolated from pristine zonal and fallow soils of southern taiga zone of North-West Russia. Different-aged soils of fallow lands represent a model of soil transformation in time and data on the transformation of soil humic acids molecular composition make a significant contribution to the understanding of soil organic matter stabilization aspects issues. In this case, the molecular structure of humic acids isolated from natural and fallow soils of North-West Russia was analyzed. To study the molecular composition of HAs, the elemental composition was analyzed and  $^{13}\text{C}$  (CP/MAS) NMR spectroscopy of HAs isolated from different aged abandoned soils and soils of different types of use was carried out. The obtained data showed that with increasing age of soils in the fallow state there is an increasing in the carbon content of humic acids, as well as a decreasing in nitrogen content. According to the data on the elemental composition of HAs, it was found that the transformation of HAs composition is directed towards HAs formed in mature soils. As a result of increasing age of soils in fallow state, there is dynamics in the content of aromatic structural fragments in humic acids, 34% for 40 years old, 28% for 80 years old and 31% for 120 years old, this is due to changes in the precursors of humification and further transformation of plant residues in the soil. Re-involved of soils of fallow land leads to an increase in the content of aromatic structural fragments in the composition of HAs in relation to HAs extracted from mature soils. The lowest content of aromatic structural fragments was observed in the humic acids of 130-year-old agriculture soil, which is associated with the long-term application of organic fertilizers.

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## **Synthesis of magnetite nanoparticles in the presence of humic substances as magnetic sorbents for cleaning water contaminated with heavy metals**

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Key words: nanoparticle magnetite, humic substances, heavy metals

Pollution of natural waters is of urgent environmental concern. Heavy metals are among the most widespread pollutants and pose particular danger to human health. An advanced method for cleaning water from metal pollution is a use of magnetic nanosorbents. The main problem in their production is stabilization in solution. Natural polyelectrolytes - humic substances (HS) - have great potential for solving this problem. In this regard, the purpose of this work was to synthesize magnetite nanoparticles in the presence of humic substances for cleaning water contaminated with heavy metals.

To achieve this goal, the following tasks were to solve:

An optimal method for synthesizing magnetite nanoparticles in the presence of humic substances was developed by varying the conditions for its production. It was shown that the optimal precursors are  $\text{FeCl}_3$  and  $\text{FeSO}_4$ , the precipitant is ammonia, an inert atmosphere and humate of oxidized coal with a high content of phenolic groups. In the presence of this humate, the minimum sizes of nanoparticles were observed. A study of their phase composition and size was performed using TEM and SEM. It was shown that the size of magnetite nanoparticles synthesized under the optimal conditions found was 5-10 nm.

To characterize the functional properties of magnetite nanoparticles stabilized by HS, their sorption capacity for copper and nickel ions was studied. It was shown that magnetite has a much higher sorption capacity for copper than for nickel: 48 and 7 mg/g, respectively.

### Conclusions

1. Optimal conditions for obtaining a pure phase of nanosized magnetite in the presence of HS were found: a use of ammonia as a precipitant and a use of inert atmosphere for carrying out the synthesis

2. The higher sorption capacity of magnetite nanoparticles obtained in the presence of HS for copper and nickel was shown, while the contribution of the humic component increases with an increase in the total acidity of the original humate.

Acknowledgements. This research was carried out within the framework of the state task "Ecology" (no. 122040600057-3).

## **Study of adsorption of polyelectrolyte complexes of humic substances with aminoorganosilanes on silica gel**

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Keywords: humic substances, sorption, aminoorganosilanes, polyelectrolyte complexes

Heavy metals are considered priority pollutants of water and soil, especially in urban areas. Natural organic matter (OM) serves as a natural barrier against the spread of these toxins, forming strong complexes with metals and reducing their mobility and toxicity. Humic substances (HS) play a major role among the OM components. Modern nature-like groundwater treatment technology that mimics natural geochemical barriers is permeable reaction barriers (PRBs). The traditional method of installing PRBs requires removal of a large volume of contaminated soil, which is not always convenient. A more promising option is injection PRBs, which require the use of special liquids capable of sorbing in significant quantities on mineral substrates. Such a liquid can be based on polyelectrolyte complexes of HS with aminoorganosilanes. The actual task is to study the sorption parameters of this complex on mineral substrates.

In this work, polyelectrolyte complexes of HS and (3-Aminopropyl)triethoxysilane (APTES) with different mass ratio were prepared. The kinetics of their adsorption on silica gel was studied and the adsorption parameters were determined. The sorption experiments were carried out in phosphate buffer medium (0.03M, pH 6) due to the maximum stability of these compositions in aqueous medium. The time of the sorption experiment was 4 hours, since kinetic experiments showed that this time is sufficient for the establishment of sorption equilibrium. Sorption isotherms were plotted in the range of concentrations of polyelectrolyte complex APTES/HS in solution from 5mg/l to 1200mg/l, because at higher concentrations aggregation and subsequent sedimentation of the whole composition is observed.

As a result, it was found that the sorption isotherms of APTES complexes are best described by the shifted quadratic Langmuir equation. The  $K_L$  adsorption constants found were  $1.8 \pm 0.2$ ,  $20 \pm 2$ ,  $11 \pm 1$ ,  $36 \pm 2$ ,  $260 \pm 30$  l/kg for samples with APTES/HS mass ratio of 0.5, 0.75, 1, 2, 3, respectively, indicating the dependence of sorption parameters on the composition of the complexes due to the increasing affinity of adsorbate to adsorbent

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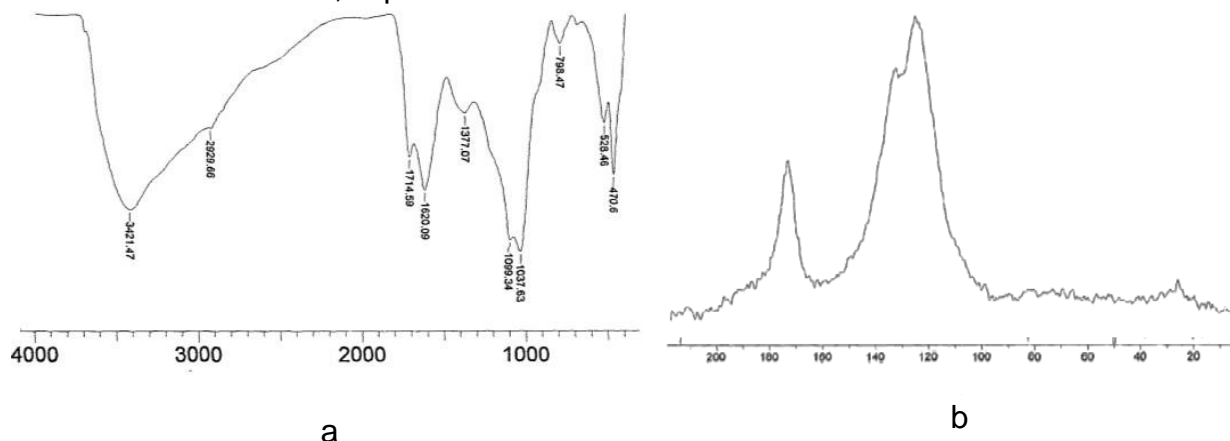
## Analysis of organic matter in pliocene soils (southern Eastern Siberia)

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Keywords: pliocene paleosols, humus substances, elemental composition,  $^{13}\text{C}$  NMR, humic acids

The Pliocene epoch (5.3-2.6 Mya) is significant for studying global warming trends. The regions of southern Eastern Siberia (Pribaikalye and Western Transbaikal) feature well-studied geological sites with subaerial Neogene-Quaternary deposits. Our research focused on the study of paleosols and coastal exposures of Olkhon Island on Lake Baikal, supported by geological and paleopedological methods. The soil organic matter was analyzed through humus substances, the elemental composition, infrared spectroscopy, and  $^{13}\text{C}$  NMR of humic acid preparations. The lower pliocene (around 5 Mya) black vertisol in Saraiskaya Bay formed under subtropical climate conditions. The soil profile shows heterogeneity, with the humic/fulvic acid ratio ( $C_{\text{ha}}/C_{\text{fa}}$ ) changing from 3.8-2.5 to 1.7-0.8 upward. The H/C ratio varies from 0.7 to 1.2 in the mid-profile and decreases to 0.8 at a depth of 5-10 cm from the surface. Humification occurred in a warm and dry climate, which then shifted to more humid conditions with decreased thermal efficiency. Later pliocene (around 3 Mya) brown soils were studied in Kharaldai Bay. Four horizons were identified with variations in humic and fulvic acid content and humin. The lower part is dominated by fulvic acids in the humus substances, with  $C_{\text{ha}}/C_{\text{fa}}$  ratios of 0.5-0.8 and atomic H/C ratios of 0.9-1.05. In the second part, the output of humic acids rises to 60-70% ( $C_{\text{ha}}/C_{\text{fa}}$  2.1-2.8; H/C decreases to 0.5), followed by a gradual increase in fulvic acids to 30-40% in the third and fourth parts, and subsequently an increase in humic acids, with humic/fulvic acid ratio ranging from 0.9 to 2.5. The atomic H/C ratio changes from 1.01 to 0.55-0.71. Materials of IR (a) NMR (b) spectroscopy of humic acids from the studied by us brown soils of Kharaldai Bay, are presented [1]. It was noted that the IRS of humic acids can be attributed to warm soils. The fragmentary composition in terms of  $^{13}\text{C}$  NMR data is as follows (in relative %): carboxyl carbon - 17.3; aromatic carbon - 68.7; polysaccharide carbon - 5.5; aliphatic carbon - 8.5.



The analysis of all humus components in the pliocene brown soils suggests a progression from warm-very humid to very warm and moderately-humid conditions, followed by a gradual shift to more arid climates amidst increasing thermal.

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## Optical Characterization of Lignin Sludge-Contaminated Water at the Solzan Landfill: Assessing Asymmetry in Fluorescence Spectra

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Keywords: sludge lignin, Baikalsk pulp and paper mill, fluorescence, UV-absorbance, humic substances

Pulp and paper mills (PPMs) are known to be major contributors to environmental pollution, primarily due to the accumulation of lignin sludge in disposal sites. At the Baikalsk Pulp and Paper Mill (BPPM), this sludge is stored in ten large concrete containers, covering an area of 105 hectares and holding up to 4 million cubic meters of waste. There is concern that potential flooding could weaken the dams, resulting in the release of harmful substances into Lake Baikal. Regular monitoring of the water above the sludge deposits is essential to assess the risk of contamination. The optical properties of dissolved organic matter (DOM), particularly its absorption and fluorescence, are highly useful for rapid environmental assessments. However, detecting the unique optical signature of lignin sludge can be challenging due to interference from the fluorescence and absorption of natural DOM and humic substances (HS).

The goal of this research was to investigate the optical characteristics of water in contact with lignin sludge at the Solzan landfill of BPPM and compare them to the properties of natural humic substance (HS) solutions. As part of the study, approximately 80 water samples were collected during a 2024 summer field trip to the landfill. These samples, along with natural HS samples, were filtered using a GFF filter (0.7  $\mu\text{m}$ ) and analyzed through fluorescence spectroscopy and UV-Vis spectrometry. Key optical descriptors were calculated based on absorption and excitation-emission matrix (EEM) spectra. Fluorescence band asymmetry was evaluated by comparing the integrated intensities at a 350 nm excitation in two spectral ranges: blue (420-460 nm) and red (550-600 nm). The findings are shown in Figure 1.

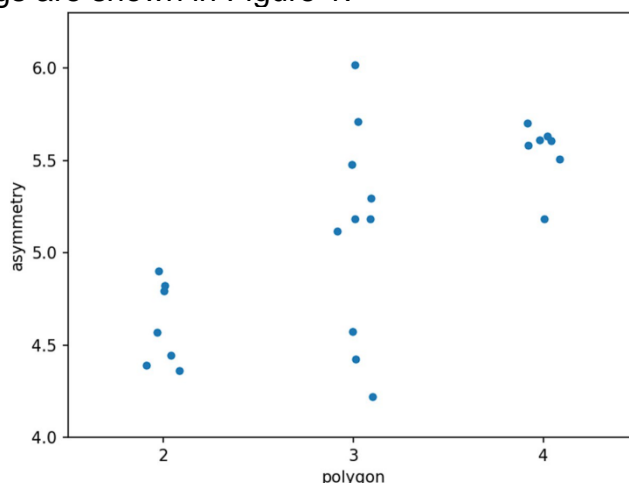


Figure 1. Asymmetry values for the sections of the Solzan landfill.

The results indicate significant differences in asymmetry values between the second and fourth sections of the landfill, while the third section displayed values that overlapped with both. This suggests that the nature of pollution in distant sections of the landfill may differ, but there is also mixing and averaging of pollutants across the site.

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## Evaluation of Membrane Filtration for the Reuse of Washing Agents in Diesel Spill Remediation

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Key words: humic substances, oil pollution, washing agents, membranes, surfactant

In 2020, a massive diesel fuel spill in the Norilsk region of Russia caused widespread environmental damage, highlighting the need for more efficient fuel spill remediation techniques. Traditional cleanup methods, including the use of washing agents, often lead to secondary pollution and increased waste. To mitigate this, the reuse of washing agents through membrane technology has gained attention as a promising solution. This study focuses on testing various membranes to determine their effectiveness in filtering contaminated washing agents, with the goal of improving diesel spill cleanup efficiency while minimizing environmental impact.

The aim of this work was to test various membranes against contaminated washing agents to identify the best membranes in terms of speed and effectiveness in removing diesel from the contaminated agents.

In the first series of experiments, studies were conducted using a range of polysulfonamide membranes: UMP-100, UPM-200, and UPM-500, which filter based on particle mass. The UMP-100 membrane allows particles with a mass of up to 100 kDa, UPM-200 allows up to 200 kDa, and UPM-500 up to 500 kDa. The UMP-100 membrane is designed for ultrafiltration, while the UPM-500 is used for microfiltration. These membranes were purchased from Vladipor Ltd. Additionally, in experiments involving ceramic filtration, a membrane made of Al<sub>2</sub>O<sub>3</sub> with a pore size of 0.05 micrometers was used. This ceramic membrane was sourced from Keramicfiltr Ltd.

Table 1 – Diesel fuel removal effectiveness using different membranes

Membrane name	Diesel fuel removal effectiveness, %	SD (n = 3), %
UPM-500	29	10
UPM -200	85	5

According to the data, the UPM-500 membrane allows some diesel to pass through, while UPM-200 completely blocks diesel but fully allows Tween-80. UPM-100 also fully blocks diesel but allows only about half of the Tween-80.

The UPM-200 membrane is the most suitable for filtration, as it blocks diesel but lets Tween-80 pass. However, its low filtration rate of around 1 ml/min is a drawback, leading to the search for a more efficient membrane.

In experiments with a ceramic membrane made of Al<sub>2</sub>O<sub>3</sub> with 0.05 μm pores, 2 liters of eluate containing ~1% Tween-80 and 0.2-0.3% diesel were filtered. The ceramic membrane was able to separate diesel with 44% efficiency, reducing its concentration. The membrane's throughput was 3.6-4.8 L/hour.

The UPM-200 membrane proved most effective in removing diesel (85%) while allowing Tween-80 to pass, though its slow filtration rate limits its practicality. The ceramic membrane, with lower diesel removal (44%) but higher throughput, offers potential for faster processing. Future work should aim to optimize membrane performance to improve both efficiency and speed, enhancing the economic viability of diesel spill cleanup.

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## **Influence of humic acid on the sorption of Pb(II) by kaolinite and muscovite**

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Keywords: kaolinite, muscovite, humic acid, heavy metal, sorption

Soil contains a large number of compounds that influence the sorption of heavy metals by the soil, and clay minerals and soil organic matter play key roles in the sorption process. The sorption of heavy metals by individual soil components has been well studied, but compounds capable of absorbing heavy metals are often present in the form of mixtures in soils, and individual components can interact with each other. Most often, compounds capable of absorbing heavy metals form films on the surface of clay minerals, which can significantly change the sorption properties of both clay minerals and compounds included in the film.

The aim of this work was to reveal the patterns and mechanisms of Pb(II) uptake by kaolinite and muscovite in different variations: untreated and surface-modified with humic acid. The objects of research were kaolinite and muscovite. Humic acid was extracted using NaOH from EL<sub>ih</sub> horizon of peaty-podzolic-gleyic soil. Minerals were modified according to [1]. Sorption experiments were carried out using lead nitrate in the concentration range from 0.005 to 1.0 mmol/l, at pH values 3 and 5 and the same ionic strength of solution.

Results of the experiment show that untreated kaolinite absorbs Pb(II) at pH 3 and 5 equally. However, at pH 5 kaolinite absorbs Pb(II) more intensively at lower concentrations than at pH 3. This is due to more favorable conditions for the formation of inner-sphere polymer complexes of Pb(II) with silanol and aluminol groups on the side chips of kaolinite and inability of kaolinite to absorb Pb(II) by the ion exchange mechanism due to the absence of a negative charge in the crystal lattice. Muscovite absorbs Pb(II) less intensively at pH 3 due to protonation of functional groups on side cleavages of mineral, and sorption occurs according to the mechanism of ion exchange. Muscovite is capable of ion exchange due to presence of a high negative charge in crystal lattice, and mechanism of ion exchange dominates at pH 3. At pH 5 sorption occurs more intensively due to involving mechanism of inner-sphere complexation. At pH 5 sorption process occurs according to mechanisms of ion exchange and inner-sphere complexation and the role of the second mechanism decreases with increasing concentration of Pb(II).

The amount of Pb(II) sorbed by kaolinite after modification of HA at pH 3 and 5 differs slightly. In comparison with unmodified kaolinite, in the region of low Pb(II) concentrations, the modification of kaolinite HA increased the sorption of Pb(II), especially at pH 3; at pH 5 the increase was insignificant. This increase is associated with addition of humic acid to kaolinite surface and HA functional groups are capable of ion exchange and complex formation. The mechanisms by which the sorption of Pb(II) by kaolinite modified by HA occurred: ion exchange and complexation. After modifying muscovite with humic acid, the Pb(II) sorption isotherms remain almost unchanged compared to untreated muscovite. Pb(II) is absorbed more intensively at pH 5, which is due to more favorable conditions for the formation of inner-sphere complexes. At pH 5 mechanism of ion exchange also takes place, because some amount of K<sup>+</sup> was released into the equilibrium solution, which was part of the interlayer cations compensating for the negative charge of the lattice. The main mechanism by which Pb(II) is absorbed at pH 3 is ion exchange, because as the concentration of Pb(II) increases, a large amount of K<sup>+</sup> was released into the equilibrium solution. Adding humic acid significantly influenced the mechanisms of Pb(II) sorption, redefining the roles of mechanisms.

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## Humic substances enhance the performance of polyelectrolyte-based formulations as soil conditioners

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Keywords: hydrolyzed polyacrylonitrile, soil structure, soil respiration, heavy metal, detoxication

Hydrophilic polyelectrolytes (PE) are considered as perspective tools to optimize soil properties and find increasing applications in agricultural technologies [1]. Among them is hydrolyzed polyacrylonitrile (HYPAN), a linear polyanion. Synthetic HYPAN mixed with humic substances in a binary polymer-humic soil amendment might have a synergistic effect enhancing their performance. The objective of this study was to examine the effects of HYPAN, two different humic products (HP) (potassium humates from lignite and lignosulfonate), and binary compositions HYPAN-HP on soil properties, microbiological activity, as well as their detoxication ability, and to reveal advantages of binary polymer-humic formulations comparably to individual polymers.

In several experimental sets, PE-solutions were applied and examined how they affect soil hydrophysical properties, soil organic matter, and activity of soil microbial community, as well as plant and microbial test-responses in bioassays. A concurrent set of studies involved spiking soil-polymer mixtures with heavy metals (Cu, Zn, Pb, and Cd).

Results. Being applied at a soil surface, binary HYPAN-humate formulations formed soil-polymer coatings resistant to the detrimental effects of water and air flows. Being mixed with the entire soil volume, all formulations affected soil aggregate composition differently. Both HP increased the proportion of large fractions, whereas HYPAN alone and in compositions with HP dispersed large soil aggregates and bound small ones, thus increasing the share of valuable 1-0.25 mm aggregates. In contrast, the effects of PE-formulations on soil organic matter were determined by the nature of HP: the one from lignite contributed to the accumulation of condensed aromatic structures, whereas humate from lignosulphonate increased the proportion of low-molecular phenolic compounds. Both HP stimulated the soil microbiological activity, expressed in increased basal respiration, microbial biomass, and metabolic quotient. Binary compositions were more efficient when combined with humate from lignosulphonate.

In HM-spiked soil-polymer mixtures, formulations decreased the content of mobile Cu, Zn, Pb, and Cd species and mitigated the toxicity of HM for plants and soil microbial community. A pronounced effect was observed for lignite-originated HP alone and in combinations with HYPAN, but not for HP from lignosulfonate.

Conclusions. Combinations of synthetic HYPAN with natural humic biopolymers improved soil hydrophysical properties, stimulated the activity soil microbial community, and mitigated the toxicity of heavy metals in the soil. The effects on soil hydrophysical properties were mainly governed by HYPAN, whereas the effects on soil chemical and biological properties were influenced by humates. The latter effects are determined by the nature and chemical structure of humates. The quality of organic matter in both humates and HYPAN was the primary determinant of the impact of the examined amendments.

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## Transformation of humic acids under long-term pollution

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Keywords: pollutants, soil, soil organic carbon, technogenic pollution

The content of soil organic matter is a vital indicator of soil health and is frequently used for monitoring and assessing soil fertility. Its composition is related to the quantity and quality of incoming organic residues, the rate of their mineralization and humification, as well as the chemical composition of soils. The impact of anthropogenic activities on the accumulation of environmental pollutants significantly contributes to a change in the composition of soil organic matter, which subsequently affects the functions and fertility of soils.

The soil (Spolic Technosols) of the Kamensky district of the Rostov region was studied to identify changes in the composition of soil organic matter. The soil was formed at the bottom of a dried-up lake, used until 1990 as a tank for industrial waste. Spolic Technosols are characterized by a high content of heavy metals, especially Zn (up to 700 mg/kg), and polycyclic aromatic hydrocarbons (PAHs) (the sum of 15 priority PAHs up to 11000 ng/g). We compared the content and composition of organic matter of Spolic Technosols with unpolluted soil (Fluvisol) located 1.7 Km from the border of the aforementioned lake.

Samples of humic acids (HA) from the surface layer (0-20 cm) of the studied soils were isolated by the IHSS method. The distribution of HA carbon among the structural fragments was determined by IR and <sup>13</sup>C NMR spectroscopy.

The IR absorption spectra of the HA of Fluvisols soil have a similar patternlike soil from the chernozem zone, while the presence of branched lateral aliphatic chains and carbohydrate components was revealed in the HA of Spolic Technosols. A distinctive feature of the HA in Spolic Technosols are the peaks at wavelengths of 2850 cm<sup>-1</sup> and 2930 cm<sup>-1</sup>, caused by valence vibrations of CH<sub>2</sub>- and CH<sub>3</sub>-groups and C-H bonds in aliphatic CH<sub>3</sub> and CH<sub>2</sub> groups, as well as the manifestation of asymmetric and symmetrical deformation vibrations of the C-H bond in CH<sub>2</sub>- and CH<sub>3</sub>-groups (1456 cm<sup>-1</sup>) and C-O bond vibrations and deformation vibrations of OH-COOH groups (1235 cm<sup>-1</sup>) corresponding to aromatic and phenolic groups. Also, the intensity of absorption bands of Spolic Technosols is higher in the region of 700-600 cm<sup>-1</sup>, corresponding to valence vibrations of C-S, and 500-400 cm<sup>-1</sup> – valence vibrations of S-S bonds.

The analysis of IR spectra revealed the inclusion of substances of an "unsoil" nature, presumably PAHs, in the HA composition. The content of various PAH groups in Spolic Technosols is 10-433 times higher than in Fluvisols, and 1.4-2.4 times higher than their concentrations in soil. Similar patterns were not found for the uncontaminated soil.

The analysis of the absorption spectra of carbon atoms in the corresponding ranges of the <sup>13</sup>C NMR spectrum confirmed the presence of aromatic and aliphatic fragments, as well as various functional groups. The structure of the HA of Fluvisols is dominated by carbon skeleton structure with a relatively small contribution of the carbohydrate periphery. There is a higher content of the carbohydrate component in the HA structure (69-75%) for Spolic Technosols, which is responsible for their increased solubility and hydrophilicity. The degree of aromaticity ( $f_a = \text{CAr-H, R+} + \text{Ar-O, N}$ ) HA of Fluvisols was significantly higher than Spolic Technosols: 38-44% vs. 12-20%. The hydrophobicity index ( $f_h/h$ ), calculated as  $f_h/h = (\text{CAr-O, N} + \text{CCOO-H, R} + \text{CC=O} + \text{CAIk-O, N}) / (\text{CAr-H, R} + \text{CAIk-H, R})$ , was higher for uncontaminated soils.

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## **Synthesis of magnetic sorbents with humic substances for the removal of heavy metals from natural waters**

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Keywords: humic substances, hematite, sorption, magnetite.

Waste from metallurgical enterprises accumulates as tailings containing hematite and residual sulfides, which can leak into the environment during accidents or malfunctions. This contamination leads to ecosystem degradation, characterized by a decrease in the pH of drainage waters, increased metal mobility, and deteriorating water quality. As a result, contaminated soils become unsuitable for plant growth, posing a threat to the survival of numerous species.

In this study, we propose the use of magnetite immobilized on a solid carrier—sawdust treated with humic substances—to create an effective sorbent with an enhanced surface area. To achieve this, iron (II) and (III) salts were mixed with sawdust, followed by the precipitation of magnetite using an ammoniacal solution of coal humic acids under heat. The resulting sorbent was then filtered and dried.

We investigated the sorbent's ability to adsorb copper and hematite from natural waters, comparing its performance to that of untreated sawdust. Characterization of the sorbents was conducted using various physicochemical methods. X-ray phase analysis and Mössbauer spectroscopy confirmed the dominance of the magnetite phase in the synthesized materials. Micro X-ray fluorescence analysis and scanning electron microscopy revealed a uniform distribution of magnetite across the surface. Additionally, magnetic field measurements indicated notable magnetic properties, which were enhanced in the absence of humic acids.

To validate the high sorption capacity of the modified sorbent, we conducted experiments focusing on the adsorption of copper and suspended hematite. The results indicated that untreated sawdust exhibited minimal adsorption capabilities: maximum copper adsorption was only 4 mg/g, while for hematite it reached 20 mg/g. In contrast, the modified sorbent displayed significantly improved adsorption rates: 7.8 mg/ml for copper and 80 mg/g for hematite. Thus, modifying sawdust with magnetite in the presence of humic acids enhances adsorption efficiency, facilitating the ecological disposal of contaminants.

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### **3. Natural and artificial humification, nature-like technologies for processing organic waste**

## Prospective *In Situ* Methods of Artificial Humification of Lignin

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Keywords: humification, humic substances, lignin, biomass valorisation

Lignin is a major source of biomass that largely goes unused, and thus accumulates in landfills. A series of such lignin landfills on the shores of lake Baikal contain over 6 million tons of lignin waste, which contaminate the lake itself [1]. In order to solve this problem while adhering to the principle of Green Chemistry of atom conservation [2], we need to look for biomass valorisation methods, i.e. converting lignin into beneficial substances, such as humic substances. In this paper we aim to give an overview of the existing applications of different approaches to the artificial humification of lignin, looking into their mechanisms and weighing the advantages and disadvantages of each in order to select the most prospective ones for the purpose of decontaminating landfills.

Different methods operate at different time scales and have been tested at different scales in terms of volume. Unfortunately, no successful large-scale application of any of the known methods has been conducted so far, besides composting [3] but owing to the specifics of the situation at Baikal, it is necessary to search for *in situ* methods, as it is economically untenable to transport such amounts of lignin waste in order to set up aerated compost piles even if combined methods would provide the best overall results [4].

More promising approaches include oxidation via laccases [5], photoirradiation [6], Fenton reactions [3], as well as superoxide-based reactions [7], as these processes can be carried out *in situ*, and they provide efficient C-C and C-O bond cleavage [6, 7], and these methods are currently being investigated. Thus a combination of enzymatic reactions, Fenton reactions, and superoxide-based reactions appears to be the most prospective method of *in situ* artificial humification of lignin for the purposes of valorising existing lignin landfills.

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## **Ability to activate humic substances of peat in twenty green technologies.**

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Key words: humic acids; peat; gas-dynamic impact; advantages.

Humic acids (HA) - humic, fulvic, humatomelanic - of organic origin, extracted from natural raw materials (peat, brown coal, organic waste, etc.). Their microstates determine: easy penetration and formation of plant and living cells; increase in crop yield up to 50%; frost resistance and reduction in their cultivation time; water retention, improved drainage and soil aeration; harmless for the production of feed diets; content of up to 20 types of amino acids.

Humic acids are the most active component of HA, but in their natural state they are inaccessible to plant cells due to their significant molecular weight and poor solubility in water. The mass of fulvic acids is a thousand times smaller, they are more active, easily soluble in water and accessible to plant cells. There are 10 times more fulvic acids in peat than in oxidized brown coal.

It is important to achieve not the maximum percentage content of HA micro fractions in fertilizers, but their biological activity, which consists in preserving, ensuring the vital activity and regenerative activity of microflora. For example, at concentrations of humic and humatomelanic acids over 0.3 g/l, the area of inhibition of the microorganisms contained in them begins. HAs act positively on plants at limited concentrations, not higher than 0.01% of the active substance.

Unlike the human body, whose organs independently remove excess microelements, plants do not have such a function and excess concentrations of microelements inhibit them. At the same time, the rate of microelement consumption by plants decreases, including their growth and development. The state of biological completeness of GC, from the point of view of their consumer properties on the part of plants, should be under constant control.

Common methods for obtaining microfractions (low-molecular) components of HA on an industrial scale are alkaline hydrolysis and mechanical activation (grinding) of natural peat.

The main disadvantages of the first method: leaching is aimed at extracting HA, not activating it; fulvic acids, which are most valuable for plant cells, remain in solution; an increase in the alkali content in the soil.

Common methods for obtaining microfractions (low-molecular) components of HA on an industrial scale are alkaline hydrolysis and mechanical activation (grinding) of natural peat.

The main disadvantages of the first method: leaching is aimed at extracting HA, not activating it; fulvic acids, which are most valuable for plant cells, remain in solution; an increase in the alkali content in the soil.

Advantages of the proposed Method:

- obtaining ballast-free microfraction of HA from peat on an industrial scale by a more efficient and cheaper method of gas-dynamic action for splitting HA supramolecules with a simultaneous increase in the biological and regenerative activity of their microflora;
- intensification of the process by vortex mixing with pressurized gas jets in a closed space, followed by settling of peat fractions – ballast (fibrous) and productive (suspension and microfractions);

significant reduction in costs due to: transportation of ballast-free peat humus; cost of activation of dry/wet peat in comparison with mechanical activation; need to use chemical reagents; preservation of the most valuable fulvic acids; adaptation of the HA structure to climate change; possibility of using biologically activated peat humus containing macro- and microelement indicators standardized for different soils.

## **Complex effect of binary polymer-humic compositions on soil properties in model experiment**

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Keywords: polyelectrolytes, hydrolyzed polyacrylonitrile, humate, soil, structure, heavy metals, phytotoxicity

Land degradation and all related processes affect the entire world and are global social, economic and environmental problems of our time, which are associated with both climate change and anthropogenic human activity. Most often, soil degradation occurs due to the destruction of the upper soil horizons, which are most valuable due to their fertility, as a result of water and wind erosion.

One of the approaches to solving this problem is the use of polymer-based stabilizing formulations to obtain protective compositions on the surface of the upper soil horizons. At present, effect of polyelectrolyte-based formulations on soil anti-erosion resistance have been well studied. However, there is insufficient understanding of how these polymers would affect other soil properties.

The aim of the study was to assess the influence of three polyelectrolytes and their mixtures on mobility of Cu and Pb, as well as on the aggregate composition of the soil and the effect on phytotoxicity in a model experiment.

In this work we used following polyelectrolytes: hydrolyzed polyacrylonitrile (HYPAN), a synthetic polymer, and two commercial humic products: Lignohumate (LH) obtained from lignosulphonate, and humate "Sakhalinsky" (SH) obtained from lignite, as well as binary compositions of HYPAN and humates at ratios 1:1 and 1:2.

The model experiment was conducted with the top horizon of cultivated podzolic soil with pH of 6.5, 4% of organic carbon content and light mechanical content. The soil was mixed with solutions of polyelectrolytes giving 0.9% by dry weight. Cu and Pb were applied as nitrate solutions at rates 66;132;198 mg/kg and 64;128;192 mg/kg for Cu and Pb respectively, incubated during two weeks, and content of mobile species of HM was determined.

The results showed that HYPAN alone and SH alone, as well as their mixtures, decreased the content of mobile forms of heavy metals in the soil. The LH has no effect on the heavy metal mobile forms amount. The use of polyelectrolytes increased the proportion of agronomically valuable and water-resistant soil aggregates. Determination of the phytotoxicity index showed a decrease in the toxic effect of heavy metals in the treatments with polyelectrolytes and humates compared to the control sample.

Conclusions. As soil amendments, binary polymer-humic compositions showed advantages comparably to individual polyelectrolytes. While humates had an impact on soil chemical and biological qualities, HYPAN primarily controlled the impacts on soil hydrophysical parameters, and reduced the mobility of Cu and Pb in soil. In combination, they provided a complex positive effect on soil properties and potential fertility.

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## Synthesis of new alkyl derivatives of peat

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Peat is a unique natural composite, a source of humic substances and raw materials for industry and agriculture. The aim of this work is to develop a new carboxymethyl derivatives from peat to study the possibility of its application in the industry oil and gas production [1]. The influence of duration mechanochemical treatment of peat on the process of carboxymethylation under the action of natrium monochloroacetic salt in the presence of NaOH, the temperature of the alkylation – 25 °C (tabl. 1) [2]. The influence of duration mechanochemical treatment of peat on the process of benzylation under the action of benzyl chloride in the presence of NaOH (tabl. 1) [2]. The chemical composition of products of benzylation of peat given in the table 2.

Table 1. The influence of the molar ratio of OH:NaOH:m-ClAcNa in the carboxymethylation of peat in conditions of intensive mechanical grinding on the properties of the obtained products

Sample	Duration carboxymethylation of peat, min	Content of carboxymethyl groups, %	Solubility in water, %
Peat	-	-	5
1	10	17.9	42
2	20	20.5	69
3	30	20.7	71
4	60	24.7	76

It was found that with an increase in the molar ratio there is an increase in the content of bound carboxymethyl groups in products and their solubility in water (tabl. 1).

Table 2. Benzylation of peat

Duration benzylation of peat, min	Content of benzyl groups, %	Solubility in chloroform, %
10	3.8	17
20	4.7	25
30	5.9	36
40	6.8	45
50	7.7	53
60	8.6	60

It is shown that the increase in the duration benzylation of peat is the increase in the content and solubility products in chloroform (tabl. 2).

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## Artificial humic substances from agriculture wastes

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Keywords: humic substances, plastics, microorganisms, biodegradation

Humic substances (HSs) are determining the basic properties of soils and play an important role in regulating the growth of plants and soil microorganisms. In nature, the formation of HSs occurs as a result of the humification of bioorganic (mainly plant) residues. However, various methods similar to natural ones are being developed for the "artificial" production of HSs from agriculture wastes (plant waste and animal excrement). accumulated annually in significant quantities (million tons/year) [1]. Conversion of these wastes could solve the problem of obtaining products containing HSs similar to natural ones and significantly reducing the waste volume and destruction of various micro-pollutants contained in them (pesticides, mycotoxins, microplastics, pharmaceutical pollutants, etc.) [1]. Initial composition of wastes and their humification methods lead to the production of various HSs containing products with different compositions and properties, widening the range of fields of their potential use (Figure. 1).

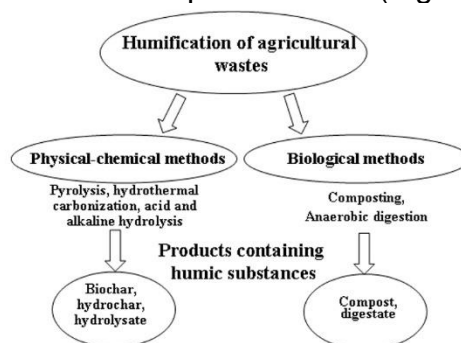


Figure 1. Various humification processes of agricultural wastes and obtained HSs containing products.

The formation of HSs is influenced by many factors (temperature, pH, C/N ratio, humidity, oxygen concentration, etc.) when using these methods. Today many researchers are searching for approaches to improving the indicators of humification (the speed and depth of the process). The use of various additives for incorporation in the reaction media (lignocellulose containing wastes, mineral particles, biochar, hydrochar, lignite, metal salts and nanoparticles, oxidizing agents, acidic or alkaline agents, conductive and dielectric materials, precursors of HSs, suspended or immobilized microbial cells, artificial consortia, etc.) is mostly studied to improve the characteristics of HF processes [1].

HSs obtained from various agriculture wastes can be effectively used in a variety of fields: organic fertilizer, soil conditioner, adsorbents, antibacterial agent and antioxidants, electrode material, feed additives, components of building materials (fresh mortars and aggregates in cementitious composites), various composite materials (wood polypropylene composites, plastics, etc.), and textiles with improved functional properties [1]. Thus, HSs obtained from various AWs using different methods of HF can be effectively used in a variety of fields along with natural HSs derived from coal and peat.

Acknowledgements. The research was supported by State Task of Lomonosov Moscow State University (122040600057-3).

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## Industrial production of humic preparation «Pochvouluchshitel» (Soil improver), its properties and results of field test

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Keywords: vermicompost, soil improver, soil fertility

The BioEra Group of companies produces industrially the humic preparation Soil Improver (Lunino village, Penza region). The vermicompost obtained by vermicomposting a mixture of cow manure and waste blocks in a vermireactor after growing oyster mushrooms *Pleurotus ostreatus* with compost worms *Eisenia fetida* is mixed with water in a ratio of 1/5 and the resulting suspension is treated in a hydraulic mill, ballast and abrasive particles are separated during hydraulic shock treatment, next, the resulting suspension is cavitated in a rotary pulse apparatus for 20 minutes, followed by alkaline extraction of humic substances with 0.5% potassium hydroxide to obtain a final product with a particle size of 10-200 microns [1].

The preparation Soil Improver is a gel-like mass with a content of organic substances – 16.27%, humic acids – 12.4%, fulvic acids – 1.37, non-hydrolyzable residue - 2.5% with a solubility index of 60%.

In 2018, in the spring, the preparation Soil Improver was introduced into the chernozems of the Engels district of the Saratov region (LLC Pokrovsk Agro) at a dose of 1,000 l/ha. It was found that the introduction of this preparation contributed to an increase in the fractions of agronomically valuable aggregates in the soil, the coefficient of structurality and the number of water-bearing aggregates, as well as the preservation of qualitative indicators of the structural composition of the soil in the second year of research. This indicates the presence of a pronounced prolonged aftereffect. It is believed that this is due to the high content of HA and FA in the composition of this preparation and their high resistance to mineralization. In addition, an increase in the activity of soil enzymes (proteases, ureases, polyphenol oxidases and dehydrogenases) was found, which indicated an intensification of the transformation processes of organic forms of N and C.

The result of the use of the humic preparation Soil Improver was a significant increase in the yield of white cabbage (*Brassica oleracea*), grade "Ammon F1" by 28% compared with the control, which provides, along with improving the physical properties of the soil, the economic effect of the use of the humic preparation "Soil Improver". Thus, the use of this preparation Soil Improver promotes structure formation, increases the water resistance of soil aggregates and, as a result, fertility and erosion resistance of soils. These results allow us to recommend the humic preparation Soil Improver as an effective means to increase soil fertility, with long-term intensive arable use, in conditions of irrigated agriculture.

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## Features of the chemical structure of humic substances of Agroverm biofertilizer

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Keywords: humic substances, biofertilizer

In the Laboratory of Humic Substances of the Department of Soil Chemistry of the Faculty of Soil Science of Moscow State University, the features of the chemical structure, composition and properties of HS in Agroverm biofertilizer obtained from vermicompost by cavitation were studied. It was shown that Agroverm biofertilizer contained 42.7 g/l of organic matter. The preparative isolation, fractionation and purification of HA and FA made it possible to determine the ash content, elemental composition and atomic ratio (Table 1).

Table 1. Elemental composition, chromaticity coefficients and atomic ratio in HA and FA from the preparation "Agroverm".

HS	Ash, %	Elemental composition, mass. % per ash-free sample					Atomic ratio			E <sub>4</sub> /E <sub>6</sub>	Formula "cells"
		C	H	N	O	S	H/C	C/N	O/C		
HA	2,4	50.1	3.7	4.1	42.0	0.2	0.88	14.4	0.63	3.9	C <sub>12</sub> H <sub>36</sub> O <sub>26</sub> N <sub>3</sub>
FA	2.6	43.5	4.5	4,1	47.9	0,1	1.23	12.7	0,83	11,8	C <sub>12</sub> H <sub>15</sub> O <sub>10</sub> N

The nature of the IR, Raman, and <sup>13</sup>C- and <sup>1</sup>H-NMR spectra, the calculation of the atomic ratios of the main elements in the composition of HA and FA indicates a developed and branched "periphery" of HA molecules, their high enrichment with various functional groups (among which the most reactive carboxylic COOH groups dominate). Gel filtration on Sephadex G-75 revealed two peaks of HA in the high molecular weight region (54000 and 41500 Da) and a dominant peak of FA in the low molecular weight region (4000-2000 Da). The content of trace elements and physiologically active low molecular weight compounds (amino sugars, amino acids, polyols, carbohydrates, etc.) were determined in HA and FA. 18 amino acids with a predominance of neutral and dicarboxylic amino acids have been identified in HA and FA hydrolysates. The assessment of the physiological activity of HA and FA fractions on plants showed the high effectiveness of AgroVerm biofertilizer as a stimulator growth and development of plants; a powerful activator of their immune system, significantly increasing the resistance of cultivated crops to adverse environmental factors and various diseases. Thus, Agroverm biofertilizer is a highly concentrated preparation of HS and physiologically active low molecular weight compounds.

## Biogeosystem Technique methodology as a GreenTech basis

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Keywords: Biogeosystem Technique, intra-soil milling, intra-soil pulse sequential-discrete watering paradigm, waste recycling, C sequestration, humic substances

A current ecosphere technology level does not provide the GreenTech implementation. To improve the soil geophysical architecture, watering, waste recycling and humic substances functioning in the environmentally sound GreenTech, we developed a transcendental (not a direct imitation of nature) Biogeosystem Technique (BGT\*) methodology providing the new high soil productivity technological framework.

BGT\* implementations are as follows.

The one time 20–50 cm layer intra-soil milling provides the stable soil fine geophysical multilevel aggregate system architecture for a period of up to 40 years. A high rate rhizosphere and soil biome long-term development ensures applied and native humic substances improved functioning, soil fertility and plant ontogenesis certainty. The crop yield is higher and stable.

Intra-soil pulse sequential-discrete watering provides soil solution matrix potential in a range from –0.2 MPa to –0.4 MPa. At this matrix potential, a plant stomatal apparatus operates in a regulation mode. Plant transpiration is reduced. The water, nutrient supply and humic substances regime provides a plant productive ontogenesis due to a stable soil geophysical architecture and a soil solution higher concentration.

The GreenTech problems are the waste recycling and the C sequestration. A BGT\* development is the municipal, industrial, biological (including agricultural, slaughterhouse, hazardous) waste and gasification byproduct intra-soil recycling in the 20–50 cm soil layer in a course of the 20–50 cm soil layer milling or/and in a course of the intra-soil pulse sequential-discrete plant watering. The intra-soil waste recycling ensures a reliable safety of environment and intensifies a nutrients and humic substances turnover. A C consumption to photosynthesis and a C reversible sequestration in rhizosphere and fresh biological plant production provide a priority functioning of soil humic substances, polymicrobial biofilms and plant stimulants. A plant resistance to phytopathogens increases. A plant ontogenesis improves. A long-term soil biological productivity and a high crop yield are achieved.

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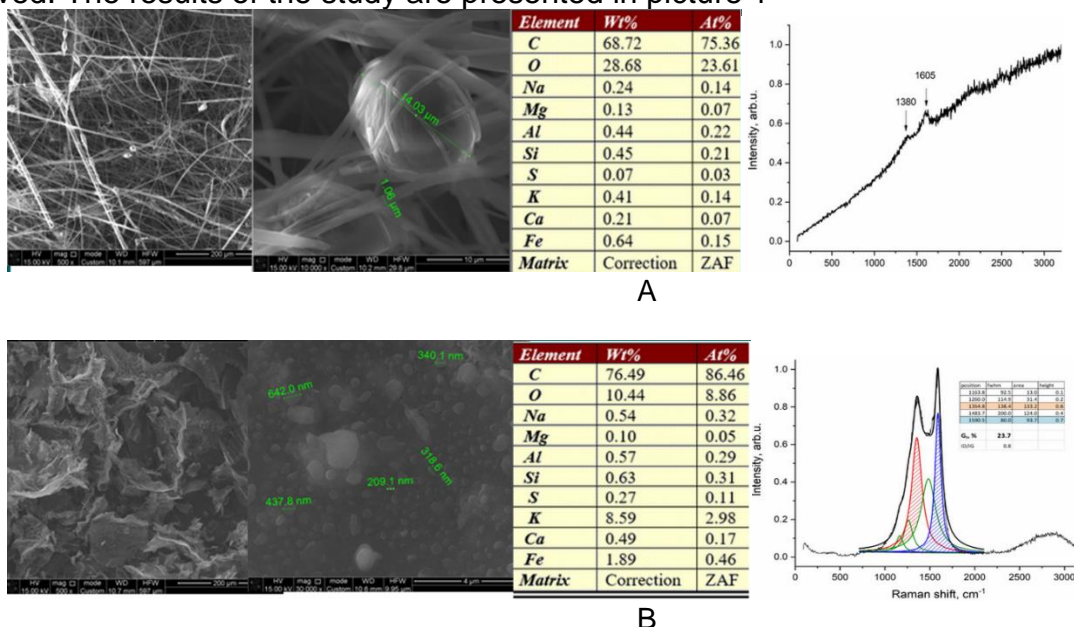
## Production of carbon nanofibers based on humic acids

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Keywords: humic acid, electrospinning, nanofibers.

Carbon nanofibers (CNFs) are sought after for their exceptional mechanical, electrical, and thermal properties, making them valuable in advanced composites and energy storage. Traditional CNF production methods, like chemical vapor deposition and electrospinning with synthetic polymers, can be complex and expensive[1].

Humic substances, such as humic acids and fulvic acids are abundant, renewable, and rich in carbon, positioning them as promising precursors for CNF synthesis. Electrospinning, a technique that uses a high-voltage electric field to produce fine fibers from a solution, can be adapted to use humic substances. This process involves electrospinning the humic substance solution to form nanofibers, which are then carbonized to create CNFs, offering an environmentally friendly and economical production method. Water was used as a solvent and the current-conducting catalyst urea was used as a polymer base; polyvinyl alcohol and humic acid were dissolved. The results of the study are presented in picture 1



Picture 1. A - SEM image, elemental composition and Raman spectra of the initial nanofiber based humic acid; B - SEM image, elemental composition and Raman spectra of the carbonized at 800°C nanofiber based humic acid

As a result, a physicochemical analysis of the composition of carbon nanofibers based on humic substances was carried out using Raman spectroscopy methods. The results of Raman spectroscopy showed the presence of graphitization after carbonization. According to the SEM patterns, fibers of different diameters and nanodots of similar diameters can be seen. Therefore, the goal for the future is the production of environmentally friendly nanomaterials.

**Acknowledgments.** This study was funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (grant No. AR19577512. Development of scientific and technical foundations for the production of microporous carbon nanomaterials for the separation and storage of hydrogen).

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## Production of carbon microporous materials based on humic substances for hydrogen storage

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Keywords: humate, adsorption, carbon adsorbent

Humic acids (HA) are stable, complex colloids from decomposed residues. The raw material, oxidized brown coal from the Sarykol deposit, was crushed to <0.5 mm. Characteristics included  $A^d$  66.09;  $W^r$  5.73;  $V^d$  17.78;  $S_t^d$  0.71;  $C_t^d$  21,01;  $H_t^d$  1,68;  $N_t^d$  2.09 and various elements. Particle sizes were 2.95  $\mu\text{m}$  (10%), 63.8  $\mu\text{m}$  (50%), and 452  $\mu\text{m}$  (90%). X-ray analysis showed halloysite, silicon oxide, and Na albite. The yield of humic substances was 56%.

For porous carbon materials, the product is crushed (6.88-401  $\mu\text{m}$ ), carbonized at 700°C and activated at 900°C, which increases surface area and strength. Steam activation modifies pore structure. Surface area was analyzed using a 3Flex 3500 analyzer with nitrogen. Figure 1(a) micrograph of sample showed heterogeneous surfaces. Elemental composition (Figure 1(b)) of the sample (%): C-24.9, O-57,4, Al-0.6, K-17.1. The Raman spectra of the activated sample (Figure 1(c)) show a signal with characteristic D and G peaks (1359  $\text{cm}^{-1}$ , and 1576  $\text{cm}^{-1}$ ). Additionally, the Raman spectrum of the sample shows a 2D peak at 2716  $\text{cm}^{-1}$ , indicating the formation of carbon nanotubes or graphene. The intensity ratio of the G and 2D peaks ( $I_G/I_{2D} = 2.7$ ) indicates a multilayer structure of the nanomaterial. The intensity ratio of the ID/IG = 0.4 indicates a low amount of defects in the material under consideration. Thus, the degree of graphitization  $G_r$  is 30.6%.

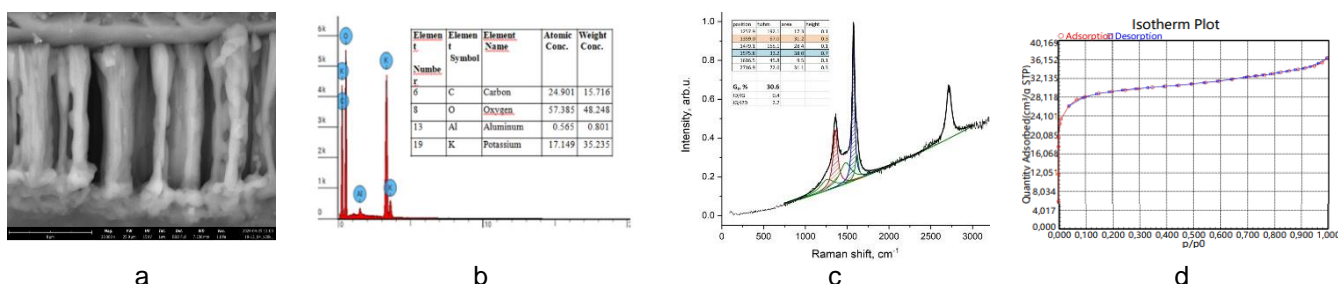


Figure 1. SEM images (a), elemental composition (b), Raman spectrum(c) and specific surface area isotherm (BET) (d) of sample

Table 1. Values of specific surface area of pores of activated adsorbent potassium humate

BET Surface Area:	113,56634(m <sup>2</sup> /g)
t-Plot Micropore Area:	102,99428 (m <sup>2</sup> /g)
t-Plot Micropore Volume:	0,04114 (cm <sup>3</sup> /g)
Average Pore Diameter (4V/A):	1,97882nm

As a result of carbonization and activation of potassium humate obtained on the basis of oxidized coal of Kazakhstan, microporous carbon materials with a specific surface area 113,56634(m<sup>2</sup>/g) were obtained, which will be used for storing hydrogen.

Acknowledgments. This research has been funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP19577512 "Development of scientific and technical bases for obtaining microporous carbon nanomaterials for hydrogen separation and storage").

## Oxidation of kraft lignin using $\text{CaO}_2$

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Keywords: humic, lignin, fenton

Humic substances (HS) contained in the soil are crucial for the quality of agroecology, improve soil properties and promote plant growth. The depletion of humus reserves as a result of erosion has caused concern worldwide, which makes the use of artificial soils vital for restoring soil fertility and maintaining the carbon cycle. To enhance humification and obtain humin-like biostimulants, various methods of humification have been developed, such as biocomposting and Fenton oxidation. However, biocomposting takes quite a long time, and Fenton oxidation faces problems such as high cost and potential phytotoxicity. Peroxide plays a key role in Fenton oxidation [1]. Recent studies show that calcium peroxide ( $\text{CaO}_2$ ) is a more effective source of  $\text{H}_2\text{O}_2$  for chemical oxidation than liquid  $\text{H}_2\text{O}_2$ . This study evaluates the possibility of oxidation of kraft lignin using  $\text{CaO}_2$ .

The oxidation was performed using a combination of the techniques described in [2,3]. For our system, we took a concentration of kraft lignin equal to 100 mg/l, 14 mg  $\text{CaO}_2$  and 0.1 M  $\text{FeSO}_4$ . oxidation was carried out for 2 hours without heating while maintaining pH = 11. determination of the degree of oxidation was carried out using fluorescence analysis by the value of asymmetry, which is the ratio of the intensity of the red region of the spectrum to the blue. The fluorescence spectra at a wavelength of  $\lambda=350$  nm are shown in Figure 1. For the initial lignin, the asymmetry value was 6.82, while for the oxidized with  $\text{CaO}_2$  it was 5.37.

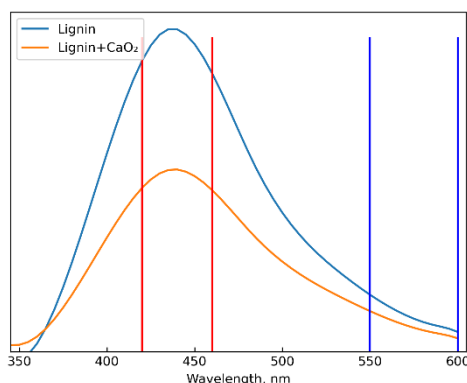


Figure 1. Fluorescence spectra at a wavelength of  $\lambda=350$  Nm for the initial (blue) and oxidized  $\text{CaO}_2$  (orange) lignins.

The results show that when synthesized with  $\text{CaO}_2$ , the asymmetry decreases, which indicates that the intensity of "red" decreases and "blue" increases, compared with the control non-oxidized kraft lignin, which may indicate oxidation.

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## Dynamics of rate and depth of biohumus humification of different composting dates

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Keywords: biohumus, humic acids

The composting of livestock products is one of the most accessible and cost-effective ways for enrich the soil with humus substances.

At present, vermicomposting is of the greatest interest due to the increasing intensification of animal husbandry in the Rostov region. The vermicomposting peculiarity is the use of epigeic earthworms, most often of the *Eisenia fetida* species, which undergo processing of organic matter to form vermicompost.

Livestock manure is often used to improve the physical, chemical and biological soil properties. However, the potential negative effects of this agronomic practice are being actively studied, as it is known that compost made from manure may contain antibiotic residues [1].

One of the main advantages of vermicompost in comparison with other organic fertilizers is the high concentration of humic substances. In addition, vermicompost fertilizers have less degree of nutrient loss and higher stability in the soil.

In the present study, microbially treated horse manure with different composting dates and different depth of humification was used. Soil samples were collected at different composting times ranging from one and a half months to nine months: 1.5, 3, 5, 7 and 9 months. The vermiculture agent was the hybrid composting red Californian worm *Eisenia foetida*. Alkaline extracts of humic compounds were isolated from the obtained mixed-age compost, with which subsequent studies were carried out for their physiological activity.

The total organic carbon content of humic compounds was determined in the extracts, with subsequent separation into humic and fulvic acids.

Nine-month vermiculture composting was expected to provide an exponential increase in humus content, with a similar increase in the humification depth factor. However, the research showed that in the first 1.5 months there is an increase in the concentration of total organic carbon with a peak in the samples of 3 months of composting, then its content gradually decreases. The same tendency to increase is observed with the content of humic acids with a peak at 3 months of composting, after which there is a gradual decrease, similar to the dynamics of total carbon.

We have concluded that the optimal composting period for horse manure in vermiculture is 3 months, as evidenced by the highest humic acids content in samples of this period relative to samples in the line with other terms of manure "maturation".

The research was carried out within the framework of the Strategic Academic Leadership Program of the Southern Federal University ("Priority 2030")

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## **Technology of organic raw material processing with production of humic substances, using the example of Lignohumate® preparations production**

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Keywords: knowledge, power

### **Relevance of the problem**

Organic waste utilization and humic substances production have become important tasks in the modern world. The use of lignin-containing plant raw materials produced during wood processing is one of the most promising solutions to the problem that allows to compensate for the organic carbon depot in nature in a short period of time. At the same time, the obtained humic preparations besides the stimulating effect on plants also affect soil productivity.

### **Processing technology**

The company A.E.T. LTD has developed and successfully uses a waste-free technology for plant raw material (lignosulfonate) processing using the method of oxidative-hydrolytic destruction, which allows producing high-quality liquid and powder humic preparations under the Lignohumate trademark.

### **Processing process**

Raw material processing with the production of Lignohumate humic preparation is carried out in industrial reactor units in periodic and continuous modes under the influence of oxygen, high pressure and temperature. Depending on the selected mode, this technology allows launching the accelerated humification of organic raw materials in 1,5-3 hours, which takes decades in the natural environment.

### **Differences in compositions**

Composition and properties of the humic preparation depend on the selected raw material processing mode and process parameters:

- in a periodic oxidation mode with increased "cooking" time, the degree of preparation humification grows ( $C_{HA}/C_{FA}$  indicator grows to 1.5), which indicates the accumulation of the humic acid fraction;
- in a continuous oxidation mode, a large amount of acid-soluble fulvic acid fraction, consisting of fulvic and low-molecular organic acids, accumulates in the product. Depending on the process parameters the  $C_{HA}/C_{FA}$  indicator varies from 0.4 to 0.8.

### **Quality control and biotesting**

To control the quality of preparations produced in different technological modes and differing in composition, the growth-stimulating activity is assessed in production conditions using comparative laboratory biotesting and "simulation of industrial seed treatment". In addition to quality assessment, these methods allow determining the optimal working concentrations and preparation dosages for agricultural production, reducing the time of field tests, seed treatment in seed treatment machines, etc.

### **Lignohumate product line**

For over 30 years, A.E.T. LTD has been producing humic preparations with different properties and characteristics under the Lignohumate trademark, monitoring production parameters and quality of products.

Today Lignohumate products are highly effective growth stimulants, anti-stress agents, adaptogens and organomineral fertilizers representing a reliable, effective and environmental friendly way to increase the yield and quality of agricultural products.



## The influence of artificially humic substances obtained from sewage sludge on biometric and biochemical parameters of cultivated plants

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Keywords: artificially humic substances, oxidative-hydrolytic destruction, urea, barley (*Hordeum vulgare* L.), white mustard (*Sinápis alba* L.), transamination.

Sewage sludge from municipal wastewater treatment plants, as a source of organic material of natural origin, can be used as a raw material to produce plant nutrient mixtures containing artificial humic substances (AHS). Neutralization and utilization of sewage sludge with obtaining a useful product for the needs of crop production is one of the actual problems. In this case two ecological tasks are solved.

AHS are a complex mixture of various dark-colored organic compounds of arylglycolipoprotein composition [1], which are products of alkaline high-temperature hydrolysis of sewage sludge organic material.

The aim of our study was to evaluate the effect of different nutrient mixtures containing AHS obtained by oxidative-hydrolytic destruction (OHD) and/or urea on barley (*Hordeum vulgare* L.) seedlings and white mustard (*Sinápis alba* L.) plants.

The content of heavy metals and radionuclides in AHS-OHD did not exceed the maximum permissible concentrations. AHS-OHD solutions (0.001%) were used as nutrient mixtures for foliar treatment of agricultural crops, both without and with the addition of urea (0.875 g/l). All obtained experimental data were subjected to mathematical processing using the variation statistics method [2].

As a result of the laboratory experiment, reliable differences between the sample average biometric parameters of barley (*Hordeum vulgare* L.) seedlings were revealed only in the case of shoot and root mass, as well as the number of roots in 10 plants. As follows from the assessment of the generalized desirability functions of E. Harrington [3], the presence of urea, AHS-OHD and their mixture in nutrient solutions had a very good effect on barley seedlings, compared to the control, the effect of which was satisfactory.

As established based on the obtained results of the small-plot field experiment, significant differences between the sample average biochemical and biometric indices of white mustard (*Sinápis alba* L.) were revealed only in the case of the content of free amino acids, amino acids included in the composition of seed proteins, the number of seeds, and the weight of seeds in one plant. Based on the assessment of the generalized desirability functions of E. Harrington, the presence of urea, AHS-OHD and their mixture in nutrient solutions had a very good effect on mustard plants, compared to the control, the effect of which was satisfactory.

In our opinion, the positive effect of AHS-OHD and/or urea on plants can be explained by the participation of amino groups of the studied organic substances in transamination, because of which, probably, an additional amount of amino acids is formed, which undoubtedly "reduces the cost" and accelerates protein biosynthesis.

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## Artificially obtained humic-like substances and symbiont *in situ* improvement of oil degradation in soil

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Keywords: hydrolysate of chicken manure (HCM); humic-like substances (HLSs); crude oil pollution; soil bioremediation

Alkaline hydrolysate of chicken manure (HCM) (~280 mg HLSs/kg dry soil) in a combination with bacteria *Rhodococcus erythropolis* (R) and microalgae *Chlorella vulgaris* (C) to oil-polluted soil was assessed during a field experiment. The introduction of HCM into the soil without additions of cells resulted in a 1.5-fold increase of initial degradation rate of oil hydrocarbons, calculated for the first 7 days of the process (from 3.3 g/kg dry soils/day to 4.8 g/kg dry soils/day), compared to the control (without any additives). The introduction of a combination of HCM and R also increased the degradation rate by 1.5 times, and the combination of HCM, R and C gave the highest rate of oil biodegradation (up to 5.91 g/kg dry soils/ day), which exceeded the control by 1.8 times. The combination of three components in the composition of the introduced additives made it possible to achieve almost the same residual concentration of oil hydrocarbons in the soil after 7 days, which was revealed in the control after 27 days under the influence of native soil microorganisms and in the presence of natural humic substances (HSs) in the soil. After 27 days of HCM introduction into the soil the content of HSs in all soil samples was higher than in the control (Figure 1). This was due not only to the introduction of HLSs with HCM, but also to the possible release of some amounts of HSs from soil agglomerates as a result of the “enzymatic activation of soil” [1].

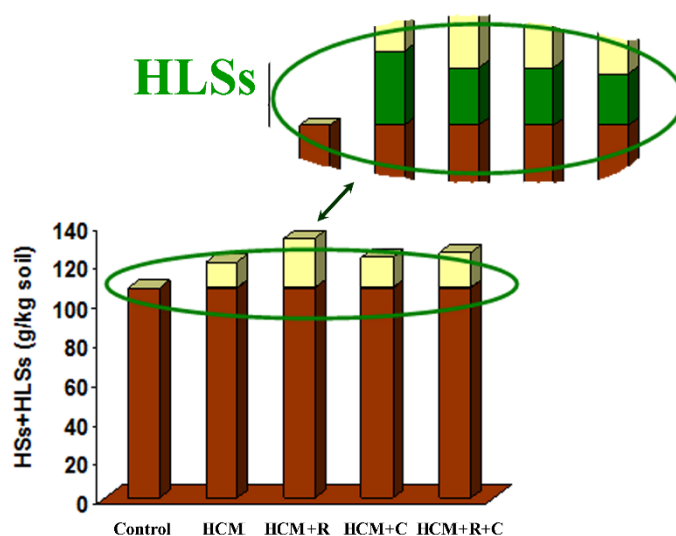


Figure 1. Changes in the concentration of available forms of HSs+HLSs after the introduction of HCM into the soil: initial HSs (brown area), added HLSs with HCM (green area), accumulated of available forms of HSs after 27 days (yellow area).

Acknowledgements. This work was carried out within the framework of the state task of the Lomonosov Moscow State University (122040600057-3)

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## Application of sodium percarbonate and calcium peroxide to remove lignin from wastewater

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Keywords: lignine, oxidation, sodium percarbonate, calcium peroxide

Recent years, pollution of water and soil by various organic substances has been increasing. On the Solzan waste deposits, as a result of cellulose production have accumulated a large amount of lignin waste, which can be a source of danger to humans and natural objects. Today, various technologies such as adsorption, reverse osmosis, electrocoagulation and others are used for wastewater treatment. A modern and actively developing trend is the In situ chemical oxidation (ISCO) based on the efficient formation of reactive oxygen species (ROS) and subsequent oxidation of organic pollutants. Therefore, in this work, the application of SPC and calcium peroxide for the oxidation of lignin was studied.

Oxidation of lignin was carried out in aqueous medium at room temperature. The reaction was carried out overnight. SPC and calcium peroxide were used as ROS sources and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  as activator. The oxidation efficiency was determined by the reduction of total organic carbon (TOC). The obtained data are presented in Figure 1.

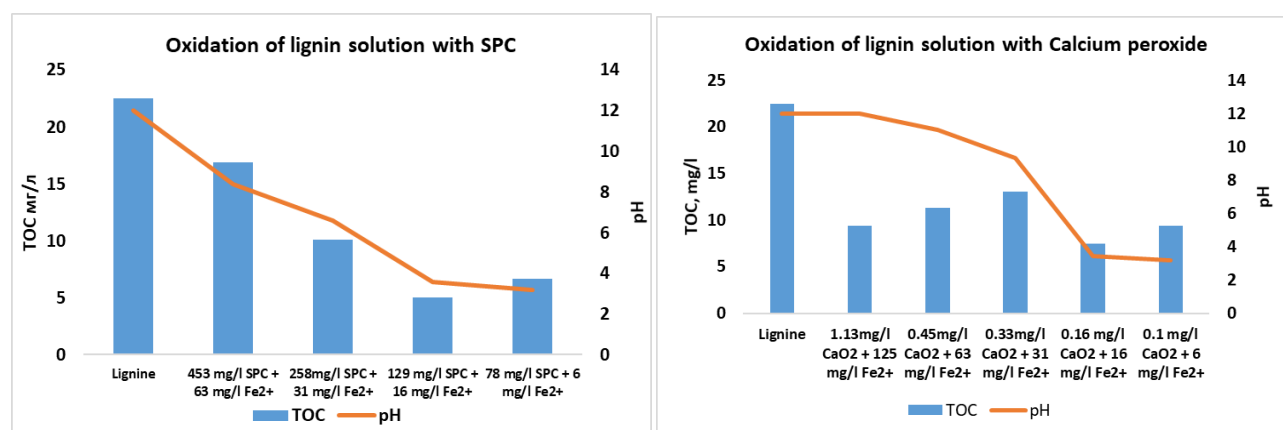


Figure 1. Reduction of TOC concentration when SPC and calcium peroxide are used as oxidising agents, and pH of the final solution

Based on the obtained data, when SPC is used as an oxidising agent, the most significant TOC reduction effect is achieved at SPC concentration of 129 mg/l and  $\text{Fe}^{2+}$  concentration of 16 mg/l. However, high  $\text{Na}^+$  concentrations and low pH in the final solution may have a negative effect on living organisms. When using  $\text{CaO}_2$ , the oxidation of lignin is less, the process is most efficient at calcium peroxide concentration of 0.16 mg/L and  $\text{Fe}^{2+}$  concentration of 16 mg/L. But when calcium peroxide is used, the oxidation efficiency does not depend on pH, and the final content of calcium ions is lower. Therefore, it can be concluded that calcium peroxide is better suited to the demands of green technologies.

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## Is there a place for speculation regarding artificial humification in the context of mechanochemical oxidation of lignite?

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Keywords: brown coal, humic acids, mechanochemistry

Mechanochemical technologies are recognized as promising and environmentally friendly, as they are highly efficient and allow using fewer production stages, as well as eliminating the use of solvents [1]. To date, mechanochemical approaches to brown coal processing are actively used, which allow us to partially oxidize the organic matter of coal, increase the share of extractable humic acids, increase the sorption properties of coal [2, 3].

The presented study aims to address a number of issues arising in the mechanochemical treatment of lignite:

1. What is the reason for increasing the yield of humic acids?
2. What can explain the increased sorption capacity of mechanochemically treated brown coal compared to native coal?
3. Can mechanochemical treatment of humic acids previously isolated from coal increase their sorption capacity and the number of functional groups?

To answer these questions, a number of experiments on mechanochemical treatment of coal and humic acids previously isolated from it were performed. Physicochemical analysis of the products and analysis of sorption capacity towards heavy metal ions ( $Zn^{2+}$ ,  $Cu^{2+}$  и  $Cd^{2+}$ ) were carried out.

It is shown that the increase in the yield of humic acids cannot be only explained by grinding and increasing the surface area of coal particles. It is shown that the increase in the yield of humic acids and the content of phenolic and carboxyl groups in lignite as a result of treatment with sodium percarbonate to date can be explained by oxidation of other (different from humic acids) fractions of organic matter of lignite.

There are examples in the literature when the application of other methods of activation of low-rank coals, accompanied by an increase in the yield of humic acids, is presented as humification [4]. If we view artificial humification as a process of obtaining humic acids from biomass or natural organic matter, mechanochemical oxidation of coal can also be considered from this point of view.

Acknowledgements. The research was funded within the state assignment to ISSCM SB RAS (project No. FWUS-2024-0002).

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## Effect of humic acid content on algotoxicity of nanocomposite (Fe<sub>3</sub>O<sub>4</sub>/HA) remediant

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Keywords: sorbent, biotest, algae bioassay, effective concentration, ecotoxicology

Magnetoactive preparations (Fe<sub>3</sub>O<sub>4</sub>) have shown their effectiveness as sorbents especially in combination in combination with humic substances [1-3]. However, the effect of the proportion of the humic component on the toxicity of composites has been little studied. Responses of living organisms in standard biotests under controlled conditions remain the most important part of the safety assessment in ecotoxicological purposes. We compared the effective concentrations of the nanostructured composite (Fe<sub>3</sub>O<sub>4</sub>/HA), a sorbent for ecotoxicants, at different ratios Fe<sub>3</sub>O<sub>4</sub> and humic acid (HA) using algotesting (FR.1.39.2007.03223). The humic acids (HA) used in this study were obtained from potassium humate (Powhumus, Humintech Ltd) by dialysis and were shown to have an ash content of 8.95%, COOH-group content of 4.2 mmol/g, and phenolic group content of 1.1 mmol/g [3]. Highly dispersed magnetite (Fe<sub>3</sub>O<sub>4</sub>) was prepared during the Elmore reaction, in three ratios (wt %/wt%) - Fe<sub>3</sub>O<sub>4</sub>/HA 20/80; Fe<sub>3</sub>O<sub>4</sub>/HA 50/50; Fe<sub>3</sub>O<sub>4</sub>/HA 80/20. Fluorescence parameters were measured with 'Fluorat-02-5M (Lumex).

Based on the inhibition of chlorophyll fluorescence and growth of microalgae *Scenedesmus quadricauda* (Turp.) Breb important toxicometric indicators were calculated. Using a probit analysis of the dose-response relationship, the following effective concentrations were obtained: EC<sub>50</sub> - the concentration of composite that gives half-maximal test response, and EC<sub>20</sub> - no observed effect concentration (NOEC) on standard test-culture (Table 1).

Table 1. Effective concentrations (mg/dm<sup>3</sup>) of nanocomposite with different humic acid (HA) content suppressing chlorophyll fluorescence by 50% (EC<sub>50</sub>) and 20% EC<sub>20</sub>.

Effective concentrations, mg/dm <sup>3</sup>	Fe <sub>3</sub> O <sub>4</sub> /HA 20/80	Fe <sub>3</sub> O <sub>4</sub> /HA 50/50	Fe <sub>3</sub> O <sub>4</sub> /HA 80/20
EC <sub>20</sub>	0,038	0,037	0,023
EC <sub>50</sub>	0,157	0,100	0,097

It has been established that the safest sorbent is Fe<sub>3</sub>O<sub>4</sub>/HA 20/80. Suppression of algae fluorescence by 50% in the presence of this preparation occurs at 0.157 mg/dm<sup>3</sup>, which is 60% - more than for Fe<sub>3</sub>O<sub>4</sub>/HA 20/80. A directly proportional dependence of algae toxicity on the HA content in the nanocomposite is observed.

Based on the results ecotoxicity of the studied substances, it is not recommended to use remediants in which the HA content is more than 20%.

Acknowledgements. This research was funded by the Russian Science Foundation (project № 23-23-00621).

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## **Chemical properties of humic biostimulant “Lignohumate” at different stages of its synthesis**

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Keywords: humic product, absorption spectra, humification, antioxidant activity, biotesting

Humic products (HPs) are increasingly used in agriculture, being considered as the main category of biostimulants. The chemical composition and efficiency of HPs as plant growth stimulators vary depending on the organic matter source, extraction processes and the technologies used to obtain the products [1]. Therefore, chemical characterization of HPs entering the market combined with verification of their efficacy as biostimulants is an urgent complex task.

The objective of this work was to characterize the chemical composition, biological and antioxidant activity of the product “Lignohumate” (LH) depending on the durability of its synthesis from raw material. A number of samples were taken at different times of the technological process, and qualitative differences in the composition of LH were analyzed.

The results showed that the pH of the solutions decreased from 10.8 to 8.1 with the duration of treatment, while the density increases from 1.08 to 1.14 g/mL. A gradual synthesis of humic-like substances (HLS) occurred: the share of HA in LH increased from 40-50% in the first period, and later reached 80%. The transformation of organic matter was evaluated by the optical properties of solutions in the UV-Vis regions. The absorption spectrum of the working solution differed from the spectra of samples subjected to artificial humification. The former was characterized by the lowest optical density, the presence of a maximum at 285 nm and a shoulder at 235 nm, indicating the presence of phenolic compounds. With increasing the oxidation time the absorbance increased, the shoulder at 235 nm disappeared, and the intensity of the peak at 285 nm became less pronounced. The calculated spectral indices indicated that molecular weights decreased with treatment time, and aromaticity increased. Examination of the antioxidant activity (AOE) trends for fast and slow centers showed that in the first period of the treatment, the fast antioxidant centers predominate over the slow centers, indicating a more fulvate character of the samples, which was also confirmed by the low humification index expressed by the low CHA/CFA ratio. The timing to obtain the maximum biological activity for the LH-product at concentration of 0.02% was evaluated in laboratory phytotest.

Correlation analysis revealed a positive correlation between seedling root length and CHA/CFA (0.84); whereas no correlation was found between antioxidant and biological activity. Therefore, depending on the purpose of use and requirements for the humic product, the treatment time can be used as a tool to emphasize either biological activity or antioxidant activity of the final product.

**Acknowledgements.** The authors are grateful to the LLC “Lignohumate” (Saint-Petersburg, Russia) for providing the samples of LH and financial support of this study.

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## **4. Humic systems and interaction with living organisms**



## Analysis of antimicrobial properties of potassium humate on microorganisms

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Keywords: potassium humate, antimicrobial properties, mold fungi

Potassium humate is a biologically active substance containing humic acids, fulvic acids, hymatomelanic acids, macro- and microelements. It is known that potassium humate has antimicrobial properties, which may be due to an increase in the bactericidal activity of blood serum, detected when introducing humic substance-based additives into the diet of animals [1]. The spectrum of biological activity of potassium humate also includes: antitoxic action, stimulation of productivity in animals, stress-protective activity, enterosorption, immunomodulatory action [2].

The aim of our work was to study the antimicrobial properties of potassium humate on microorganisms.

The following cultures were sown on Sabouraud's nutrient medium: opportunistic fungi *Candida parapsilosis*, *Rodotorula*, mold fungi *Aspergillus niger*. After 24 hours of incubation, wells were made, the bottom was sealed with a thin layer of Sabouraud's nutrient medium. The wells were filled with: UMBC+Potassium Humate 0.5%, Potassium Humate 1% and an emulsion based on potassium humate. They were placed in an incubation thermostat at 28°C.

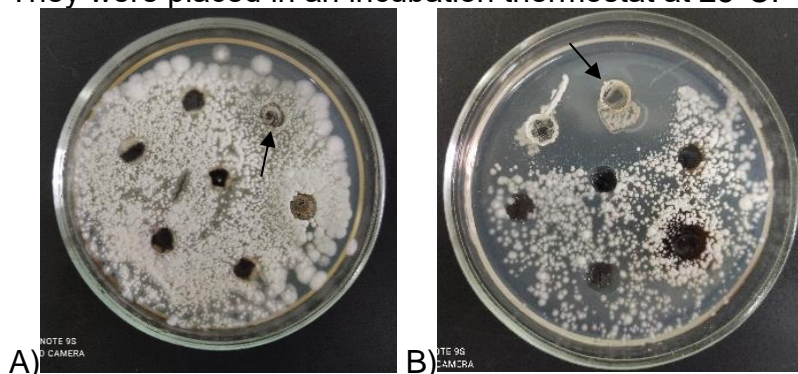


Figure. A-fungistatic effect of 1% potassium humate to *Rodotorula*; B-fungicidal effect of 1% potassium humate to *Aspergillus niger*

As a result, the presence of 1% potassium humate affected the growth pattern of *Aspergillus niger*, *Rodotorula* fungi. 1% potassium humate had a fungistatic effect, reducing the mold fungus *Aspergillus niger*, *Rodotorula*. No changes were observed with respect to *Candida parapsilosis*. Also, 1% potassium humate had a fungicidal effect with respect to *Aspergillus niger*. Thus, the presence of fungicidal properties of potassium humate was revealed, which may be promising for the treatment of skin mycoses caused by fungi of the genus *Aspergillus niger*.

Acknowledgements. The work was conducted within the framework of the project AP23489001 "Genetic monitoring and analysis of pathogenicity of new pathogens of opportunistic mycoses of farm animals in Kazakhstan", 2024-2026.

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## Magnesium deficiency and antioxidant activity of food

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Keywords: humic acids, antioxidant, magnesium, *Lactuca sativa*

The role of magnesium deficiency in the formation of various pathological conditions in the human body has been demonstrated based on the results of large meta-analyses. Among food products, green salads are of particular importance, being an essential component of a healthy diet. Lettuce leaves contain not only magnesium but also a high quantity of antioxidants, including carotenoids, folic acid, and vitamin C, which support normal cardiovascular function and help strengthen the immune system.

The primary source of magnesium for plants is the soil. The role of humic substances in plant and soil health is well known: humic acids improve the physical, chemical, and biological characteristics of soils. They enhance the bioavailability of nutrients in the soil, particularly micronutrients, through chelation and co-transport of micronutrients into plants [1].

Our study focused on the leaves of lettuce (*Lactuca sativa*) varieties "Armholt" and "Iceberg," which were cultivated using humates and magnesium sulfate. In this research, model solutions of humic acid were prepared (0.1 mL of humic acid and 100 mL of distilled water), to which solutions of magnesium sulfate were added. Potentiometric, conductometric and spectrophotometric methods were used to determine the optimal humate-magnesium ratio. The soluble complex "humate-magnesium" was formed by mixing 100 mL of a 0.01% humic acid solution with 187.5 mg of magnesium sulfate (heptahydrate). Treatment of the lettuce with the aforementioned solution increased the magnesium content in the green leaves of the "Armholt" variety from 19.2 to 38.4 mg/100 g; however, the magnesium content in the "Iceberg" variety decreased from 36 to 28.8 mg/100 g.

The biochemical significance of magnesium in plants is unique: it plays a direct role in photosynthesis, respiration, protein synthesis, and many other physiological processes. Magnesium deficiency delays chlorophyll formation in plant leaves, enhances oxidative processes [2]. It was hypothesized that an increase in magnesium in the leaves would also enhance the antioxidant properties of the lettuce. However, antioxidant activity significantly decreased with high magnesium content in the green leaves.

The antioxidant content in aqueous extracts from "Armholt" lettuce leaves was 14.1 mmol/L before treatment with humates and magnesium sulfate; it dropped to 8.9 mmol/L after treatment. For "Iceberg" lettuce, the antioxidant content was 8.1 mmol/L before treatment and 7.2 mmol/L after treatment. This may be explained by the fact that excess magnesium and the "humate-magnesium" complex could hinder the uptake of other macroelements and biologically active substances, which might otherwise serve as prosthetic groups for enzymes or enhance the expression of antioxidant genes.

Therefore, it is advisable to establish criteria that optimize the composition and properties of irrigation solutions for green salads, taking into account the botanical characteristics of the variety to preserve their antioxidant properties.

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## The release of iron from various iron-containing humic acid derivatives

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Keywords: humic substances, iron deficiency anaemia, iron content, ferrozine

Iron deficiency anaemia is a significant public health problem with a global prevalence. Novel iron-containing humic derivatives represent a promising new class of drug candidates for the anaemia treatment. An essential aspect of the screening process for anti-anaemic activity is the evaluation of the ability to release iron in an *in vitro* test with the use of the ferrozine reagent.

After incubation of Caco2 cells with the tested humic derivatives (final concentration 50 µg/ml as calculated for iron) for 24 h, concentrated hydrochloric acid was added to the cells and incubated for 1 h (60 °C) and then for 12 h at room temperature, followed by quantification of iron content in the cells by the ferrozine method. The calculation was performed using the calibration curve constructed for the FeCl<sub>3</sub>\*6H<sub>2</sub>O standard. All experimental data were subjected to statistical analysis. All calculations were performed using Prism GraphPad 8.0 software (USA).

The results of cytotoxicity assessment are presented in Figure 1.

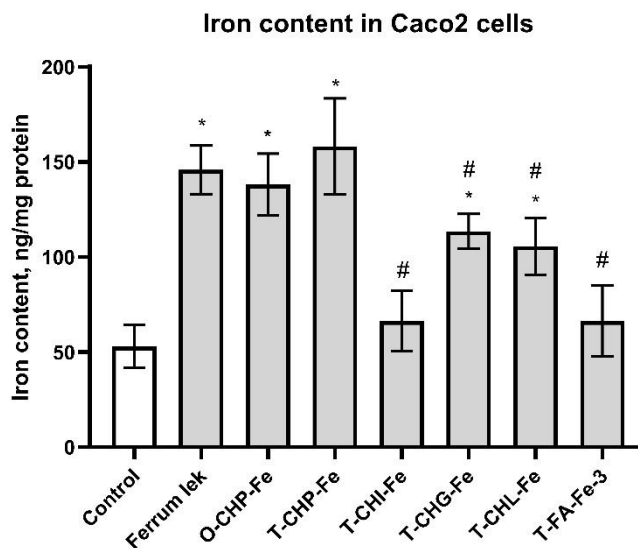


Figure 1 - Iron contents (ng/mg protein) in Caco2 cells after incubation with 50 µg /ml of different humic acid derivatives. \* - represents the difference with the control group (p<0.05), # - represents the difference with the FerrumLek group (p<0.05).

The results of the experiments demonstrated that four of the investigated derivatives (in addition to the comparison drug FerrumLek) exhibited a notable accumulation of iron in Caco2 cells (O-CHP-Fe, T-CHP-Fe, T-CHG-Fe, T-CHL-Fe). Concurrently, two samples (O-CHP-Fe, T-CHP-Fe) demonstrated the capacity to release iron at a level comparable to that of the reference drug FerrumLek. The four substances tested (T-CHI-Fe, T-CHG-Fe, T-CHL-Fe, T-FA-Fe-3) demonstrated significantly diminished activity compared to FerrumLek. Consequently, this study revealed that two compounds exhibited the greatest capacity for iron release, which was comparable to that of the comparison drug.

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## Interaction of humic substances and exopolysaccharides of microorganisms

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Keywords: humic substances, bacterial cellulose, exopolysaccharides

The study of the interaction of humic substances (HSs) and exopolysaccharides (EPs) is interesting for a number of reasons. First of all, a similar phenomenon is observed in the environment when HSs, as sources of reactive oxygen species, affect the cells of microorganisms, which in turn stimulates increased EPs formation. Accumulated EPs increases cell surface adhesion, which promotes biofilm formation or cell immobilization on accessible surfaces.

HSs can be specifically used to modify the surface of various EPs to create composite materials with special properties. EPs such as bacterial cellulose can be used to create composite materials. Since HSs are able to inhibit the metabolism of microorganisms and the activity of their enzymes, it is possible to create polymers with antimicrobial properties [1]. It is known that the introduction of HSs into the composition of polymers contributes to the initiation of photodegradation of the obtained composites under the action of UV [2].

Composites based on HSs and EPs can be interesting as the basis for the development of food packaging, providing safety of foods and their long-term storage. Moreover, the initial experiments confirm the high capacity of such materials in relation to water. Since then, such materials can be oriented on the prevention of spoilage development from one side, and from another side, the keeping of food freshness can be prolonged in perspectives.

The addition of the antimicrobial agents (including the enzymes with antifungal and antimicrobial quorum activity [3-5]) permitted in food industry to the polysaccharide matrix, as it follows from firstly obtained experimental results can guaranty the long enough safe storage and transportation of the products. That can be useful in solution of technical questions appeared during the export/import of fruits/vegetables between different countries guaranteeing the microbial safety of the supplied products.

Acknowledgements. The research was funded by the Russian Science Foundation (23-14-00092).

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## **The effect of the liquid humic preparation "AgroVerm" on crop productivity**

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Keywords: biofertilizer, spring wheat, sunflower, corn, productivity

The liquid humic preparation "AgroVerm" is a highly concentrated preparation of HS obtained from vermicompost by cavitation. It contained 42.7 g/l of organic matter. A field experiment in 2017 was conducted at a pilot site located in the UNPO "Povolzhie" (Stepnoye village) Engelsks district of the Saratov region. The predominant type of soil on the territory of the farm is dark chestnut, slightly saline, clay and heavy loamy in mechanical composition. The purpose of the research is to establish the effect of the preparation "AgroVerm" on the biological yield of spring wheat, sunflower and corn hybrids in the conditions of the Saratov region. The use of the liquid humic preparation "AgroVerm" on spring wheat had a positive effect on plant height, ear length, the number of grains in the ear and the weight of grain in the ear. The maximum biological yield was obtained with a single leaf dressing with 1% solution of the preparation — 1.68 t/ha. The high efficiency of the use of the preparation "AgroVerm" on sunflower has been established. In the SUR variety, the number of plants under control before harvesting was 4.51 pcs/m<sup>2</sup>, the number of seeds in the basket was 221.3 pcs; the weight of seeds from the basket was 14.0 g; biological yield was 0.63 t/ha. In the variants with the use of the preparation, there was a noticeable increase in the number and weight of seeds from one basket. As a result of the experiment, it was found that the most effective use of the preparation is for single treatment of crops - the yield reached 0.78 t/ha (an increase in control - 0.15 t/ha). The yield of the Megasan hybrid at the control was 0.76 t/ha, and when the seeds were soaked, it increased to 0.83 t/ha. The maximum biological grain yield of the studied corn hybrids was obtained by soaking seeds in a 1% solution of the preparation and double application of leaf treatments — 3.89 t/ha for the Falcon hybrid and 5.61 t/ha for the P9074 hybrid.

## Synthesis of [1-hydroxy(3,4,5-trimethoxyphenyl)methylene]bis(phosphonic acid)

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Keywords: bisphosphonates, humic substances, bone diseases

Bisphosphonates are of great interest from the point of view of pharmacology. The most famous representatives of the bisphosphonate group - 1-hydroxy-1,1-diphosphonic acids are widely used in medical practice for the treatment of bone diseases. Modification of humic substances by a bisphosphonic group in order to increase their chelating properties is of interest.

The introduction of the 1-hydroxy-1,1-bis(phosphonic) group requires a practical and effective method suitable for working with multifunctional substrates such as humic substances. This is a method based on the reaction of tris(trimethylsilyl)phosphite with carboxylic acid chlorohydrides [1]. In the synthesis was used gallic acid - low molecular weight compound which modeling humic substances.

As a result of the work, [hydroxy(3,4,5-dimethoxyphenyl)methylene]bis(phosphonic acid) was synthesized according to the proposed scheme:

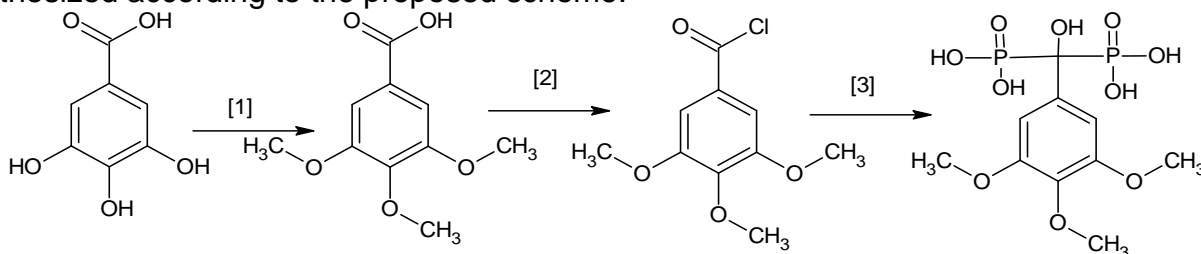


Figure 1. Synthesis scheme of [hydroxy(3,4,5-dimethoxyphenyl)methylene]bis(phosphonic acid).

The following precursors were used: gallic acid, dimethyl sulfate, tris(trimethylsilyl)phosphite, thionyl chloride, methanol.

The separation of the final product was carried out by precipitation with 90% ethyl alcohol. The synthesis products were characterized by using NMR spectroscopy on <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P nuclei. NMR spectra contain signals characterizing the structure of [hydroxy(3,4,5-dimethoxyphenyl)methylene]bis(phosphonic acid), which confirms the successful synthesis.

The conclusions are that the successful synthesis of [hydroxy(3,4,5-dimethoxyphenyl)methylene]bis(phosphonic acid) has been carried out. In the future, this method of introducing the 1-hydroxy-1,1-bis(phosphonic) group will be used to develop synthesis methods of bisphosphonates of humic substances.

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## Humic substances as radioprotective agents

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Keywords: low-dose radiation, radiotoxicity, humic substances, radioprotection, luminous marine bacteria, bioassay, reactive oxygen species

It is known that microorganisms of soils and aqueous media are sensitive to the presence of humic substance (HS), which play a role of natural attenuators of environmental toxicity. We studied bioeffects of alpha- and beta- emitting radionuclides (americium-241, uranium-(235+238), thorium-232, and tritium) in the presence of HS under the conditions of low-dose exposures (<0.1 Gy). Luminous marine bacterium *Photobacterium phosphoreum* was applied as a model unicellular water microorganism to monitor toxicity and activation ability of the radionuclide solutions. To imitate the marine environment for bacterial cells and to balance osmotic processes, the 3% NaCl solutions were used. The bioeffects of the radionuclides were compared to those of salts of heavy metals (salts of Ce, Sm, Gd, Eu).

The bioluminescence response of the marine bacteria to the radionuclides corresponded to the "hormesis" model: it included stages of bioluminescence inhibition and activation, as well as the absence of the effect. HS were shown to decrease the inhibition and activation effects of the radionuclides on the bacterial luminescence. The correlations between the bioluminescence intensity and the content of Reactive Oxygen Species (ROS) were found in the radioactive bacterial suspensions in the presence of radionuclides, thus revealing an involvement of ROS to radiomodifying effects of the radionuclides and HS.

The results demonstrate an important role of HS in natural processes in the regions of low radioactive contaminations: HS can mitigate radiotoxic effects and adaptive response of microorganisms to low-dose radioactive exposure of alpha- and beta- types. The involvement of ROS to these processes was demonstrated.

The results can provide a basis for predicting a response of living organisms to radiation at large territories infected with low-intensity radiation after accidents, discharges of nuclear plants, or underground mining of natural resources.

The radioprotective effect of HS was found in the organism of higher level of organization – agricultural animals, rabbits, under low-dose exposure to tritiated water: HS neutralized the toxic effect of tritiated water by bringing rabbit' physiological parameter (phagocytic activity of leukocytes) closer to the control. Hence, the bacteria-based bioassay can be applied to predict (1) changes in rates of cellular processes in higher organisms under low-dose radiation exposures, and (2) radioprotective activity of HS in different radiation environments.

Acknowledgements: Author are thankful to the Russian Science Foundation (No. 23-26-10018) and Krasnoyarsk Regional Science Foundation for funding the study of biological responses of rabbits.

## Probiotic effect of a feed additive based on potassium humate

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Keywords: bacillus, feed additive, probiotic, potassium humate

It is known that humates have a wide range of biological activity, which manifests itself in the effect on metabolic processes in the body of animals. Humates supply trace elements, strengthening the immune system and preventing diseases. In addition, humic acids inhibit the growth of pathogenic bacteria and molds, reducing mycotoxin levels and improving protein digestion and absorption of calcium, trace elements and nutrients. The result is a high body condition and disease immunity [1]. Antimicrobial activity has previously been identified in Kazakh humic acid preparations [2]. The research aims to develop a feed additive with a probiotic effect for preventing and treating gastrointestinal diseases in farm animals.

The developed feed additive "Gumibac" contains spore-forming bacteria of the genus *Bacillus* with a pronounced probiotic effect against opportunistic intestinal microflora and potassium humate with the presence of antimicrobial activity and a mass fraction of humic acids up to 50-56% by dry matter. Analysis of the biomass accumulation of *B. subtilis* and *B. amyloliquefaciens* showed that the number of cells per unit volume of culture fluid increases in the first 8-10 hours of cultivation. The number of cells at different time intervals was  $280 \times 10^9$  cells/ml after 24 hours of cultivation,  $306 \times 10^9$  cells/ml after 48 hours, and  $274 \times 10^9$  cells/ml after 72 hours. Thus, the exponential phase in the cultivation of bacilli lasts 48 hours.

An analysis of the growth of probiotic *B. amyloliquefaciens* and *B. subtilis* at a potassium humate concentration gradient of 1% to 100% showed that the bacilli grew well in the presence of humic substances, withstanding concentrations from 1% to 50%. The optimal concentration of potassium humate for them is 1-10%. Based on the data obtained, the biological product was prepared by deep cultivation of microorganisms in modified oat broth in the presence of humic substances for 48 hours and was used as a feed additive on laboratory and farm animals. The analysis of the toxicity of the feed additive showed that it is harmless and non-toxic to animals, causing an increase in the body weight of laboratory animals. Analysis of the morphology and mass of the internal organs of the control and experimental groups of animals during the autopsy showed that in the experimental animals, the weight of the heart changed insignificantly; liver weight decreased markedly, which indicates a decrease in the toxic load; the weight of the spleen has increased by two times, which is a sign of an increase in the body's immune defence; The weight of the kidneys increased by 1.6 times, which indicates an improvement in the filtration capacity of the kidneys. There were no significant morphological differences in parenchymal organs between the groups.

Analysis of the effect of the feed additive "Gumibac" on farm animals showed that after the first intake of the biological product, sick calves and lambs became calmer, stopped moaning, lay down, rested, defecation was frequent, and colic was not pronounced. After the second dose of the drug, the calves noticeably improved the state of the gastrointestinal tract (GIT), defecation was painless, and diarrhoea practically stopped. After the third intake of the biological product, the calves had an appetite, motor activity intensified, and the signs of intoxication and gastrointestinal disorders disappeared within a week. In piglets, an improvement in the general condition was noted after the third dose of the drug.

Thus, the feed additive "Gumibac", which is a biological product based on probiotic bacilli and potassium humate, has a positive effect on farm animals, namely, on beef calves, lambs and piglets, which indicates the presence of probiotic properties of the feed additive.

Acknowledgements. Thank you to Zhamantaev R.M. for the research carried out.

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## **The effect of humates on the yield of crops in the open-field: do they really work? A systematic review and a meta-analysis**

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Keywords: field trials, crop sensitivity, soil properties

Despite huge amount of publications on the beneficial effects of humic substances on crop growth and productivity over more than six decades, the use of humates, which are humic-containing commercial products, in agriculture varies and there is skepticism about their effectiveness. The first attempt to generalize the results of the humates efficiency was carried out in [1] and included mainly laboratory experiments. Another study related to the assessment of the effect of humates on yield was limited to data from Russian scientists [2]. In light of the potential benefits of humates, together with their inconsistent performance under field conditions, we sought to improve the understanding of the effects of humates on crop yield under open-field conditions by conducting a systematic review and a meta-analysis of the published literature. More specifically, our objectives were (i) to quantify the magnitude of plant-growth promotion resulting from humates application, in terms of yield; (ii) to determine the influence crop type, enrichment of humates with macro- or microelements, soil properties, and the manner of application on plant-growth response to humates. To reach these goals, ISI Web of Science and eLIBRARY databases search for the period of 1992-2022 has been conducted. A combination of searched terms included "humic" AND "field" AND "yield" or Russian-language equivalents. From a total of 407 papers originally found, 124 were retained for the review and meta-analysis, which provided over 575 data points on which to base the performed analysis.

The effectiveness of humates, estimated as yield as a percentage of control, ranged from 41% (suppression) to 659%, averaging 117%. It is interesting to note that the humates enriched with microelements had a significantly ( $p < 0.01$ ) lower average efficiency (113%) compared with the unenriched ones (119%). The observed unexpected phenomenon is probably explained by the fact that the distribution of efficiency values is not normal. Indeed, a comparison of the distributions showed that the mode value of the humate efficiency lies in the range of 100-110%, and enriched humates in the range of 110-120%. The established phenomenon indicates the impossibility in some cases to carry out a comparative assessment of humates based on a comparison of arithmetic averages and the need for a preliminary assessment of the distribution of the estimated indicator.

Oilseeds and cereals turned out to be the most sensitive to humates, while fiber crops were the least responsive. An increase in efficiency with an increase in the application dose of humates was found only on sandy soils and up to no more than 25 kg/ha, while for loamy and clay soils there was no such relationship. Humates are most effective, apparently, on soils with organic carbon (OC) content below 1%. The effectiveness of humates above 110% for such soils was noted for 55% of cases, whereas for soils with higher OC content it varied from 26% to 49%. Finally, the analysis allows us to conclude that among the manner of humates application, combined application to the soil and foliar treatments is the most effective. In this case, the effectiveness of humates exceeding 110% is observed in 95% of cases.

Acknowledgements. This research was funded by the Federal budget of the Russian Federation (CIT&S no. 121041300098-7).

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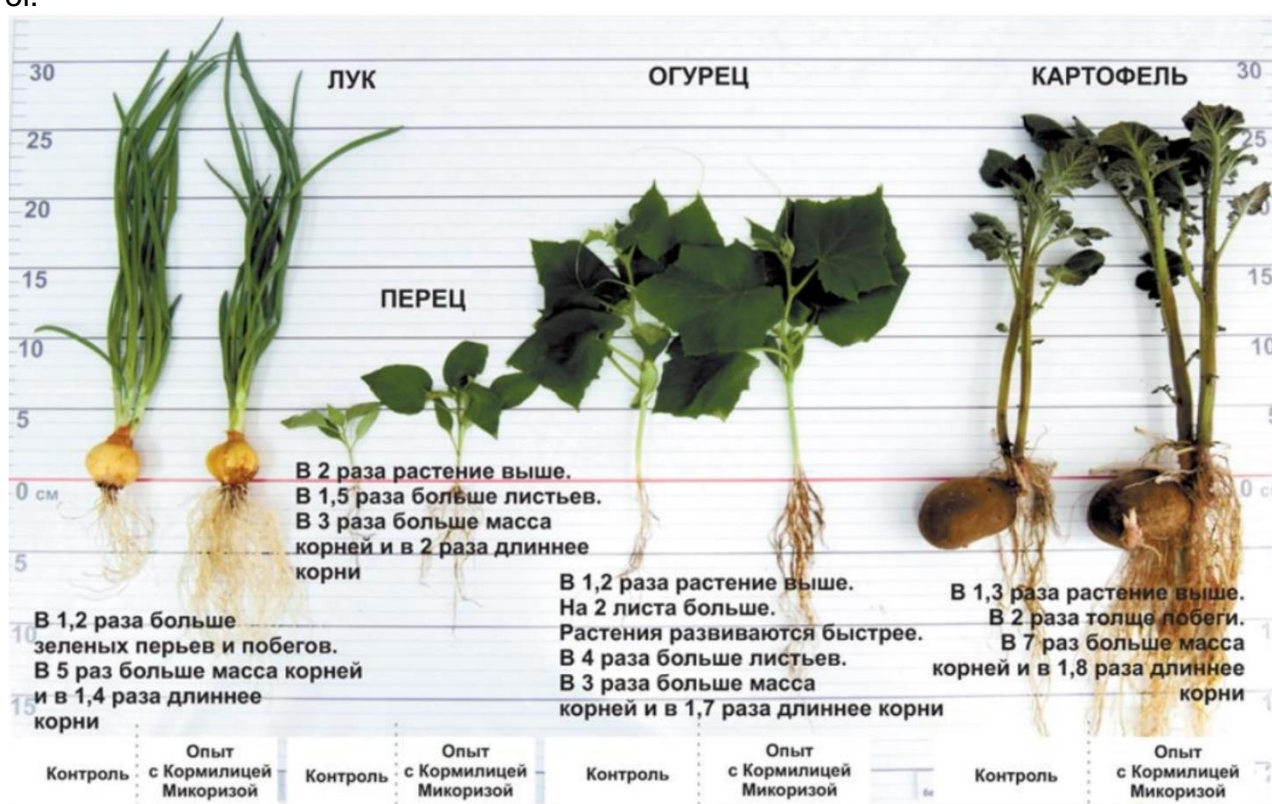


## A new Strategy in Agriculture from LLC «S.I.E. Bashlnkom»

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Keywords: humic acid, fitosporin, fungi of the genus Glomus

The company LLC "S.I.E. Bashlnkom" is developing a new direction in its product line related to "green technology" - GreenTech in agriculture. Preparations containing humic acid salts, fitosporin, endomycorrhizal fungi of the genus Glomus and more than 40 strains of beneficial soil microorganisms have been developed and tested. The tests were carried out on vegetable and berry crops, as well as on agricultural crops. The tests were carried out in a darkroom, in greenhouses and on plots in the open ground. The growth rates of the root system and the green mass of plants were investigated and analyzed. It was found that the use of our preparations allows to increase the root system of plants by 20-85%, and the green mass up to 90% relative to the control.



## Humic preparations to reduce phytotoxic aftereffects of herbicides

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Keywords: humic preparations, phytotoxic aftereffects, herbicides, toxicity reduction, protective properties, crop production.

The State Catalogue of Agrochemicals (as of 18.09.2024) registered 315 fertilizers based on humic acids, including organic 185, organomineral 92, mineral 24, complex 14. In addition, 4 more preparations have been registered as growth regulator pesticides based on humic acids. To investigate the influence of humic substances on the phytotoxicity of herbicide after-effects, an experiment was conducted, including preparations for seed treatment, treatment of vegetative plants and for remediation - cleaning from pollutants.

The effects of herbicides on subsequent crops in the rotation often cause significant yield reduction risks for sensitive crops. Reduction of crop rotations to a de facto two-link rotation system further increases these risks. The imidazolinones are a widely used group of herbicides. The half-lives of these highly toxic chemical compounds of this class depend on the conditions of the main degradation pathways (photolysis, hydrolysis and enzymatic degradation). For imazethapyr can range from 10 to 30 days, for imazamox from 10 to 45 days. The variability of drug residues, depending on the conditions of the year and soil type can be from 2 to 30%. By the next field season, their amount will already be below the sensitivity level of the chromatographic method of determination. However, minimal amounts of imazapyr can persist in soil for up to two years and manifest as severe phytotoxicity to sensitive crops. Imazamox is extremely toxic to higher aquatic plants and algae. On experimental sunflower crops, herbicides were used as weed control agents in the recommended and double maximum (as a simulation of overlapping "traces" of spraying). After harvesting the crops, winter triticale of Tornado variety was sown as a sideral crop with treatment of seeds and sowing with growth-stimulating agents of humic nature. After sideration operations on experimental plots soil samples were taken for phytotoxicity study. Indicators of germination reduction were determined according to GOST 32627-2014 "Methods of testing chemical products posing a threat to the environment. Terrestrial plants. Phytotoxicity test". In 3 weeks after incorporation of green mass of winter triticale, soil samples were taken and tested by germination of 25 white mustard seeds in Petri dishes in 5-fold repetition. The highest sensitivity, close to the control, was shown by the plants grown on the soil where the plants were treated only during the vegetation period. In the variant with the use of remediation preparation (humic complex liquid fertilizer of "Phoenix" brand), phytotoxic aftereffects were slightly above the experiment error for control oat seeds and within 8% toxicity for white mustard seeds. A continuation of the soil phytotoxicity evaluation experiment was conducted for the seeds of the tested plants. All 7 tested seed treatment preparations significantly reduced the toxicity index from 14 to 65%, however, when the same preparations were used after day 5-7 of the experiment, the toxicity index for mustard was practically unchanged, but with a noticeable tendency to increase. The toxicity index determined using oat seeds was practically not affected by treatment of seedlings with humic preparations. Short-term (according to GOST) experiments to establish toxicity, does not make it possible to assess possible delayed effects. The conducted experiments make it possible to draw positive conclusions about a promising approach to the use of preparations based on humic acids in the system including three directions of application - soil application, seed treatment, foliar treatment. The analysis of variance allowed to establish synergism of action at the level of 37%.

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## Synthesis and characterization of biologically active zinc compounds with different humic ligands

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Keywords: humic, zinc, wound healing, complexes

Wound treatment is a significant healthcare expense, often referred to as a "silent epidemic" due to its widespread impact on patient well-being and mental health. An estimated 1-2% of the population suffers from chronic wounds. Effective wound healing requires a combination of systemic and local therapies, including zinc-containing medications. Zinc plays a crucial role in human physiology, acting as a cofactor for enzymes involved in cell membrane repair, growth, proliferation, and immune function, all essential for wound healing.

Recent research focuses on enhancing the properties of biologically active metals by using ligands to create hybrid molecules. Humic substances, natural compounds with immunostimulatory and antioxidant properties, have emerged as promising ligands for zinc-based wound treatments. These substances exhibit good biocompatibility and can be used as stabilizers or for synthesizing coordination compounds. Their varying biological activity allows for fine-tuning therapeutic applications across different wound healing stages.

The goal of this study was to create and characterize biologically active zinc compounds using fractions of humic substances with different ligand properties. The research synthesized three types of compounds: zinc oxide nanoparticles stabilized with coal-derived humic acids (HAs), zinc complexes with coal HAs, and peat-derived fulvic acids (FAs).

The coal HAs proved to be effective ligands for synthesizing zinc oxide nanoparticles. The process allowed control over nanoparticle size, and the moderate zinc release rate in hydrophilic gels made these nanoparticles suitable for use in wound dressings at the scarring (remodeling) stage, potentially replacing conventional zinc oxide ointments. Both humic and fulvic acids also showed promise as ligands for zinc complexes, with the ligand profile determining their biological activity.

FA-based zinc complexes stimulated monocyte differentiation into macrophages, promoting antibacterial activity, making them suitable for early wound healing stages. In contrast, HA-zinc complexes inhibited macrophage formation and exhibited anti-inflammatory properties, useful in later stages to prevent excessive collagen formation.

The research demonstrated that the three types of zinc-based compounds with humic ligands can be applied at different stages of wound healing, supporting faster recovery as confirmed by in vivo tests. This approach could lead to a range of zinc-based treatments tailored to specific healing stages, improving overall wound care.

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## **Development of Methods for Standardizing the Active Pharmaceutical Ingredient Based on Humic Substances and Silver Nanoparticles**

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Keywords: humic substances, silver nanoparticles, standardization

**Introduction.** The problem of registering humic-based drugs is due to their complex structure and stochastic composition. Nanocomplexes of humic substances with silver (HS-AgNPs) exhibit antibacterial, wound healing and anti-inflammatory activities. To develop a drug based on these, it is necessary to develop methods for standardizing the main active components of the active pharmaceutical ingredient (API). Therefore, this study represents the first step towards solving the problem of standardizing humic preparations. The test sample (HS-AgNPs) was synthesized in the Laboratory of Natural Humic Systems of the Faculty of Chemistry, Lomonosov MSU. The goal of this study is to develop methods for standardizing the API and the finished dosage form to form a set of regulatory documents for a pilot-industrial regulation and a registration dossier.

**Materials and Methods.** The development of methods for quality control of the pharmaceutical substance and the finished dosage form is based on the general pharmacopoeial principles described in the State Pharmacopoeia of the Russian Federation, General Pharmacopoeial Monograph 1.1.0006 "Pharmaceutical substances" and in the pharmacopoeial monographs of individual types of drugs (gels, solutions, ointments, etc.). Given the nanostructure of the pharmaceutical substance, additional parameters characterizing quality, and hence the efficacy and safety of the drug, should include characteristics such as particle size and zeta potential. The initial stage of the study involved the development of general pharmacopoeial quality parameters for the substance: description, solubility, authenticity, transparency and color of the solution, pH of the solution of the substance.

**Results.** The following results were obtained when determining the quality parameters of the API. The substance samples are dark (almost black) crystalline powders, well soluble in water (with ultrasonic treatment) and aqueous alkali solutions, forming a dark brown colloidal solution. The particle size of the colloidal solution and zeta potential were determined under experimental conditions. It was shown that solutions in the lower concentration range, where spectrum analysis is possible, have acceptable optical densities. To determine the authenticity by UV spectroscopy, the method of calculating relative optical densities (ROD) 300/500; 350/500; 400/500; 450/500 was proposed. For color determination, the solution was diluted to a concentration of 0.05 mg/ml, and the color intensity should not exceed the intensity of solution B0. The pH value was determined to be between 6.8 and 7.20. The loss on drying should not exceed 10%.

**Conclusion.** Thus, approaches for standardizing the API based on humic substances and silver nanoparticles are proposed, which is a necessary step in the process of developing pharmaceuticals.

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## **The release determination of silver nanoparticles from different types of topical pharmaceutical form**

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Key words: silver nanoparticles; humic substances; ointment; gel; release

**Introduction.** Silver nanoparticles (AgNPs) have strong antibacterial and antiseptic properties, which makes them promising for medicine in the treatment of purulent-inflammatory and infectious processes, as well as the development of various ointments based on them. Silver as a heavy metal can have toxic effects, but toxicity is greatly reduced when using humic ligands in the production of bionanomaterials with AgNPs.

The goal is a study the release of AgNPs from an adsorption-based ointment with lincomycin and a hydrophilic carboxymethylcellulose-based gel, as well as to evaluate their potential therapeutic effect.

**Materials and Methods.** Two topical pharmaceutical forms have been developed: an emulsion ointment on the adsorption basis of vaseline and anhydrous lanolin with lincomycin and a hydrophilic gel based on carboxymethylcellulose. The active substance is bionanomaterial based on AgNPs and coal humic substances (CHP-AgNPs), synthesized in the Natural Humic Systems Laboratory of the Chemical Faculty of Lomonosov MSU. The release study of AgNPs was carried out using a 7 mL Franz vertical diffusion cell of closed type. A dialysis hydrophilic polyethersulfone membrane with a porosity of 450 nm, 25 mm in diameter, with a plastic ring placed on it in the range of 410-425 nm was used for the analysis. The contents of the cells were stirred using a magnetic stirrer at 400 rpm. The quantitative content of AgNPs was determined on a PE-5400UV spectrophotometer in 10 mm quartz cuvettes in the range of 410-425 nm in 2 nm steps. The concentration of released AgNPs from the SNP-AgNPs sample was estimated from the calibration graph.

**Results.** As a result of the study of AgNPs release from the emulsion ointment on the adsorption basis, the mean value was 0.63%, indicating the low systemic toxicity of Ag as a heavy metal, and the possibility of long-term application and staying ointment on the wound surface. The result of AgNPs release study from hydrophilic carboxymethylcellulose-based gel was 11.13%, indicating the high ability of AgNPs to be released from the dosage form and exert rapid antiseptic effect by mixing in the wound with biological fluids.

**Conclusion.** Thus, the first dosage form (adsorption-based ointment) is the most preferable for the treatment of sluggish chronic purulent-inflammatory processes and bedsores. The putative mechanism of action of this ointment is most likely that the ointment adsorbs the wound contents along with infectious agents and within the ointment, the active ingredient CHP-AgNPs together with lincomycin exerts antibacterial and antiseptic effects. The second dosage form (hydrophilic carboxymethylcellulose-based gel) is the most preferable for the treatment of open wounds, including those that are large in area and require frequent application.

**Acknowledgements.** This work was supported by the financial Russian Science Foundation (Grant No. 20-65-47052).

## **New biopreparations based on bacteria and humates to increase carbon sequestration by woody plants**

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Keywords: biopreparation, humic substances, rhizosphere bacteria, bacteria stimulating plant growth, carbon deposition, woody plants

Improving the quality of tree planting material for carbon sequestration through reforestation can help solve environmental problems, including the need to reduce concentration of carbon dioxide in the atmosphere.

The object of the study is woody plants - seedlings of common pine (1-4 years old), nonstandard pine (1 year old), pyramidal poplar planted in the open ground, as well as plants grown in containers - linden (broad-leaved, Caucasian), horse chestnut, oak, aged 1-3 years.

The aim of the research is to develop and test complex preparations for agroforestry ecosystems, increasing carbon storage based on bacteria *Pseudomonas protegens* DA1.2, *Pseudomonas* sp. 2, *Pseudomonas* sp. 4CH and humic substances.

As a result of the work, we observed higher efficiency of application of humates and bacteria in combination compared to the application of each separately. It is noted that one strain of bacteria (DA1.2) had a growth stimulating effect on some species of woody plants (pine, linden - up to 160 and 58 % respectively), another strain (4CH) - on others (chestnut up to 58 %). The influence of the age of woody plants was studied on the example of common pine (1-4 years old). It is shown that the maximum growth stimulating synergetic effect of application of humates and DA 1.2 bacteria is observed for non-standard (less than 8 cm) annual pines - increase in length by 350 % and shoot and root mass by 109 and 171 %, respectively; in pines 2-4 years old the effect is less significant (49-147 %).

On the example of common pine under the action of preparations, not only increase in length and mass of woody plants is shown, but also an increase in carbon content (up to 16,4-17,4 %) in plant biomass, which is very important for solving the problem of carbon sequestration.

Increase in NBI and chlorophyll in horse chestnut and red oak (13-23 %) was detected under the influence of humate and bacteria-based biopreparation, but growth-stimulating effect was observed only in chestnut. The most susceptible to biopreparation treatment were common pine, broadleaf linden and horse chestnut, while poplar and oak were not susceptible.

An assessment of the combined influences of humates and bacteria on the productivity of agricultural plants showed previously their greater effectiveness compared to the use of each of them separately. This prior study demonstrated the additive effect of a combination of bacteria and humates on pine seedlings. In the present study, this pattern was revealed on a larger number of plant species (Scots pine, large-leaved linden, and horse chestnut seedlings). However, the applied treatments did not exhibit a growth-stimulating effect on all studied species. Plants of poplar, rowan, and red oak turned out to be unresponsive to treatments. At the same time, the fact that one strain of bacteria showed a growth-stimulating effect on some plant species and had a different influence on others indicates the need for selecting the necessary bacteria for each species of woody plant, to exert the appropriate growth-stimulating activity towards each. To date, information has been accumulated on the growth-stimulating effect of a huge number of rhizosphere bacteria, among which bacteria have been found that can stimulate the growth of woody plants in combination with humates; this can lead to an improved quality of tree planting material for reforestation and increased carbon sequestration. Our results indicate promising research in this direction.



## The impact of binary polymer-humic compositions based on xanthan gum on heavy metals mobility in a model experiment

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Keywords: polyelectrolytes, phytotesting, soil detoxication

One of the most important problems of our time is erosion and land degradation. In this regard, techniques and technologies aimed at preserving soil and their fertility are actively developing. One of the promising methods is the usage of synthetic and natural polymers. One of these polymers are humic substances, in the form of industrial preparations, which are widely used as biostimulants. It is also possible to use other biopolymers as soil meliorants, in particular heterofunctional polysaccharides such as xanthan gum. Due to the property of forming net structures, it is able to retain moisture, and also has a beneficial effect on the soil structure.

The aim of the study is to evaluate the impact of two-component polyelectrolyte compositions based on xanthan gum (XG) and 3 types of humic products (HP) on the detoxifying properties of sod-podzolic soil in a model experiment with heavy metal (HM) pollution and to identify their potential as soil meliorants in comparison with individual polymers.

The object of the study was the arable horizon of a sod-podzolic soil. Following 4 polyelectrolytes have been used: XG and 3 HP different in organic matter source: "Sakhalin humate" from lignite (Sh), "Peat gel" from peat (Pg) and "Lignohumate" from lignosulphonate (L) and combinations: XG + Sh, XG + Pg and XG + L.

HPs were examined for several properties such as content of organic carbon, elemental composition, content of acidic functional groups.

The model experiment was carried out as follows: 100 grams of soil were mixed with 1 gram of dry polymers, then moistened with 15 milliliters of water. Incubated for 2 weeks at room temperature. In a parallel series of experiments, soil-polymer mixtures were spiked with nitrate solutions of Cu, Zn, Pb at a dose of 150 mg/kg of each element. The experiment was carried out in three parallels. After incubation soil pH, content of organic carbon and mobile species of heavy metals were determined. Also phytotoxicity of soil-polymer mixtures was assessed in bioassay with a test culture (*Raphanus sativus*).

The following results were obtained during the study:

1. The highest content of organic carbon belonged to L (29,81%), the lowest belonged to Pg (8,36%), but Pg had the highest content of nitrogen (1.49%). Also Sh had the largest number of acidic functional groups (4,12 mg\*eq/g).

2. The introduction of all types of studied polymers in a dose of 1g/100g of soil increases the total carbon content in soil (by 0.5%-0.9% compared with the control).

3. Among the individual polyelectrolytes the most effective binding of Cu, Pb and Zn was showed by Sh and made up accordingly 34%, 21% and 20% of binding. Pg and L alone performed less effective but in binary composition with XG their efficiency in decreasing mobility of heavy metals enhanced by an average of 10%.

4. Both individual polyelectrolytes and their binary compositions had a stimulating effect on the test culture. This influence affected the length of the stems of the seedlings more than the roots. L alone was the most effective polyelectrolyte in this case and enlarged stems by 2,2 times. The compositions with XG did not show a better effect on the growth of seedlings compared to individual polyelectrolytes.

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## Effect of leonardite humate as a priming agent on the yield and quality of radish under open-field conditions

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Keywords: Box-Behnken design, field experiment, Sakhalin humate, sugars, ascorbic acid

Currently, a transition to environmentally sound technologies of crops cultivation that do not harm the environment is of urgent issue. Therefore, it is relevant to search for new approaches and materials in the field of agriculture that allow increasing crop yields.

Seed priming has been numerously reported to be a promising way to increase crop productivity due to promoting the rapid germination and emergence of seedlings, and increasing resistance to stress in various adverse environmental conditions. Various substances are used as priming agents, in particular, humic substances. They are multifunctional biostimulants protecting plants from environmental stress. Though many laboratory studies demonstrated beneficial effect of priming, field experiments are still lacking. The results of laboratory studies often cannot be extrapolated to field conditions, so the result of a field experiment can be unexpected. The aim of the study was to assess the effect of Sakhalin humate (SH) as a priming agent on the yield and quality of radish crops.

Radish seeds (*Raphanus raphanistrum* ssp. *sativus* L, cv. "Sophit") were used for the study. In laboratory conditions, optimal seed priming conditions (SH concentration, duration and temperature of priming) were determined using Box-Behnken design. The field experiments were conducted on Urban Technosol (pH 7.4, 38 g/kg OC, 570 mg P<sub>2</sub>O<sub>5</sub>/kg and 172 mg K<sub>2</sub>O/kg). Radish crop was harvested at the 24<sup>th</sup> day after sowing (DAS) or at the 32<sup>nd</sup> DAS. During radish cultivation, the rate of germination was monitored. At the end of the experiment, germination, weight of root crops were estimated, and yield was calculated. To assess the quality of root crops, the content of dry matter, pigments (carotenoids and chlorophyll), sugars and ascorbic acid were measured.

Depending on the optimized parameter (vigor index, germination, root and shoot length), the optimal concentration of SH for priming radish seeds lay in the range from 0.5 to 1.0 g/l. For the field experiment, a concentration of 0.5 g/l HS was used, at which optimal germination values were obtained. SH treatment reduced the final germination of radish in field conditions, while the yield did not differ significantly from the control. Depending weather conditions, the content of sugars or ascorbic acid changed due to seed priming with SH indicating partial adaptation of plants to unfavorable temperature and water conditions.

The conducted studies showed lack of SH efficiency as priming agents in the case of using priming as the only method of stress mitigation.

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## Natural substances with antibacterial and regenerative effects

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Keywords: humic substances, silver nanoparticles, kalanchoe, thyroid hormones, antibacterial activity, wound healing

Nowadays, there is a tendency to search for natural compounds that have wound healing and antibacterial action. Such compounds are humic substances, kalanchoe (*K.pinnata*) and thyroid hormones (thyroxine and triiodothyronine). The present study summarizes the gels under development with wound healing and antibacterial effects.

The gel containing humic acids stabilized by silver nanoparticles was found to have antibacterial activity against to the methicillin-resistant strain of *Staphylococcus aureus* (MRSA). In experiments on laboratory animals, the gel showed proliferative activity (Figure 1).

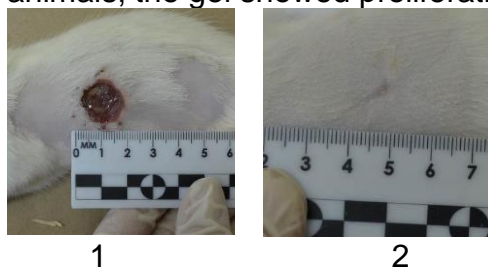


Figure 1. Dynamics of healing of burn wounds in rats on the background of treatment with the developed gel containing humic acids stabilized by silver nanoparticles (1 – 8 days; 2 – 27 days)

The results of *in vivo* studies with modelling of a burn wound on rats and a limited clinical trial showed that local application of the developed gel based on *K.pinnata* juice as a part of complex therapy is characterized by high therapeutic efficacy (Figure 2).



Figure 2. Dynamics of healing of burn wounds in rats on the background of treatment with the developed gel containing *K.pinnata* (1 – 7 days; 2 – 14 days; 2 – 27 days)

A gel containing thyroid hormones in its composition has shown good wound healing activity in preliminary experiments on laboratory animals on the model of thermal burns.

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## Responses of plants and microorganisms to soil treatment with polymeric ameliorants

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Keywords: sorbent, humate, hypan, bioassay, phytotest, microbiome, emission CO<sub>2</sub>, toxicology

The use of polymeric materials (PM) as soil structure stabilizers has been shown to help prevent nutrient loss, soil erosion, and soil deformation (Sikder et al. 2021). PM include both synthetic and natural PM. In addition, it is often suggested to use binary formulations. It is believed that humic substances improve efficiency and safety of synthetic polymers. The objective of this study was to perform an ecotoxicological assessment of PM. The work assesses the phytoeffect of hydrolyzed polyacrylonitrile (HYPAN) and its composite with humate "Sakhalinsky" (SH) on sod-podzolic soil contaminated with heavy metals (HM) at 2, 4 6 approximately permissible concentrations (APC) of copper, zinc and lead.

The introduction of HM into the soil in doses of 2 and 4 stimulates the growth of white mustard *Sinapis alba* L. roots. Inhibition was observed only at 6 APC. The positive effect of polymers was observed at all levels of HM load. The greatest detoxifying effect was observed against the background of 6 APC.

Microbial respiration (MR) is a sensitive measure of soil contamination and soil health. Based on MR the microbial biomass carbon content (C<sub>mic</sub>) and the microbial metabolic quotients QR were calculated. As it can be seen from Figure 1, polymers improved the condition of the microbiome. Moreover, at doses 4 and 6 HM the effect of the binary structure was higher than that of HYPAN alone.

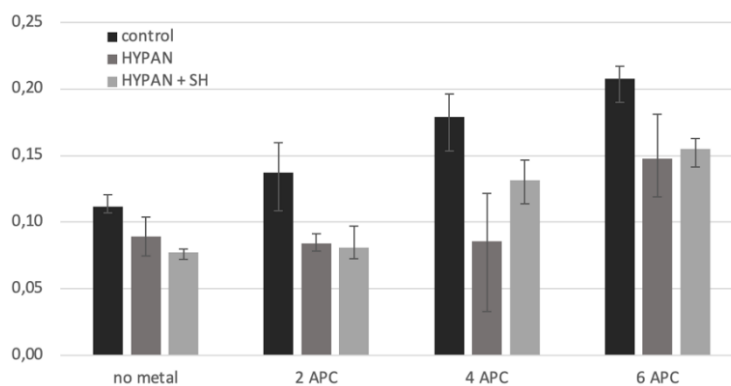


Figure 1. Effect of HM and polymers on the microbial metabolic coefficient of soil

Thus, the positive effect of polymeric ameliorants in polluted soil was demonstrated, while at high doses, the best effect is achieved by the combined use of a synthetic polymer and humic product.

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## The Influence of Silver-Containing Bionanomaterials Based on Humic Substances on Biofilm Formation in Opportunistic Pathogens

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Keywords: humic substances; silver nanoparticles; opportunistic pathogens; antibacterial activity; biofilm formation

**Introduction.** The uncontrolled use of antibiotics has led to a global problem of antimicrobial resistance. One of the main mechanisms of bacterial resistance is the formation of biofilms. In order to prevent the growth of antimicrobial resistance, it is crucial to develop new antibacterial agents that are capable of inhibiting the formation of biofilms. Promising candidates for these antibacterial agents are new bionanomaterials made from natural humic substances and silver nanoparticles. These substances have the potential to not only directly kill microorganisms but also penetrate biofilms and inhibit their formation.

The goal of this study is to research influence of silver-containing bionanomaterials based on humic ligands on biofilm formation in the most dangerous opportunistic pathogens.

**Materials and Methods.** To study the antibacterial effect, 12 samples of the active pharmaceutical substances (HS-AgNPs) were taken, which are bionanomaterials based on silver nanoparticles ultradispersed in a matrix of humic substances. These bionanomaterials were synthesized in the Laboratory of Natural Humic Systems of the Faculty of Chemistry, Lomonosov MSU.

For the study, there were used standard strains of opportunistic microorganisms: *Escherichia coli*, *Staphylococcus aureus*, *MRSA (Methicillin-resistant Staphylococcus aureus)*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa* and clinical isolates of following types of bacteria: *Escherichia coli*, *Staphylococcus aureus*, *Acinetobacter baumannii*, *Pseudomonas aeruginosa* and *Klebsiella pneumoniae*, isolated in the bacteriological laboratory of SSMU clinics from various patient materials (urine, sputum, wounds, the uterine cavity, and blood). A panel of microorganisms relevant to clinical practice and capable of forming biofilms was selected. Then, the studied substances were screened for antibacterial properties. We also studied the effect of bionanomaterials on the bacterial cell wall, biofilms, and the viability of bacteria inside them.

**Results.** As a result of screening the antimicrobial activity of bionanomaterials, an antibacterial effect was discovered for 11 of the 12 substances studied. The substances with the highest antimicrobial activity are sample CHP-pHQ-FE-AgNPs (p-hydroquinone derivative of HS-AgNP synthesized by Fenton reaction) against gram-negative bacteria and sample CHP-AgNPs-MW (microwave-synthesized HS-AgNP) against gram-positive bacteria. Sample CHP-oHQ-FE-AgNPs (o-hydroquinone derivative of HS-AgNP synthesized by Fenton reaction), being a sample with the broadest spectrum of antimicrobial activity, damages the cell wall of bacteria such as *MRSA*, *K. pneumoniae* and *P. aeruginosa*. Sample CHP-pHQ-FE-AgNPs suppresses the biofilms formation and destroys biofilms of all studied gram-negative microorganisms. Sample CHP-AgNPs-MW suppresses biofilm formation and destroys biofilms of all studied gram-positive microorganisms. Sample CHP-pHQ-FE-AgNPs reduces the viability of gram-negative bacteria in biofilms. Bionanomaterial CHP-AgNPs-MW reduces the viability of gram-positive bacteria in biofilms.

**Conclusion.** Thus, bionanomaterials based on silver nanoparticles ultradispersed in the matrix of humic substances demonstrated antibacterial properties against all selected opportunistic microorganisms capable of forming biofilms.

## The use of humic substances to suppress the vital activity of mycelial fungi as part of a consortium

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Keywords: fungi, humic substances, inhibition

There is a pool of studies confirming the inhibitory effect of HSs on various mycelial fungi (Table 1 [1-4]). The inhibition of fungi is carried out, among other things, due to the non-covalent binding of hydrolytic enzyme molecules to HSs and the inactivation of these biocatalysts, leading to a decrease in the number of available substrates entering fungal cells [5,6]. At the same time, sufficiently high concentrations of HSs (5-10 g/l) must be introduced into the system.

Table 1. Inhibition of growth of filamentous fungi by the HSs

Fungi	Influence of HSs	Reference
<i>Aspergillus</i>	Inhibition of cell growth and enzyme synthesis	[1]
<i>Penicillium</i>	Inhibition of cell growth	[2]
<i>Fusarium</i>	Inhibition of growth	[3]
<i>Alternaria</i>	No growth inhibition in presence of 200 mg/L of HSs	[4]

When suppressing cells in stable consortia, great efforts are required [6]. Thus, in addition to the introduction of HSs, potassium persulfate and hexhistidine-containing organophosphate hydrolase were additionally introduced to suppress the metabolism of landfill consortia containing fungi of the genera *Aspergillus*, *Trichoderma*, *Penicillium*, *Fusarium*, *Alternaria*, hydrolyzing lactose-containing molecules responsible for quorum in the consortium [6].

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## Application of the salting-out method for extracting Fe(III) complexes with humic substances from aqueous solutions for additional purification from salts

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Keywords: Humic substances, salting-out, iron deficiency anemia, iron(III) complexes

Humic substances (HS) are natural compounds with high complexing ability due to the presence of multiple functional groups. They exhibit antioxidant properties, are non-toxic within natural concentration ranges, and could serve as an alternative to polymaltose iron supplements for the treatment of iron deficiency anemia (IDA), particularly for patients with sugar intolerance. The salting-out method effectively extracts Fe(III)-HS complexes from aqueous solutions with minimal inorganic salt content.

The aim of this study is to develop a method for synthesizing and purifying Fe(III)-HS complexes with high bioavailable iron content and a high degree of salt removal. Two synthesis methods for Fe(III) complexes with macroligands (peat fulvic acids (FA), polymaltose (PM)) were considered.

The one-step method involves the hydrolysis of Fe(III) in the presence of macroligands in an alkaline medium followed by lyophilization. The two-step method involves precipitating Fe(OH)<sub>3</sub>, adding it to the macroligand in an alkaline medium, and drying the precipitate in an oven. The target product was precipitated using organic solvents with varying polarity (ethanol, isopropanol, acetone).

The composition and iron content of the samples were analyzed using X-ray diffraction and inductively coupled plasma atomic emission spectrometry. Results showed that the two-step synthesis method using isopropanol (V(alcohol:water) = 0.5) yielded samples with the highest iron content of 33.5%, while ethanol resulted in an iron content of 15.6-27.2%. Comparison of FA-Fe complexes obtained with and without the salting-out method demonstrated that salting-out provides a purer product due to a significant reduction in salt content. The mass of dry samples after salting out with ethanol (V(alcohol:water) = 2) decreases from 14.7 to 7 g and from 17.5 to 10 g, indicating successful purification of the complexes from impurities and inorganic compounds, thereby increasing the concentration of the target component — the Fe(III)-HS complex.

The polymaltose sample, despite the absence of a salt phase, exhibited lower iron content compared to humic ligands (Table 1).

Table 1. Characteristics of samples obtained through one-stage (O) and two-stage (T) synthesis, extracted using salting-out (s) and without salting-out (k).

Code	C(Fe), %	I(NaCl) integral
O-FA-Fe-k	6.7-7.5	2281-2648
O-PM-Fe-s	7.8	-
O-FA-Fe-s	18-22	31
T-PM-Fe-s	11-15	-
T-FA-Fe-s	12.7-33.5	6-24

Thus, salting-out is a promising method for isolating water-soluble iron(III) oxyhydroxides with humic macroligands, offering potential for their use in the treatment of iron deficiency anemia.

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## Application of humic substances for inhibition of hydrolytic enzymes of filamentous fungi

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Keywords: antifungal effect, hydrolytic effects, water and soil humic substances, inhibition

Filamentous fungal hydrolases represent one of the most important and potential targets for the development of antifungals, as they provide these microorganisms with accessible nutrients outside the cell [1]. It is known that some humic substances (HSs) are capable of inhibiting hydrolytic enzymes of fungi (Table 1).

Table 1. Inhibition of fungal enzymes by HSs

HSs [References]	Enzymes	Inhibition
Commercial HSs, 20 % [1]	$\alpha$ -amylase	59%
	proteinase	86.7%
Commercial humic acid (HA), 2 g/L [2]	cellulase	reversible inhibition
	protease	reversible inhibition
HSs from Peat [3]	$\beta$ -glucosidase	75 % competitive inhibition
HSs from soil [4]	protease	EC <sub>50</sub> = 153 mg/L for soil HSs EC <sub>50</sub> = 6360 mg/L for aqueous HSs
Humic-like compounds from manure 0.5-5 g/L [5]	cellulase	Inhibition of anaerobic cellulose hydrolysis
	lipase	enzymatic tributyrin hydrolysis was inhibited
HA from soil [6]	$\beta$ -glucosidase	13%
Fulvic acids from soil 0,2 g/L [7]	$\beta$ -glucosidase	25.7%
Commercial HA, 10 g/L [8]	cellulase	36.3%

The inhibition of various enzymes can be due to several reasons, namely: partial shielding of the active centers of enzymes by HSs molecules, modification of the conformational structure of the enzyme during the formation of humic-enzyme complexes [7], as well as preferential complexation of metals entering the active center of enzymes with HSs.

Acknowledgements. The research was funded by the Russian Science Foundation (23-14-00092).

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## Study of compositions of silver nanoparticles- humic substances to minimize nanotoxicity

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Keywords: humus, nanosilver, nanotoxicity

With the progress of nanomedicine, various nanobiomaterials with antibacterial properties have been developed and began to be used in clinical practice. Among them, the leading positions belong to silver nanoparticles (AgNPs). This is due to the fact that AgNPs have a strong inhibitory effect on most pathogenic bacteria and can retain antibacterial properties for a long time. In addition, cases of resistance to silver nanoparticles are much less common than to antibiotics. One of the main problems in the synthesis of silver nanoparticles with high antibacterial activity is the control of size below 10 nm while maintaining their aggregative stability. In this regard, the choice of ligands and stabilizers in the synthesis of silver nanoparticles is of particular relevance.

Humic substances (HS) are natural polyelectrolytes with unique physico-chemical and biological properties. They are complex molecular ensembles of the oxidation products of biomacromolecules. The presence of aromatic structures highly substituted by carboxyl and hydroxyl groups provides good complexing and reducing properties of GW. In this regard, they are widely used for the synthesis of metal nanoparticles. A unique property of HS is a very favorable biosafety profile: they are non-toxic in a very wide range of concentrations. This property is very important for overcoming the effect of "nanotoxicity", which is especially important when silver nanoparticles enter the environment with "hospital waste".

In this work we synthesized silver nanoparticles in the solutions of sodium humates (12 g/L) and silver nitrate (6 g/l) as a precursor using conventional heating (water bath) under various temperatures. The antibacterial activity of the synthesized AgNPs was measured with regard to resistant strain of MRSA. The obtained results are shown in Table 1.

Table 1. Antimicrobial activity of AgNP obtained in the solutions of HS with a use of conventional heating at different temperatures

Medication	Temperature, °C	IC50, μM (Ag)	IC90, μM (Ag)
CHP-Ag-40	40	195	282
CHP-Ag-50	50	209	293
CHP-Ag-60	60	490	803
CHP-Ag-70	70	628	905
CHP-Ag-80	80	753	944

The obtained data show that antibacterial activity of the synthesized silver nanoparticles diminishes along an increase in the synthesis temperature. This could be connected with the larger size of the AgNPs synthesized under elevated temperatures. This phenomenon should be further investigated.

Acknowledgements. This work was supported by the Russian Science Foundation (grant #20-63 47070)

## Effect of the EldORost humic preparation on the resistance of wheat plants to root rot

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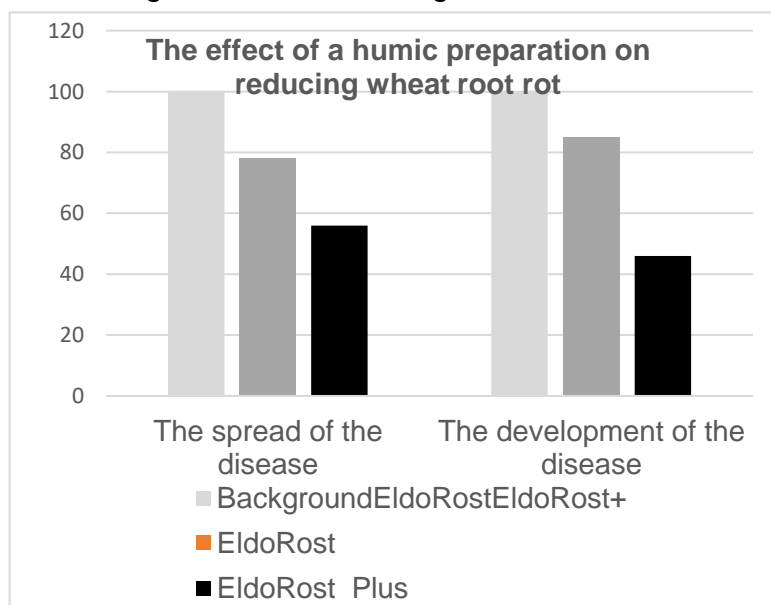
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<sup>3</sup>InterAgroTech LLC, Almaty, Kazakhstan

Keywords: humic preparation, EldORost, wheat plants, root rot

It is known that wheat grown in Kazakhstan is the main crop for the republics of Central and Central Asia. One of the main ways to increase wheat productivity in Kazakhstan is the transition from extensive to highly intelligent farming systems. The studies were carried out in the conditions of northern Kazakhstan "(N51 ° 32'51.77"; E71 ° 03'27.50 ") since 2017 on the land use of nonprofit institution LLP "NPTsZH im. A.I. Baraev.

In the experiments of 2019-2020, spring wheat of local selection was cultivated. The research was carried out at the precision farming landfill in the southern carbonate chernozems in field experiments with the size of accounting plots of at least 100 m<sup>2</sup>. The seeds of the plants were etched before sowing using recommended mordants such as Inshur Perform, 12% 0.4 l/t + Tabu, 0.5 l/t. This option acted as a background. The studied humic preparations EldORost and EldORost + were administered together with the background variant in recommended doses.



It was found that the treatment of wheat seeds with EldORost provides a reduction in the development and spread of root rot by 22 and 15%, and with EldORost Plus by 44 and 54%. Conclusions: As a result of field trials of EldORost humic preparations, their positive role has been revealed as a means of reducing the spread and development of root rot in spring wheat. Thus, in the conditions of northern Kazakhstan, the protective role of EldORost humic preparations in the damage of wheat plants by pests and diseases has been revealed.



## Development of effective organic fertilizers on the basis of humic substances in cultivation of maize and sorghum crops for seeds

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Keywords: organic fertilizers, foliar treatment of plants, humic substances, maize, sorghum crops.

Currently in Kazakhstan, more than 95% of farms in the country use expensive industrial mineral fertilizers. Excessive use of mineral fertilizers in the southern regions of the country has led to almost complete destruction of species diversity of native soil biota and, as a consequence, to the degradation of the qualitative composition of soil organic matter. The problem of effective use of mineral fertilizers is central to crop production. Intensive chemicalization, although it allowed solving the problem of crop yields, but at the same time disrupted the ecological balance of species diversity of terrestrial biota.

The use of organic fertilizers containing humic substances has a favorable effect on the growth and development of plants, are not toxic to insects, animals and humans. In the presence of humic substances, the coefficient of assimilation of mineral nutrition elements by plants increases sharply.

Humic substances for the new-generation domestic organic-mineral fertilizer were isolated from highly oxidized brown coal using special neutral salt solutions, rather than by shelling, in order to reduce the content of the lipid fraction harmful to plants. In addition to humic substances, the new fertilizer contains a full complex of vital (or essential) trace elements and stimulating starter (initial) amounts of basic plant nutrition elements (NPK) in a form readily available to plants. Universal Organic Mineral Fertilizer is fully soluble in water and environmentally safe. It can be used for all types of crops in different agroclimatic zones, the optimal concentration is only 0.0001 % (mass).

Organic fertilizer can be used for pre-sowing seed treatment, foliar treatment during the growing season as an independent fertilizer and post-harvest soil treatment. Its application does not require changing existing agro-technologies, it is compatible with any plant protection preparations and other agrochemicals. It requires 0.2 l/t for pre-sowing seed treatment, 0.15 l/ha for grain spraying, and 0.4 l/ha for post-harvest soil treatment.

The effect of universal organic-mineral fertilisers in the production of maize (*Zea mays L.*) seeds and sorghum crops: sugar sorghum (*Sorghum saccharatum Jakushev.*) and Sudan grass (*Sorghum sudanense Jakushev.*) was studied. Corn in Kazakhstan is the main source of succulent fodder and mixed fodder, as well as various food products. Sorghum can be used in the food industry, fodder production and bioenergy. Sorghum plants are characterized by high and stable yield and exceptional drought and salt tolerance. The main advantage of sorghum grain is its high-energy value due to its high starch content. Sudan grass is the third promising high-yielding agricultural crop suitable for cultivation in the conditions of semi-arid and arid zones Sudan grass is among the most promising fodder crops due to its high ecological plasticity and herd ability, ability to form green mass during the summer depression of perennial grasses.

The conditions of pre-sowing treatment of seeds of cucurbit, sorghum and Sudan grass with new universal organic-mineral fertilizer both alone and together with dressing agents taking into account the norms of their application have been selected.

Preliminary data allowed characterizing the new organic-mineral fertilizer as a promising one with pronounced properties of plant growth and development regulator. As, it was experimentally established, the yield of cucurbit, sorghum and Sudan grass increased on average by 30-50 % and more, chlorophyll synthesis was accelerated, and maturation of the crop was reduced by 10-12 days.

## **The influence of humic substances and based on them bionanomaterials with silver nanoparticles on the type of immune response**

Zykova M.V.<sup>1</sup>, Trofimova E.S.<sup>1,2</sup>, Danilets M.G.<sup>2</sup>, Ligacheva A.A.<sup>2</sup>, Mihalyov D.A.<sup>1</sup>,  
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Keywords: humic substances; silver nanoparticles; immune response

**Introduction.** Screening studies that allow identifying leading molecules are of great importance in the creation of new medicinal substances. One of the very important parameters of a medicinal substance is also its effect on the type of immune response. Macrophages, which are heterogeneous and universal cells and can undergo both phenotypic and functional changes in response to microenvironment signals, are very effectively used for these purposes. The type of developing immune response depends on the type of macrophage activation in the first phase of immune inflammation: by producing IL-12 or IL-10, they contribute to the development of Th1 or Th2 type of immune response.

The goal of this study is a comparative study of the humic ligands influence and created on their basis bionanomaterials with silver nanoparticles (AgNPs) on the type of immune response in a culture of mouse peritoneal macrophage cells.

**Materials and Methods.** A study was conducted of humic ligands, as well as bio-nanomaterials with AgNPs synthesized on their basis (HS-AgNPs). Among the basic matrices were humic substances (HS) from various types of peat and coal, as well as coal HS modified with various quinones. These bionanomaterials were synthesized in the Laboratory of Natural Humic Systems of the Faculty of Chemistry, Lomonosov MSU.

In immunotropic activity study C57BL/6 female mice aged 8-10 weeks were used. Peritoneal macrophages were harvested by lavaging the mouse peritoneal cavity with ice-cold physiological saline. After 48 hours of incubation, nitric oxide (NO) production was assessed based on the nitrite content in the supernatant, cell proliferation, and arginase activity. Nitrite levels in the cell supernatants were determined by the Griess reagent method (Sigma-Aldrich, USA). Arginase activity was assessed in the macrophages' lysates using method of urea concentration determination using the Urea-450 test system (Bio-La-Test, Czech Republic) according to the protocol provided with the test system, applying the ChemWell 2910 analyzer (Awareness Technology, USA) at a wavelength of 540 nm.

**Results.** It was established that some HS samples promote the antigen-presenting cells polarization according to the classical type (M1) by increasing the activity of NO synthase and inhibition arginase. Moreover, all these samples don't have a toxic effect on cells. The functions of macrophages (M1), which are traditionally associated with such activation as phagocytosis of microorganisms, microbicidal activity, induction of inflammation, antitumor activity, are stimulated by Th1 cytokines, primarily IFN- $\gamma$ , as well as IL-1 $\beta$ , IL-6, TNF- $\alpha$ , IL-8, IL-12. But, some HS-AgNPs samples on the contrary, activate the alternative properties of macrophages (M2). Moreover, almost all of these samples, cause a significant inhibition of the proliferation of the tested cells. The properties of M2 activators are aimed at the formation of the extracellular matrix, repair and remodeling of tissues, suppression of inflammation, stimulation of vascular formation, phagocytosis of apoptotic cells, synthesis of anti-inflammatory cytokines - IL-10, TGF- $\beta$ , IL-4, IL-1ra.

**Conclusion.** The conducted screening study made it possible to identify leading molecules for the development of medicinal products with antibacterial, anti-inflammatory and wound-healing properties.

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для анализа природных объектов на содержание органических веществ (в том числе ПАУ, пестицидов, микропластика, ПХБ, нефтяных углеводородов) и элементов (Al, As, Sb, Cd, Ca, Cr, Co, Fe, Cu, Pb, Mg, Mn, Hg, Ni, V, Zn).

### 2 Оборудование для автоматизированной пробоподготовки

системы микроволнового разложения проб, системы упаривания растворителей в токе азота и в вакууме, системы твердофазной и жидкостной экстракции под давлением, гомогенизаторы и др.

### 3 Системы очистки воды HyperPureX

позволяют получать воду I, II, III типа для различных задач лаборатории и в любом количестве.

### 4 Расходные материалы для аналитических приборов

колонки для ВЭЖХ и газовой хроматографии, лампы с полым катодом, дейтериевые лампы для спектрометров, кварцевые и стеклянные кюветы для спектрофотометрии и спектрофлуориметрии.

### 5 Автоматизированные анализаторы

для процессов «мокрой» химии и определения неограниченного числа параметров в объектах окружающей среды: щелочь, аминокислоты, аммиак, анионные поверхностно-активные вещества (ПАВ), карбонаты, ХПК, хлориды, общий органический углерод, цианиды, железо, мочевины и многие другие.

### 6 Флэш-хроматографы и препаративные хроматографы

для очистки продуктов органического синтеза, а также выделения биологически активных веществ из природного сырья.

### 7 Оборудование для твердофазного пептидного синтеза

а также реагенты для его проведения.

**По вопросам подбора, поставки и запуска оборудования обращайтесь в компанию ООО «ЭЛЕМЕНТ»!**



**Sakhalin Humates Group of Companies was established in 2000 and exclusively produces and distributes environmental friendly natural organo-mineral fertilizer Humate Sakhalinsky. The goal of Sakhalin Humates GC is manufacture and development of highly effective and environmental friendly products based on leonardite.**

Leonardite mining is carried out on the Sakhalin island, Russian Federation. All stages of extraction and selection of raw materials are carefully monitored by our specialists.



Sakhalin Humate GC products have a high content of humic substances and are available in various formulations (powder, aqueous solution, granules).

Especially for agriculture, the SAKHALIN HUMATES Group of Companies developed Potassium Humate and Sodium Humate. These preparations are produced under the brand name AGRO and are positioned as a line of professional agrochemistry.

Distinctive features of humates of this line are high degree of oxidation of hydrocarbon chains and increased content of low molecular weight humic acids.

Humate "Sakhalinsky" under the AGRO trademark contain an optimum set of microelements in chelated form: silicon, iron, magnesium, sulfur, zinc, cobalt, copper, manganese, etc.

It goes well with fungicides, herbicides, growth regulators, with urea and alkaline microelement solutions.

The preparations have successfully passed a full range of agrotechnical tests and are recommended for widespread implementation, both for reclamation and restoration of depleted and infected lands, and as an effective accelerator of plant growth and development.



The use of humates significantly increases uptake of mineral nutrition and productivity of plants. The high effectiveness of their use is confirmed both with the facts and figures of scientific reports of the best agricultural chemists and soil scientists of Russia, as well as by the positive reviews of agricultural enterprises that already use Potassium Humate and Sodium Humate ® AGRO. Humate "Sakhalinsky" is fully suitable for organic farming.

Contacts:

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LLC «Scientific and Innovation Enterprise «BashInkom» was established in 1991. The «SIE BashInkom» enterprise has its own modern certified scientific and production laboratories: agrochemical, microbiological, plant physiology and selection of microorganisms and phytopathology. The company also has modern production and raw material bases for the production of humic and bioactivated fertilizers, production microbiological laboratories for the production of biofungicides, probiotics and feed additives for livestock.



The main activities of the company:

- Production of natural fertilizers and plant protection products, which can increase the yield several times without the use of pesticides;
- Introduction of effective biotechnologies for crop cultivation;
- Creation of multi-strain biologics for veterinary medicine, feed production, stubble processing, manure and storage of agricultural products;
- Development of high-performance drilling reagents for the oil and gas industry.

The RDE BashIncom LLC actively cooperates with local, regional and central research institutes of agricultural profile, many institutes of the Russian Academy of Sciences, plant protection stations and agricultural producers.

The RDE BashIncom LLC welcomes any mutually beneficial cooperation in the development, production and marketing of agro-technical products that meet our concept of Organic Live Farming, Anti-Stress High-Productivity Farming, Anti-Stress High-Productivity Livestock.

**Our main products:**

Integrated microbiological bioproducts for protecting plants from diseases and pests of the Fitosporin series.

Complex bioactivated humic preparations enriched with micro-, meso- and macroelements.

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premium organic products

Edagum SM Rus LLC specializes in the development and production of humic preparations from environmentally friendly plant materials, including humic fertilizer and feed additive EDAGUM®SM.

The high efficiency of the EDAGUM® brand of preparations has been confirmed by studies of 35 specialized Russian and foreign research institutes, as well as by practical application since 2006 in Russia, the CIS countries, Europe, Asia, Africa, and Latin America.

As a result of using the EDAGUM®SM fertilizer when treating vegetative plants, an increase in yield was achieved: on wheat up to 34%, rice - up to 30%, potatoes - up to 63%, tomatoes - up to 34%, soybeans - up to 56%, cotton - up to 45%, etc.

The results of studies of the biological characteristics of the EDAGUM®SM humic fertilizer at the All-Russian Research Institute of Agricultural Microbiology of the Russian Agricultural Academy confirm the high efficiency of the drug's impact on soil properties and the ability to stimulate plant growth and development, which is due to the high number of physiological groups of microorganisms contained in the drug. It was found that when EDAGUM®SM is added to the soil, microorganism respiration increases by 28.8%, the decomposition of organic nitrogen and phosphorus compounds accelerates, and their bioavailability increases.

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Research by scientists from the Soil Science Faculty of Moscow State University. M.V. Lomonosov on wheat crops showed that the effect of soil treatment with 1 liter of EDAGUM®SM fertilizer is equivalent to the introduction of 5-10 tons of cow compost, and the IR spectra of humic substances of the fertilizer and compost show their high similarity in the nature of the functional groups. As a result of the effect of EDAGUM®SM fertilizer, the processes of formation of the so-called "young humus" (pro-humic substances and non-specific organic compounds) are accelerated and intensified, the preparation has a positive complex effect on the physical properties of the soil and its structure. These and other scientific studies and applications in farms allow us to conclude that systematic soil treatment with EDAGUM®SM fertilizer allows us to restore its fertility and environmental parameters, improve its physical properties and structure, and make the manufactured products higher quality and more environmentally friendly.

According to research data from SNIIZhK, VNIKO RSHA, the use of the feed additive EDAGUM®SM gives a weight gain of farm animals, poultry up to 21.4%, their immunity increases, the morphological composition of the blood improves, the quality of products increases, and many others.

Thus, the use of humic preparations EDAGUM®SM on a national scale is not only help in solving the food problem, but also the health of the nation!



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 more than 100 members and is the largest chapter of the IHSS. The membership includes scientists, students, engineers, practitioners, and business representatives from Belarus, Kazakhstan, Kyrgyzstan, Russia, and Ukraine. 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/>. Information about the IHSS you can find at the website: <http://www.humicsubstances.org>

You are very welcome to join us!

Irina Perminova  
Regional Coordinator of the CIS IHSS

Olga Yakimenko  
Secretary of the CIS IHSS

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