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Detoxification of oil-contaminated soils by using humic acids

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Abstract. The paper deals with the study of the effect of peat mechanoactivation on the structure and biostimulating and detoxifying properties of isolated humic acids (HA) in of oil-contaminated soil. It is shown that the mechanical activation of peat leads to an increase in the HA yield by a factor of 2-3. In this case, the changes in the fragment composition of HA are observed. Hence, the percentage of aromatic and oxidized alkyl fragments increases, while the amount of oxygen-containing functional groups decreases. The binding of petroleum organic compounds occurs due to the presence of an aromatic skeleton in the structure of HA. The increase in the proportion of aromatic fragments in the structure of mechanically activated HAs increases their affinity for hydrophobic oil compounds, thereby providing them a detoxifying ability. The maximum detoxifying ability of mechanically activated HA determines their biostimulating properties in the wheat seed germination experiment. The biostimulating effect from the use of mechanically activated HA samples is manifested itself to a greater degree in the increase in the height of the sprout stem and the dry mass of the aerial part of the plant. The processes of biodegradation of oil in the soil in the presence of HA are investigated. It is shown that the amount of bitumoids extracted from the soil in the presence of HA is reduced by 30%. The content of hydrocarbons in bitumoids decreases by 50% due to the biodegradation of low molecular weight alkanes. At the same time, the degree of branching of hydrocarbon chains increases, which suggests a microbiological activity. An increase in alcohol-benzene resins in the composition of bitumoids indicates the stimulation of hydrocarbon-oxidizing bacteria by humic acids. According to the data of IR spectroscopy, the content of paraffin hydrocarbons has decreased during the destruction of oil by soil microflora.

1. Introduction

Oil and petroleum products are widely spread pollutants in nature. Hence, the most important and urgent task in the activities of oil producing and oil refining enterprises is detoxification, cleaning and restoring the properties and fertility of soils polluted by oil and oil products. In the environment, the processes of soil self-purification are extremely slow and need to be stimulated. To remediate the oil-polluted soils, a combination of mechanical, chemical and biological methods is used. When using microbiological methods, complex problems arise in the interaction of populations introduced into the soil with the natural microflora. Microflora includes hydrocarbon-oxidizing microorganisms, which are permanent components of soil biocenoses. It is possible to increase the catabolic activity of microorganisms by introducing peat humic acid-based preparations into contaminated soil.

Humic substances make up 50-80% of the soil organic matter and solid fossil fuels. The presence of a wide spectrum of functional groups in molecules of humic acids (HA) in combination with aromatic fragments determines their ability to enter into ionic and donor-acceptor interactions, to form hydrogen



bonds, bind toxic substances (pesticides, polycycloaromatic hydrocarbons, heavy metals, etc.), and actively participate in sorption processes [1-7].

The complex composition of macromolecules of humic acids (HA) and their stochastic nature require the establishment of the relationship of the sorption and detoxifying properties of HA with their structure. One of the methods for the structural modification of HA is the method of mechanical activation of solid caustobioliths. It was previously found that the mechanical activation of solid caustobioliths results in a change in the structural parameters of the isolated HA and increases their efficiency when interacting with ecotoxicants and heavy metals [8-10].

The purpose of this work was to study the detoxifying and biostimulating ability of humic acids in relation to oil.

2. Experimental part

The objects of the study were HA of sphagnum peat, HA1 of the mechanically activated peat without additives, and HA2 of the mechanically activated peat with the addition of solid alkali – 3% NaOH of analytical grade. Mechanical activation of peat was carried out under following experimental conditions: the rotational speed of the drums – 1820 rpm⁻¹ and centrifugal acceleration – 600 m/s². Grinding bodies were steel balls of 8-10 mm diameter. The weight of balls per one drum loading was 0.2-0.5 kg, sample weight was 15-20 g, and time of treatment was 2 minutes. Humic acids were isolated from peat by treating it with 0.1 n NaOH at a temperature of 90 °C in an amount of 150 ml of solution per 1g of the sample weight for 1 hour. Alkaline extraction was repeated three times. Humic acids in an alkaline solution were precipitated with 4% HCl to pH 2. The brown amorphous HA precipitate was separated by centrifugation and then washed with distilled water to pH 7 and dried in a Petri dish in a vacuum oven to constant weight.

The elemental composition of HA was determined using a Carlo Erba Strumentazione 1106 analyzer (Italy). The analysis of fragment composition was performed via NMR¹³S spectrometry using a Bruker 300 radiospectrometer (Germany) at an operating frequency of 100 MHz via the fast Fourier transform accumulation method. Spectral sweep width was about 26000 Hz, the time of registration of the free induction decay signal (FID) was 0.6 s, the interval between pulses (Td) was 8 seconds at a pulse width of 90°, and the duration of spectrum accumulation was 24 hours. The quantity of preparation weighed 50-70 mg was dissolved in 0.7 cm³ of 0.3 M NaOD.

To assess the detoxifying properties of humic preparations, laboratory-based vegetation experiments were conducted on the soil contaminated with a crude oil. A universal, uniform soil from Einheitserde Werkverband E0 (Germany) was used as a model soil. To simulate pollution a crude oil at a concentration of 1.5 wt% was used. The dose of nutrient substrate applied per 100 g of soil was 2 ml of the HA solution with a concentration 0.5 g/l. In this case, the calculated amount of HA was dissolved in a small volume of alkali (0.1 N NaOH), neutralized with 1 M HCl solution to pH 7.0, and made with distilled water up to one liter. The HA solutions were applied to the soil on the 3rd and 5th days of cultivation. Wheat of a genetically unmodified cultivar variety Samurai served as a test object. The duration of the experiment was 20 days at a temperature of 23-27 °C with natural light, daily watering or irrigation with appropriate solutions of HA. The physiological activity of humic preparations was assessed by their effect on the height of the stem of a seedling and its biomass using the standard procedure described in [11].

After the experiment, the content of residual oil in the soil was determined by extraction with chloroform. To determine the group composition of crude and residual oil, the method of column chromatography was used. Destructive changes in oil hydrocarbons were analyzed by IR spectroscopy using a Nicolet 5700 spectrophotometer (FT-IR) in KBr tablets at a ratio of 1:300 within the range from 400 to 4000 cm⁻¹. Based on the results of IR spectroscopy, spectral coefficients were calculated. They represent the normalized optical densities of the following absorption bands: D₁₆₁₀/D₇₂₅ – coefficient of aromatization, D₇₂₀/D₁₃₈₀ – content of paraffin structures, D₇₅₀/D₇₂₀ – content of condensed aromatics, D₇₂₅/D₁₄₆₅ – content of paraffin structures, and D₁₃₈₀/D₁₄₆₅ – branching coefficient.

3. Results and discussion

In Table 1 the results of studies of the effect of peat mechanoactivation (MA) on the yield in HA and their elemental and fragmentary composition are presented. Preliminary mechanical activation of peat promotes an increase in the yield of HA by a factor of 2-3 compared with the initial peat. The highest amount of HA is isolated from peat by MA with 3% NaOH. The increase in the yield of HA is possible due to the destruction of hardly hydrolyzable substances. It is evident from the data of elemental analysis that the H/C and O/C atomic ratios are decreased in HA. This suggests an increase in the degree of aromaticity.

Table 1. Effect of peat mechanoactivation on the yield in HA and their elemental and fragmentary compositions.

Parameter	HA	HA2	HA3
Content, wt%	8.5	15.3	25.4
Content of elements in HA, wt%			
C	53.4	55.6	57.3
H	6.6	5.6	5.4
N	3.1	2.9	3.0
O	36.9	35.8	34.3
H/C	1.48	1.21	1.13
O/C	0.52	0.48	0.45
Content of C atoms, rel. %			
C=O 160 ppm	17.8	15.3	14.0
CarO 160-140 ppm	13.2	14.6	13.6
CarCH 140-113 ppm	15.9	16.7	16.8
CalkO 107-54 ppm.	26.8	27.9	28.3
Calk 54-0 ppm	26.3	25.5	27.9

The structural parameters calculated from the results of ^{13}C NMR spectroscopy are shown in Table 1. Data analysis indicates a change in the distribution of carbon atoms by the structural fragments of HA depending on the conditions of mechanochemical activation. The percentage of carbon in aromatic and oxidized aliphatic fragments in the HA1 and HA2 molecules from mechanically activated samples is higher than that in HA of the initial peat. The number of oxygen-containing groups has decreased.

An analysis of the chemical composition of oil-contaminated soil in a month after the introduction of HA from the initial peat into it showed a decrease in the amount of bitumoids under extraction by 30% (Table 2).

Table 2. Changes in the content of bitumoids and n-alkanes extracted from the oil-polluted soil.

Content, wt%	Soil + oil	Soil + oil + HA	Soil + oil + HA1	Soil + oil + HA2
Bitumoids of	55.4	39.5	29.4	32.3
n-alkanes	38.7	30.1	20.5	22.5
Benzene resins	1.5	2.5	2.5	3.5
Alcohol-benzene resins	2.1	4.0	7.5	6.5

The amount of extracted bitumoids decreased by 42-47% after the introduction of mechanically activated samples HA1 and HA2 into the soil. A decrease in the percentage of paraffin-naphthenic fractions, in particular, n-alkanes, was observed in the composition of bitumoids (Table 2). At the same time, the content of resins, in particular, acidic alcohol-benzene resins increased due to the new

formation of oxygen-containing compounds. This suggests the destructive oxidative activity of microorganisms, stimulated by the introduction of HAs into the soil.

Based on the results of the analysis of the hydrocarbon composition of bitumoids extracted from the soil, the biodegradation coefficients were calculated (Table 3). A decrease in the $n\text{-C}_{17}/n\text{-C}_{27}$ ratio in bitumoids, extracted from the soil with the addition of HA suggests a decrease in the percentage of low molecular weight n-alkanes, which are subject of biodegradation in a greater degree. The index $i\text{-C}_{19}/i\text{-C}_{17}$, which characterizes the degree of branching of hydrocarbon molecules increases in samples with HA additives and confirms the occurrence of more intensive processes of oil biodegradation. The index $2\text{C}_{29}/\text{C}_{28}+\text{C}_{30}$ reflects the degree of destruction of high molecular weight n-alkanes. The values of this index are similar for hydrocarbons isolated from soils containing HA.

Table 3. Indices of hydrocarbon biodegradation.

Objects	Indices of hydrocarbon biodegradation		
	$n\text{-C}_{17}/n\text{-C}_{27}$	$i\text{-C}_{19}/i\text{-C}_{17}$	$2\text{C}_{29}/\text{C}_{28}+\text{C}_{30}$
Soil + oil	3.3	0.13	1.1
Soil + oil + HA	2.1	0.19	0.8
Soil + oil + HA1	1.6	0.19	0.8
Soil + oil + HA2	1.9	0.25	0.8

In Table 4 are presented the spectral coefficients characterizing the processes of oil biodegradation by soil microflora and HA additives. As follows from the Table 4, the oil biodegraded by soil microflora, stimulated by the addition of HA2, is characterized by increased coefficients C1, C2, which indicates an increase in the fraction of aromatic structures in oil. Biodegradation of paraffin hydrocarbons is confirmed by a decrease in C3 and C4 coefficients and an increase in the branching degree of C5.

Table 4. Spectral coefficients of oil before and after degradation.

Spectral coefficients	Initial oil	After destruction by indigenous soil microflora	After destruction by indigenous soil microflora + HA2
$C_1=D_{1610}/D_{720}$	0.3	1.1	1.5
$C_2=D_{750}/D_{720}$	0.6	1.3	1.6
$C_3=D_{720}/D_{1380}$	0.5	0.2	0.2
$C_4=D_{725}/D_{1465}$	1.9	0.7	0.03
$C_5=D_{1380}/D_{1465}$	0.9	1.7	4.2

The biostimulating and detoxifying effect of HA solutions was manifested in an increase in the height of the stem of seedling and dry weight of the aerial parts of plants compared to the control (Figure 1). The greatest effect was obtained when treating the soil with solutions of mechanically activated samples HA1 and HA2.

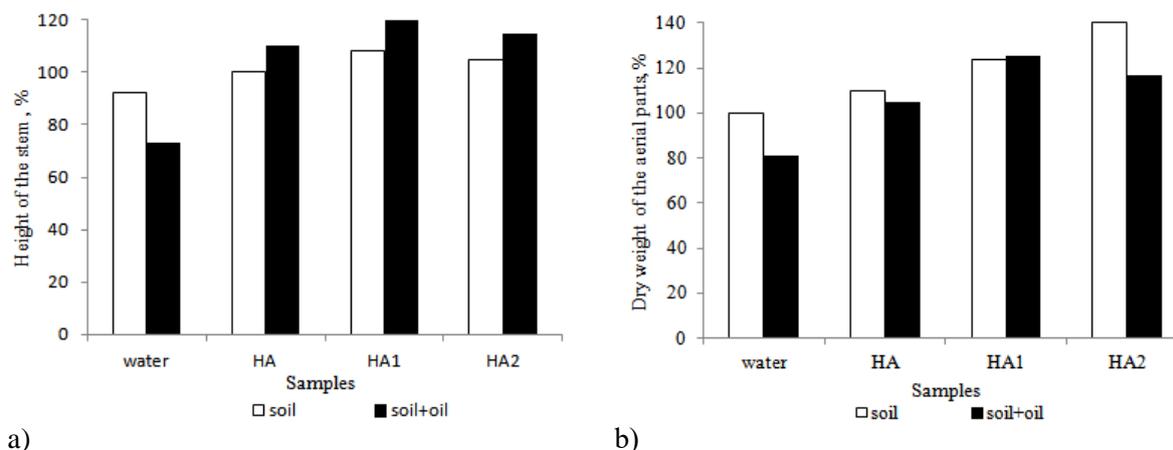


Figure 1. Effect of humic acids on the height of the stem (a) and the dry weight of the wheat seedling (b).

Thus, it has been found that HA exhibit biostimulating and detoxifying properties under conditions of oil-contaminated soil. The greatest effect in this case has been provided by HA of peat, mechanically activated in the presence of alkali. The presence of the aromatic framework provides the ability of HA to bind organic compounds, therefore, as the contribution of the aromatic framework to the HA structure increases, their affinity for hydrophobic organic compounds increases. Maximum aromaticity is characteristic of HA, which determines their high binding and detoxifying ability with respect to oil under the conditions of vegetative experiment.

The processes of oil biodegradation in the presence of HA are accompanied by a decrease in the amount of bitumoids and low-molecular hydrocarbons, and the new formation of high-molecular-weight hydrocarbons. The increase in alcohol-benzene resins in the composition of bitumoids indicates a stimulating effect of humic acids on hydrocarbon-oxidizing microorganisms.

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