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RESEARCH ARTICLE
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Effectiveness of Oil-Contaminated Soil Reclamation with Humic Preparations

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ABSTRACT

The study aimed to assess the environmental effectiveness and determine the technological principles for oil-contaminated soil reclamation using basic humate and modified humic preparations with N, Fe, and Si. The modified humic preparations were obtained via an ultrasound method, containing colloidal ultrafine particles with a high energy charge, which predetermined the high activity of humic preparations for oil-contaminated soil reclamation. Those soils were mixed with the obtained preparations and analyzed using multiple methods. Following the treatment of O-soil with humic preparation solutions, there was a significant percentage reduction in the levels of all heavy metals (Cd, Pb, Cr, Zn, Cu). Experimental studies showed a significant decrease in the content of petroleum products and heavy metals in the soil after treatment with humic preparations. These results suggest that humic preparations are effective for reclaiming contaminated soils. Further research is needed to optimize their composition and application. Based on the findings, the authors recommend the development of an optimized humic preparation to refine treatment strategies and advance soil reclamation technologies. These results have important implications for both the scientific community and the practical implementation of environmental protection and management strategies.

Keywords: Soil; Petroleum products; Heavy metals; Environmental assessment; Atomic absorption analysis

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INTRODUCTION

Oil pollution has become a global environmental problem in recent years. Oil spills on land affect entire ecosystems, change vegetation, fauna, and soil characteristics, and affect microbiological processes. Oil and petroleum products are characterized by high hydrophobic properties, stability, and difficult extraction from environmental components. When oil enters the soil, the physical, chemical, and biological properties of the soil change (Nikolopoulou et al., 2013).

Oil is considered one of the main soil pollutants due to the intensive development of the oil production and processing industries. Oil-contaminated soils contain hydrocarbons and their derivatives, among which polycyclic aromatic hydrocarbons (PAHs) are of particular concern. They are characterized by a diverse structural configuration, low biodegradability, hydrophobic nature, strong sorption phenomena, and high resistance. Apart from PAHs, halogenated hydrocarbons are also dangerous. They are characterized by a strong odor and toxicity (Alimbaev et al., 2020).

The issue of soil oil pollution is urgent in West Kazakhstan. The rapid development of the oil and gas complex leads to an increase in the number of accidental and technical emissions of petroleum products into the soils and waters of the region. As a result, soil pollution with petroleum products and heavy metals in West Kazakhstan is a serious environmental problem that requires special attention and the development of effective reclamation methods (Akhmetov et al., 2022).

The soil reclamation technologies necessary after such pollution can be divided into physicochemical, chemical, thermal, and biological ones, depending on their basic principle of operation (Lan et al., 2023). Before starting any reclamation work, the supply of petroleum products and

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highly mineralized wastewater should be stopped. The residual liquid part of petroleum products has to be purified and transferred to refineries or used as primary raw materials in road construction. Then the land should be drained, and reclamation works should start directly with removing layers of contaminated soil and further soil backfilling with sands and organic fertilizers. After plowing the reclaimed area and saturating it with fresh water, the land is left in a fallow state for two years to activate the biological degradation of petroleum products (Nizamzade, 2014).

A widespread method of cleaning oil-contaminated lands is sorption. Oil and petroleum product spills are covered with sorbents that absorb them. This method is most effective for use on a hard surface. Currently, there are about 200 different types of sorbents in the world. Clay, wood chips, brown humic coal, granulated polystyrene foam, nylon, etc. are used as sorbents (Benza, 2006).

Thus, the study (Kokorina et al., 2009) highlights the sorption properties of a natural biopolymer sorbent chitosan for the detoxification of soils contaminated with petroleum products. In an organic environment, it swells and can firmly retain the solvent in its structure and the substances dissolved in it. Its sorption capacity is due to the presence of free amino groups in the chitosan macromolecule that contribute to the formation of complex compounds with organic compounds.

The reclamation of oil-contaminated soils using a new generation of sorbents based on humic substances and aluminum alloys shows a decrease in the concentration of oil in soil samples by 12-22%, depending on the concentration of reagents and the oil content in the soil (Akhanova et al., 2023). In bioremediation, humic substances are important for binding heavy metals to form a complex when obtaining a sorbent with aluminum, indium, gallium, and tin.

Humic acids, as a key organic component of soils, natural waters, and peats, exhibit heightened reactivity toward oil and its constituents PAHs due to their hydrophobic aromatic structure. This reactivity enables humic acids to play a vital role in self-purification processes and in mitigating the environmental impact of oil pollution. The efficiency of bioremediation for oil-contaminated water bodies can be significantly enhanced by utilizing biological formulations that combine humic acids with microorganisms capable of degrading crude oil. Acting as dispersants, humic acids facilitate the breakdown of petroleum emulsions into smaller components, which are then more readily degraded by microorganisms. Under abiotic stress, when the processes of consumption of essential nutrients by microorganisms slow down, humic acids are a substrate that supplies the necessary components for the vital activity of bacteria (Dmitrieva et al., 2022). Microorganisms can partially utilize the molecule of humic substances and peripheral fragments represented by oligosaccharides and peptides, thereby supplying nutrients (Dmitrieva et al., 2017).

Researchers in (Fomicheva et al., 2022) also note that the soil microflora stimulated by humic preparations has increased destructive oil-oxidizing activity, as evidenced by the indicators of hydrocarbon biodegradation.

During the elimination of soil pollution by oil and petroleum products, humic substances are also used in soil improvement. Humic fertilizers are introduced into the soil to stimulate the native oil-degrading microbiota. They have a stimulating effect on enzymatic activity and the release of carbon dioxide at oil concentrations of 1 and 5% (Minnikova et al., 2019).

Due to the demonstrated effectiveness of humic substances in soil purification in other regions, it is advisable to consider their use in West Kazakhstan, which has an increased risk of oil pollution.

The objectives of this study were to assess the extent of soil oil pollution in West Kazakhstan and to evaluate the effectiveness of humic preparations as a means of soil reclamation. Given the rapid development of the oil and gas industry in the region, which has led to significant contamination of soils with petroleum products and heavy metals, this research aims to explore the potential of humic substances in mitigating such environmental impacts.

MATERIALS & METHODS

Methods

To identify the effectiveness of humic preparations for the purification of oil-contaminated soils in West Kazakhstan, soil samples were treated with potassium humate with modifiers (Suchshikh et al., 2023). Concerning the variants of the experiment, we performed the analysis of the original soil, the soil after treatment with basic potassium humate, and after treatment with three variants of various modified humic preparations (with added nitrogen (N), iron (Fe), or silicon (Si)). Each experimental sample was obtained by mixing soil with certain percentages of potassium humate solution (1, 10, 30, 50%) and the modified preparations.

The characteristics of the initial samples and soil samples obtained as a result of mixing with preparations were described by laboratory elemental analysis methods such as the Pregl-Dumas technique, gravimetry, infrared (IR) spectroscopy, and atomic absorption spectrophotometry (AAS) of heavy metals (Zhyrgalova et al., 2024).

Sampling

Samples of oil-contaminated soils for analysis were collected from the territory of the Makat field of the Dossormunaigas Company in West Kazakhstan (Atyrau region).

Potassium humate was obtained from oxidized brown coal from the Sarykol deposit (Kazakhstan), pre-ground to a size of less than 0.5 mm and having the following characteristics (wt.%): 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; Na 0.61; Al 0.89; K 0.58; Ca 0.31; Ti 0.22; Fe 1.11; Zr 0.08. The size of coal particles was: 2.95 microns (10%), 63.8 microns (50%), or 452 microns (90%). Humate was obtained using a rotary pulsation apparatus by processing raw materials in an ultrasonic reactor to bring the size of coal particles to 19.2 nm and 3.57 microns. In both cases, air was supplied to oxidize coal and increase the content of humic substances. During dispersion and ultrasonic exposure, the mixture's temperature reaches no more than 50-55°C. This temperature is acceptable for the oxidation of coal with oxygen in the air and the extraction of the formed salts of humic, fulvic, and other acids. In the process of oxidation by air, a myceloid dispersed system is formed, i.e., a solution of humic substances with a particle size less than a micrometer. This technology is based on cavitation dispersion of humate-containing substances (coal) by electrophysical action (Ermaғambet et al., 2017, 2021, 2023).

Further, four biological preparations were prepared for various variants of the experiment: Potassium humate, Potassium humate with Fe, Potassium humate with molybdenum (Mo), and Potassium humate with Si. The resulting solution was stirred on an IKARH basic 2 magnetic stirrer for 30 minutes. After that, treatment was performed in a GRAD ultrasonic bath for 30 minutes at 30˚C; the resulting humic preparations were sent for cooling and bottling. The production of chelate complexes with components (N, Fe, Mo, Si) followed the complex formation mechanism inherent in all carboxylic acids starting with the lower analogs of monocarboxylic acids (formic and acetic acid). To the greatest extent, it is manifested in those acids where the molecules, next to the carboxyl group (in α-, β-, ortho-positions), contain electron-donating groups: $-NH_2$, -OH, >C=O, -COOH, -SH, >NH, =N. Using this method, modified biological preparations based on humic polyelectrolytic acids were obtained without decomposition of the humic framework, which enhances their main positive and nutritional properties (Ermaғambet et al., 2017, 2021, 2023).

Stages of Analysis

Elemental analysis of the original oil-contaminated soil and its mixture with various concentrations of humic preparations was performed on the Elementar Unicube device. The analysis is based on the classical technique of organic elemental analysis (Pregl-Dumas technique) and consists of a series of sequential steps: combustion (reduction), homogenization of products, separation of products, and their detection.

Soil samples were burned in an analyzer at high temperature in the presence of oxygen. During the combustion process, gases (CO_2, H_2O, N_2, SO_2) containing the elements were released. These gases were then passed through various detectors to measure their volume. The Pregl-Dumas technique is the basis for many modern methods of elemental analysis of organic compounds, and it remains an important tool in chemical analysis (ASTM International, 2016). With the help of this standard, the carbon (C), hydrogen (H), N, and sulfur (S) content in the studied samples was determined.

The subsequent analysis to determine the percentage of humus in the samples of the studied soils was carried out according to State Standard (GOST) 26213-2021 (2021), and the pH in the soils was determined according to GOST 26483-85 (1986).

Then the content of the mass fraction of petroleum products in the soil with the addition of humic preparations was determined by the gravimetric method following ruling document (RD) 52.18.647-2003. The content of petroleum products in the soil was determined on the 5th, 30th, and 60th day, depending on the duration of exposure to various concentrations (1, 10, 30, 50%) of basic potassium humate and modified humic preparations (N, Fe, Si) for initial soil samples. According to the same scheme, a study of the soil treated with humic substances was carried out using IR-Fourier spectroscopy.

The final analysis involved determining the heavy metal content in the soil using atomic absorption spectroscopy (AAS) with a Shimadzu device. The samples were prepared according to the standard protocol for the Shimadzu device, which included sample digestion, the production of atomized metal vapors, and analysis at the characteristic wavelengths specific to each metal (Kuzyakov et al., 1990; Zyrin & Obukhov, 1977). AAS is a technique used to determine the concentration of various elements in samples by measuring the absorption of light by atoms in the gas phase. The Shimadzu device employs a monochromatic light source that passes through the vaporized atoms of the sample, and the level of light absorption is measured, allowing for precise determination of element concentrations (Obukhov & Plekhanova, 1991; Orlov, 1993; Welz, 2005). This method is highly accurate, sensitive, and capable of analyzing multiple elements within a single sample. The use of AAS with the Shimadzu device enabled a detailed analysis of heavy metal content in soil samples, facilitating the evaluation of various soil treatment methods, including the application of humates, in the reclamation of contaminated soils (USSR State Committee for Hydrometeorology, 1990).

RESULTS

The results of the elemental analysis of oil-contaminated soil samples are shown in Table 1.

The results of determining the percentage of humus in the samples of the studied soils and their pH values are shown in Table 2.

Table 2 shows that different concentrations of solutions of basic and modified potassium humate had a slight effect on the pH of the control and treated soils, the range of pH values ranged from 7.33 to 7.97.

The humus content in the original soil was 7.68%. After applying various concentrations (1, 10, 30, 50%) of basic potassium humate solutions and their modifications (with N, Fe, Si), we observed an increase in the humus content. The addition of a 1% basic potassium humate solution raised the humus content to 9.77%, while a 30% concentration further increased it to 11.31%. Similarly, the use of potassium humate modified with nitrogen (Potassium humate-N) resulted in a humus content of 12.03% with a 30% solution. The potassium humate modified with iron (Potassium humate-Fe) also showed positive effects, with the humus content reaching 12.12% after the application of a 50% solution. The observed concentrations of petroleum products in the soil following the addition of humic preparations are detailed in Table 3 and illustrated in Fig. 1 and 2.

Table 1: C, H, N and S content in the control and experimental soil samples

No.	Sample name	C, %	H, %	N, %	S, %
1	Original oil-contaminated soil (O-soil)	0.59	10.36	0.55	0.20
2	O-Soil + 1% Basic potassium humate solution	1.36	9.69	1.44	0.15
3	O-Soil + 10% Basic potassium humate solution	1.49	10.05	2.25	0.00
4	O-Soil + 30% Basic potassium humate solution	0.84	10.09	1.29	0.13
5	O-Soil + 50% Basic potassium humate solution	0.87	9.99	1.27	0.12
6	O-Soil+ 1% Potassium humate-N solution	0.82	8.84	1.51	0.14
7	O-Soil+ 10% Potassium humate-N solution	0.86	10.35	1.24	0.16
8	O-Soil+ 30% Potassium humate-N solution	0.54	10.11	2.20	0.08
9	O-Soil+ 50% Potassium humate-N solution	0.77	9.37	1.06	0.11
10	O-Soil+ 1% Potassium humate-Fe solution	0.82	9.73	1.19	0.17
11	O-Soil+ 10% Potassium humate-Fe solution	0.56	10.31	2.06	0.13
12	O-Soil+ 30% Potassium humate-Fe solution	1.24	9.34	1.26	0.14
13	O-Soil+ 50% Potassium humate-Fe solution	1.19	11.03	0.96	0.07
14	O-Soil+ 1% Potassium humate-Si solution	0.74	7.95	1.09	0.06
15	O-Soil+ 10% Potassium humate-Si solution	0.85	9.28	1.04	0.11
16	O-Soil+ 30% Potassium humate-Si solution	0.56	9.71	1.77	0.12
17	O-Soil+ 50% Potassium humate-Si solution	1.0	10.56	1.58	0.14

*where O-Soil is oil-contaminated soil.

Table 2: Results of pH and humus content determination in the control and experimental soil samples

No.	Sample name	Soil pH	Humus content, %
1	Original O-soil	7.97	7.68
2	O-Soil + 1% Basic potassium humate solution	7.39	9.77
3	O-Soil + 10% Basic potassium humate solution	7.29	9.51
4	O-Soil + 30% Basic potassium humate solution	7.40	11.31
5	O-Soil + 50% Basic potassium humate solution	7.38	9.51
6	O-Soil+ 1% Potassium humate-N solution	7.88	9.13
7	O-Soil+ 10% Potassium humate-N solution	7.85	9.51
8	O-Soil+ 30% Potassium humate-N solution	7.82	12.03
9	O-Soil+ 50% Potassium humate-N solution	7.73	11.39
10	O-Soil+ 1% Potassium humate-Fe solution	7.89	10.92
11	O-Soil+ 10% Potassium humate-Fe solution	7.87	8.23
12	O-Soil+ 30% Potassium humate-Fe solution	7.81	11.61
13	O-Soil+ 50% Potassium humate-Fe solution	7.75	12.12
14	O-Soil+ 1% Potassium humate-Si solution	7.57	11.86
15	O-Soil+ 10% Potassium humate-Si solution	7.55	11.48
16	O-Soil+ 30% Potassium humate-Si solution	7.68	11.56
17	O-Soil+ 50% Potassium humate-Si solution	7.70	11.48

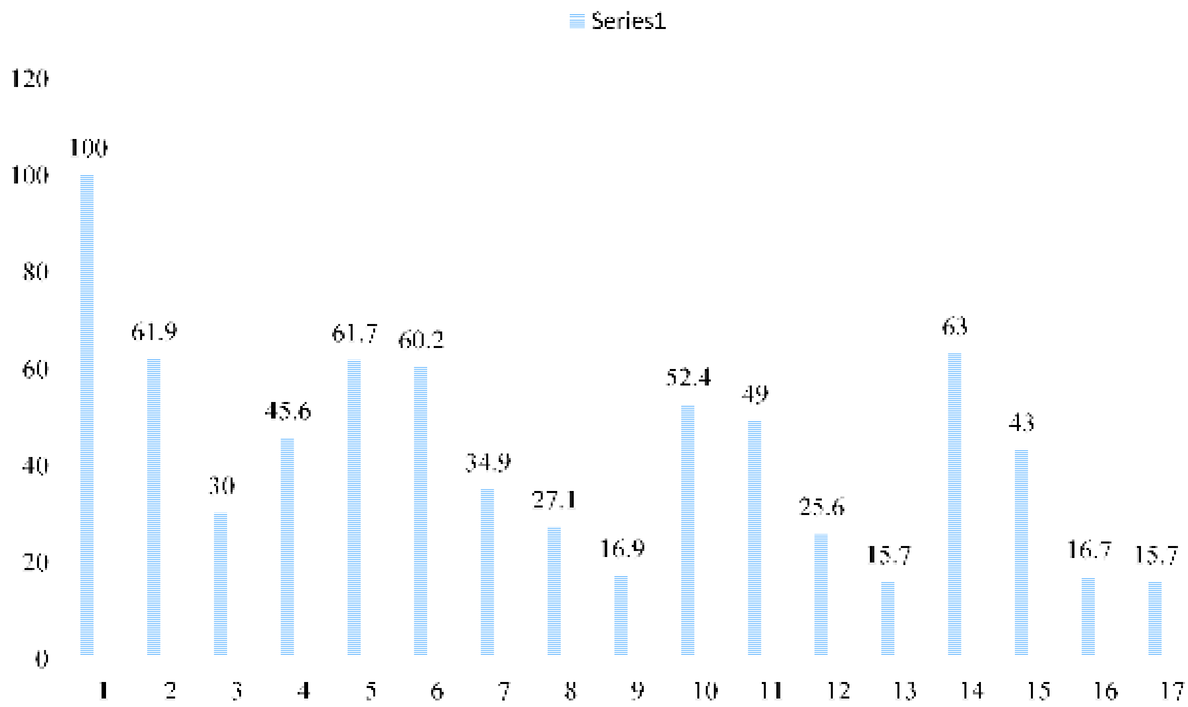


Fig. 1: The petroleum product content in the control and experimental samples in the soil.

The following humic preparations showed the best result in reducing the content of petroleum products in the soil after 60 days: 1) 50% potassium humate +Fe (the degree of purification was 84.3%); 2) 30% Potassium humate + Si (83.3%); 3) 50% potassium humate +N (83.1%); 4) 10% basic potassium humate (70%). Table 4 and 5 show the results of the IR Fourier analysis of oil-contaminated soil on the 5th, 30th, and 60th day.

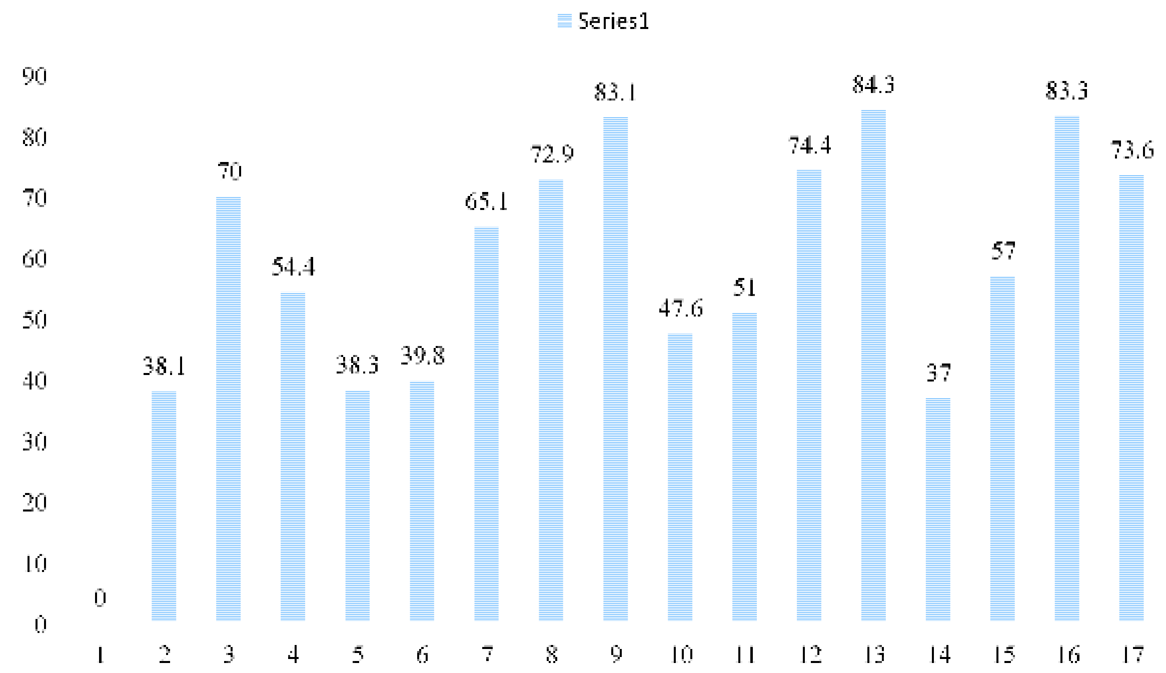


Fig. 2: Purification degree from of petroleum products in the control and experimental samples in the soil.

Table 3: The content of petroleum products in the control and experimental samples in the soil

Sample	Mass fraction of petroleum products in the soil sample, mg/kg, day 5	Mass fraction of petroleum products in the soil sample, mg/kg, day 30	Mass fraction of petroleum products in the soil sample, mg/kg, day 60	Content of petroleum products in %	Degree of purification %, Day 60
Original O-soil	72.000	72.000	72.000	100	0.0
O-Soil + 1% Basic potassium humate	76.200	59.700	44.600	61.9	38.1
O-Soil + 10% Basic potassium humate	65.800	48.200	21.600	30	70.0
O-Soil + 30% Basic potassium humate	73.000	55.400	32.800	45.6	54.4
O-Soil + 50% Basic potassium humate	69.200	57.600	44.400	61.7	38.3
O-Soil+ 1% Potassium humate+N	58.750	50.620	43.370	60.2	39.8
O-Soil+ 10% Potassium humate+N	52.300	40.030	25.120	34.9	65.1
O-Soil+ 30% Potassium humate+N	40.260	32.890	19.540	27.1	72.9
O-Soil+ 50% Potassium humate+N	36.260	26.720	12.180	16.9	83.1
O-Soil+ 1% Potassium humate+Fe	60.670	41.230	37.740	52.4	47.6
O-Soil+ 10% Potassium humate+Fe	57.250	44.833	35.280	49	51
O-Soil+ 30% Potassium humate+Fe	48.790	30.040	18.438	25.6	74.4
O-Soil+ 50% Potassium humate+Fe	25.630	19.451	11.320	15.7	84.3
O-Soil+ 1% Potassium humate+Si	67.000	53.000	46.000	63	37
O-Soil+ 10% Potassium humate+Si	58.000	46.000	31.000	43	57
O-Soil+ 30% Potassium humate+Si	42.000	25.000	12.000	16.7	83.3
O-Soil+ 50% Potassium humate+Si	44.000	36.000	19.000	26.4	73.6

As a result of IR spectroscopic studies, the search area in samples at various concentrations of potassium humate was 400-4,000 cm^{-1}; wave numbers: 3,907-413.17 cm^{-1}; alkanolamines (OH): 3,200-3,650 cm^{-1} (OH groups), alkanes (paraffins): 2,800-3,000 cm^{-1} (CH bonds); alkenes (olefins): 1,600-1,680 cm^{-1} (C=C bond); aromatic compounds (benzene, toluene): 1,450-1,600 cm^{-1} (C=C); functional groups: ketones (C=O): 1,700-1,750 cm^{-1}, aldehydes (C=O): 1,700-1,750 cm^{-1}, carboxylic groups (C=O): 1,600-1,700 cm^{-1}, halogen-containing compounds: CX (where X is F, Cl, Br, I) 500-1,600 cm^{-1}, silicates: Si-O 800-1,200 cm^{-1}, alkanolamine groups: OH (3,200-3,650 cm^{-1}), OH groups in water (3,200-3,650 cm^{-1}), S dioxide (SO_2): S=O 1,000-1,200 cm^{-1}, methyl groups (CH) and ethyl groups (CH): 2,800-3,000 cm^{-1}, arenes: 1,450-1,600 cm^{-1} C=C, ammonia (NH_3): 1,400-1,600 cm^{-1} NH, Fe: 400-600 cm^{-1}. The presence of Fe ions was detected within the 400-600 cm^{-1} range.

Table 6 shows data on the content of heavy metals in the soil before and after treatment with humic preparations in 1, 10, 30, and 50% concentration.

Fig. 3 shows a practical decrease in the concentration of heavy metals in O-soil after treatment with solutions of humic preparations.

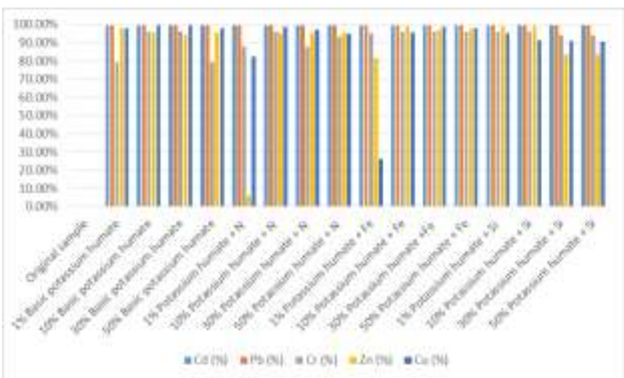
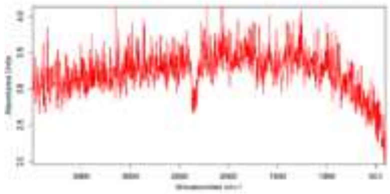
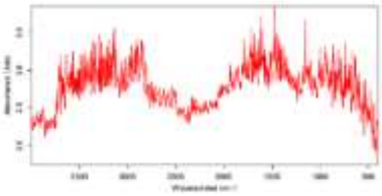
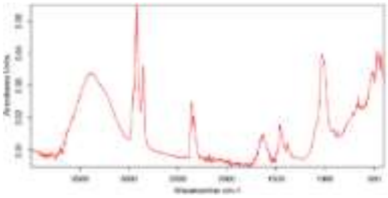
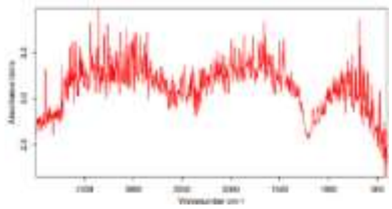
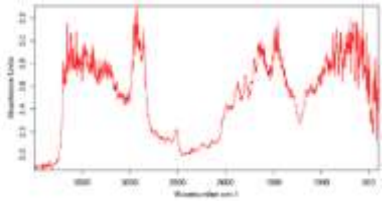
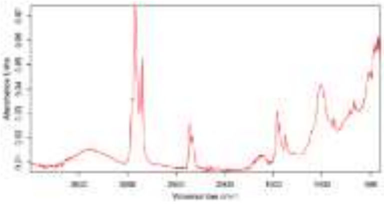
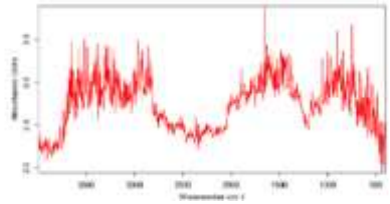
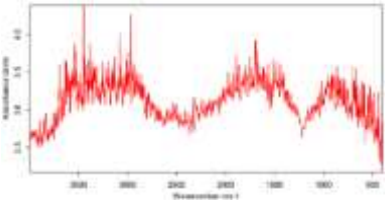
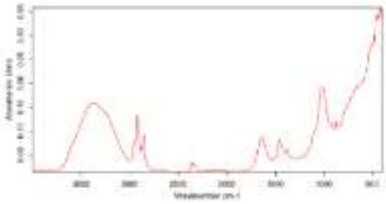
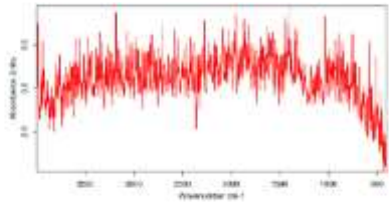
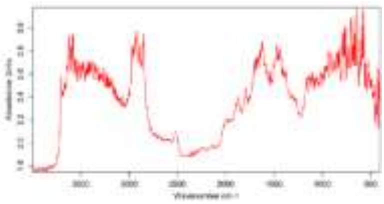
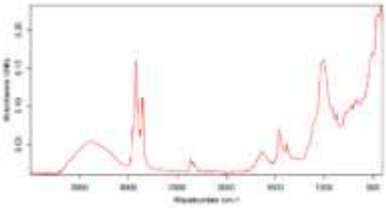
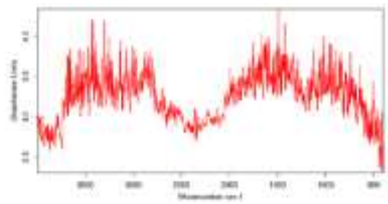
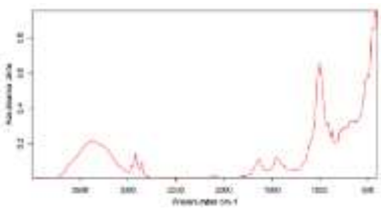
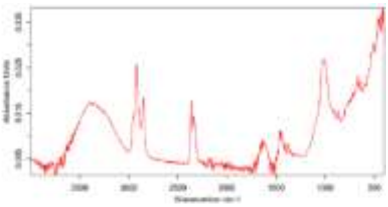
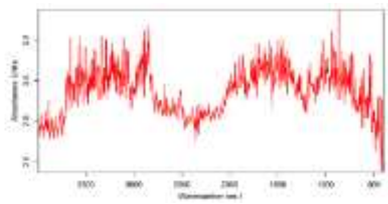
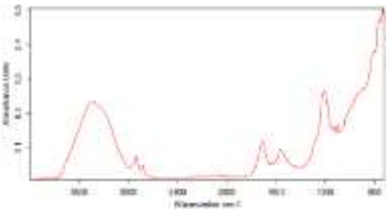
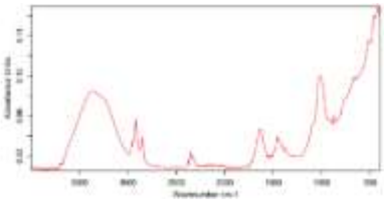
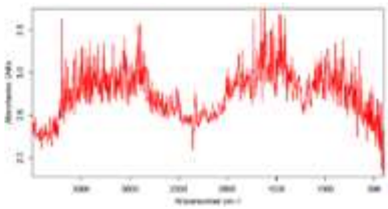
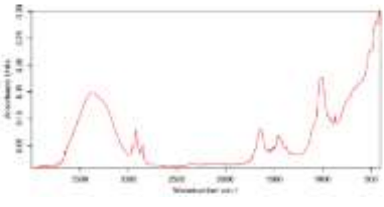
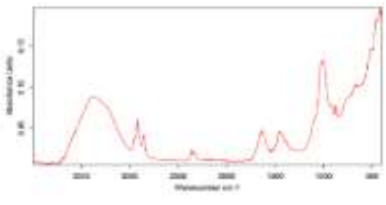
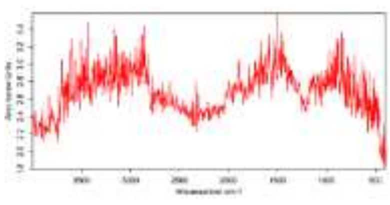
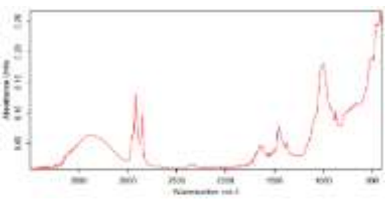
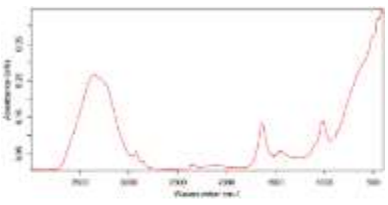
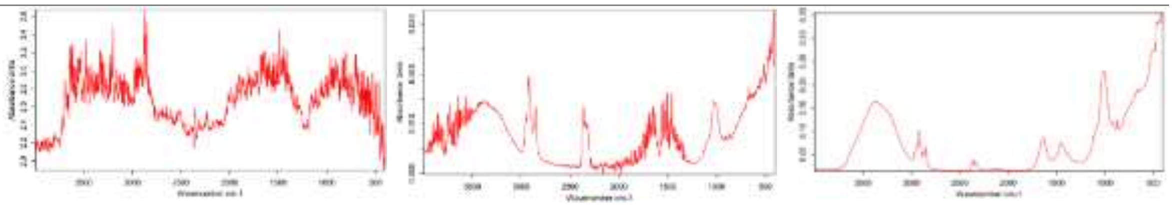
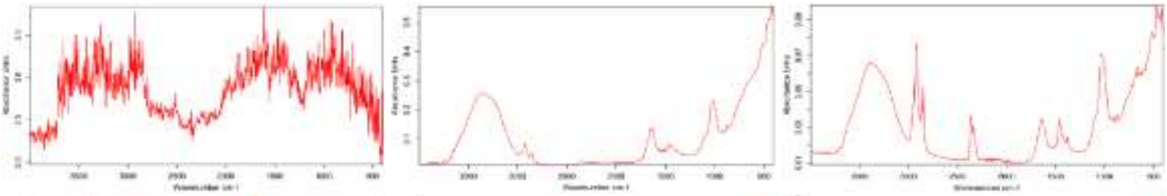
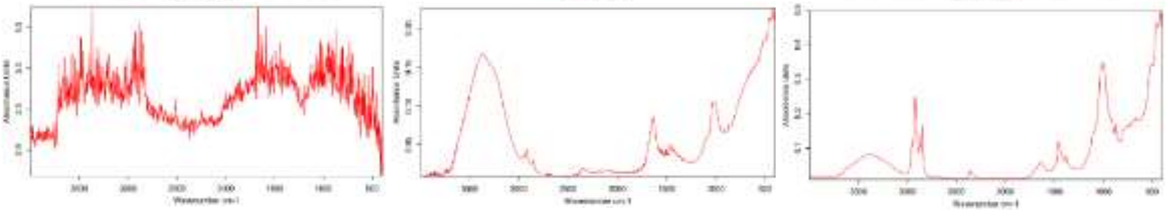
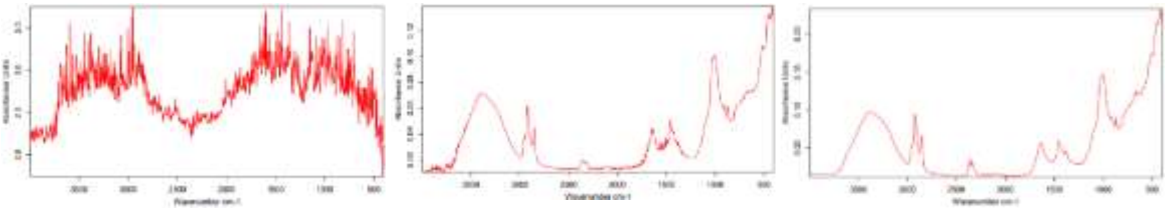
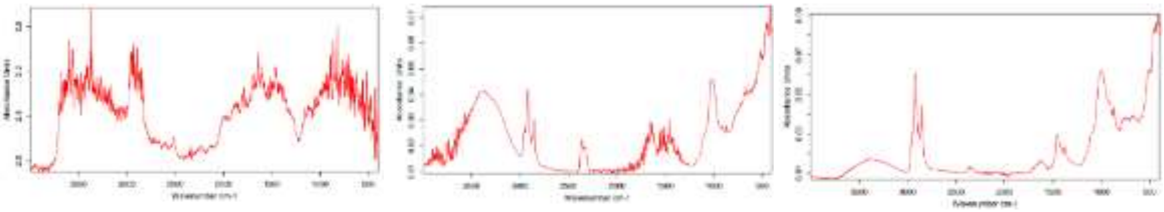
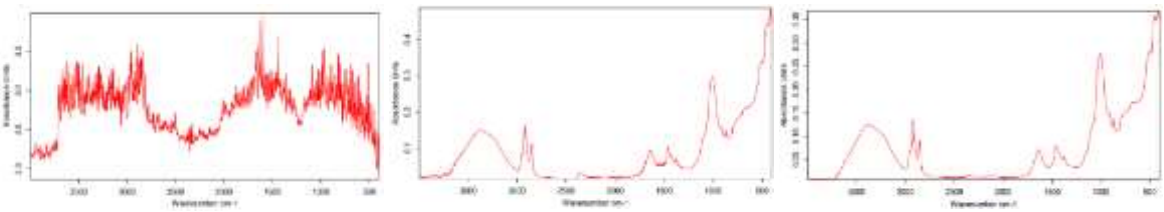
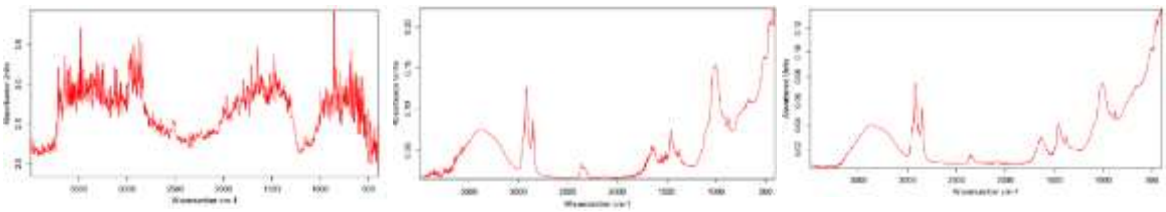
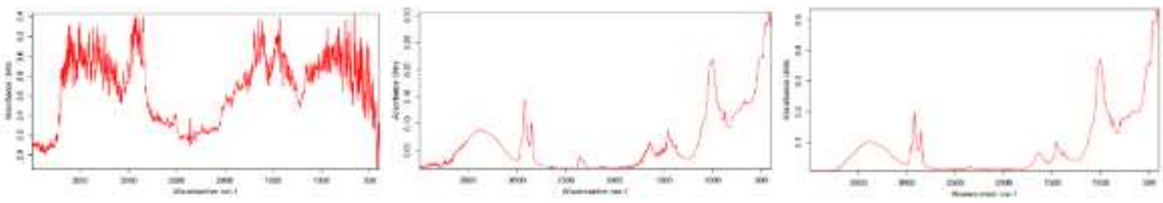


Fig. 3: Percentage decrease in the concentration of heavy metals in the soil before and after treatment with solutions of humic preparations

Table 4: Peaks of the IR-Fourier spectra of oil-contaminated soil on the 5th, 30th, and 60th day

No.	Sample	Day 5	Day 30	Day 60
1	1% Basic potassium humate			
2	10% Basic potassium humate			
3	30% Basic potassium humate			
4	50% Basic potassium humate			
5	1% Potassium humate+N			
6	10% Potassium humate+N			
7	30% Potassium humate+N			
8	50% Potassium humate+N			

9	1% Potassium humate+Fe	
10	10% Potassium humate+Fe	
11	30% Potassium humate+Fe	
12	50% Potassium humate+Fe	
13	1% Potassium humate+Si	
14	10% Potassium humate+Si	
15	30% Potassium humate+Si	
16	50% Potassium humate+Si	

The concentrations of heavy metals in the original soil before treatment were high. As can be seen from Fig. 3, after treatment of O-soil with solutions of humic preparations, high rates of percentage reduction in the level of all heavy metals (Cd, Pb, Cr, Zn, Cu) were observed.

Table 5: Results of IR-Fourier spectroscopy of oil-contaminated soil on the 5th, 30th, and 60th days

No.	Sample	Day 5	Day 30	Day 60
1	1% Basic potassium humate	Total peak: 276 Search area: 400-4,000 cm^{-1} Wave numbers: 3,976-407 cm^{-1} 1. Acyclic aromatic hydrocarbons: Cyclohexane: 2,800-3,000 cm2. Solid phases and mineral components: Silicates, oxides: 400-,1200 cm^{-1} 3. Organic acids and ethers: C=O in acids: 1,700-1,750 cm^{-1} - C in ether: 1,000-1,300 cm^{-1}. 4. Saturated and unsaturated hydrocarbons: CC and CH: 600-3,000 cm^{-1-1} CH.	Total peak: 97 Search area: 400-4,000 cm^{-1} Wave numbers: 3,907-413.17 cm^{-1} 1. Alkanolamines (OH): 3,200-3,650 cm^{-1} (OH groups). 2. Alkanes (paraffins): 2,800-3,000 cm^{-1} (CH bonds). 3. Alkenes (olefins): 1,600-1,680 cm^{-1} (C=C bond). 4. Aromatic compounds (benzene, toluene): 1,450-1,600 cm^{-1} (C=C). 5. Functional groups: Ketones (C=O): 1,700-1,750 cm^{-1}. Aldehydes (C=O): 1,700-1,750 cm^{-1}. Carboxyl groups (C=O): 1,600-1,700 cm^{-1}.	Total peak: 13 Search area: 400-4,000 cm^{-1} Wave numbers: 3,393-418 cm$^{-1.}$ 1. Alkynes: 2,100-2,260 cm^{-1} C≡C 2. Saturated and unsaturated hydrocarbons: 600-3,000 cm^{-1} CH and C=C. 3. Organic acids: 1,700-1,750 cm^{-1} C=O. 4. Non-protonoid components of the oil: various bonds, including CH and C=C, form a complex spectrum in the range of 600-3,000 cm^{-1}.
2	10% Basic potassium humate	Total peak: 183 Search area: 400-4,000 cm-1 Wave numbers: 3,985-410 cm$^{-1.}$ 1. Cyclohexane (acyclic aromatic hydrocarbon): 2,800-3,000 cm^{-1} CH. 2. Silicates (solid phases and mineral components): 400-1,200 cm^{-1}. 3. Carboxyl groups in organic acids (C=O): 1,700-1,750 cm^{-1}. 4. Saturated hydrocarbons and alkanes: CH 2,800-3,000 cm^{-1}. 5. Phenolic groups (C-OH) in phenols and cresols: 3,200-3,600 cm^{-1}.	Total peak: 48 Search area: 400-4,000 cm^{-1} Wave numbers: from 3,694 to 411.51 cm$^{-1.}$ 1. Acyclic aromatic hydrocarbons: - Cyclohexane: 2,800-3,000 cm^{-1} CH 2. Solid phases and mineral components: - Silicates, oxides: 400-1,200 cm^{-1} 3. C=O bonds in acids: 1,700-1,750 cm^{-1}; OC bonds in ether: 1,000-1,300 cm^{-1}. 4. Saturated and unsaturated hydrocarbons: CC and CH: 600-3,000 cm^{-1}.	Total peak: 13 Search area: 400-4,000 cm^{-1} Wave numbers: 3,287-423 cm$^{-1.}$ 1. Acyclic aromatic hydrocarbons: 2,800-3,000 cm^{-1} CH. 2. Benzene: C=C 1,450-1,600 cm^{-1}. 3. S compounds: SH and S=O 1,000-1,200 cm^{-1}. 4. Solid particles (e.g. asphaltenes): 600-1,600 cm^{-1}.
3	30% Basic potassium humate	Total peak: 177 Search area: 400-4,000 cm^{-1} Wave numbers: from 3,935 to 408 cm$^{-1.}$ 1. Alkynes (acetylene): C≡ C2,100-2,260 cm^{-1}. 2. Methoxyl groups (O-CH_3): O-CH_3 2,800-3,000 cm^{-1} 3. Water-soluble components and alkanolamines: O-H 3,200-3,650 cm^{-1}. 4. Composition of water: OH groups in water: 3,200-3,650 cm^{-1}. 5. Methoxy groups (O-CH_3): 2,800-3,000 cm^{-1}.	Total peak: 98 Search area: 400-4,000 cm$^{-1.}$ Wave numbers: from 3,889 to 410.85 cm$^{-1.}$ 1. Phenols and cresols: Phenolic groups (C-OH):* 3,200-3,600 cm^{-1}. 2. Alkyne (acetylene): C≡C: 2,100-2,260 cm^{-1}. 3. Halogen-containing compounds: CX bonds: 500-1,600 cm^{-1}. 4. Methyl groups (C-H) and ethyl groups (C-H) 2,800-3,000 cm^{-1}. 5. Aromatic compounds (benzene, toluene): C=C 1,450-1,600 cm^{-1}.	Total peak: 6 Search area: 400-4,000 cm^{-1} Wave numbers: 3,373-1,006 cm$^{-1.}$ 1. Alkyl mercaptans: BC 2,550-2,650 cm^{-1}. 2. Deformed alkenes: 1,600-1,680 cm^{-1} C=C. 3. S compounds: 1,000-1,700 cm^{-1} SH, S=O.
4	50% Basic potassium humate	Total peak: 281 Search area: 400-4,000 cm^{-1} Wave numbers: 3,985-414 cm$^{-1.}$ 1. Functional groups (ketones, aldehydes, carboxyl groups): C=O 1,600-1,750 cm^{-1} 2. Alkenes (olefins): C=C bonds 1,600-1,680 cm^{-1}. 3. Halogen-containing compounds: C–X bonds (where X is F, Cl, Br, I) 500-1,600 cm^{-1} 4. The O-H groups in water are 3,200-3,650 cm^{-1}. 5. C in alkanes-C : 600-1,500 cm^{-1}.	Total peak: 38 Search area: 400-4,000 cm^{-1} Wave numbers: 3,698-409 cm$^{-1.}$ 1. Alkanolamines (OH): 3,200-3,650 cm^{-1}. 2. Alkanes (paraffins): 2,800-3,000 cm^{-1} (CH). 3. Alkenes (olefins): 1,600-1,680 cm^{-1} (C=C). 4. Aromatic compounds (benzene, toluene):1,450-1,600 cm^{-1} (C=C). 5. Functional groups: Ketones (C=O): 1,700-1,750 cm^{-1}. Aldehydes (C=O): 1,700-1,750 cm^{-1}. Carboxyl groups (C=O): 1,600-1,700 cm^{-1}.	Total peak: 7 Search area: 400-4,000 cm^{-1} Wave numbers: 3,384-859 cm$^{-1.}$ 1. Phosphorus (P) compounds: 1,000-1,300 cm^{-1} PH and P=O. 2. Silicates: Si-O peaks in the area of 800-1,200 cm^{-1}. 3. Amides: 1,600-1,750 cm^{-1} C=O.

5	1% humate+N	Potassium	Total peak: 137 Search area: 400-4,000 cm^{-1} Search area: 3,973-417.72 cm^{-1} 1. Alkane (paraffin): 2,800-3,000 cm^{-1} (CH bond). 2. Alkenes (olefins): 1,600-1,680 cm^{-1} (C=C). 3. Aromatic compounds (benzene, toluene): 1,450-1,600 cm^{-1} (C=C).	Total peak: 20 Search area: 400-4,000 cm^{-1} Wave numbers: 3,372-413 cm^{-1} 1. Alkanes (paraffins): 2,800-3,000 cm^{-1} (CH). 2. Alkenes (olefins): 1,600-1,680 cm^{-1} (C=C). 3. Functional groups: Ketones (C=O): 1,700-1,750 cm^{-1}. Aldehydes (C=O): 1,700-1,750 cm^{-1}. Carboxyl groups (C=O): 1,600-1,700 cm^{-1}. 4. Functional groups: Ketones (C=O): 1,700-1,750 cm^{-1}. Aldehydes (C=O): 1,700-1,750 cm^{-1}. Carboxyl groups (C=O): 1,600-1,700 cm^{-1}.	Total peak: 10 Search area: 400-4,000 cm^{-1} Wave numbers: 3,384-417 cm$^{-1.}$ 1. Aromatic compounds C=C (1,450-1,600 cm^{-1}) and solid phases (400-1,200 cm^{-1}). 2. Organic acids: C=O (1,700-1,750 cm^{-1}) and halogen-containing compounds: CX (500-1,600 cm^{-1}). 3. Methoxyl groups: O-CH3 (2,800-3,000 cm^{-1}) and phenols: (C-OH) 3,200-3,600 cm^{-1}.
6	10% humate + N	Potassium	Total peak: 135 Search area: 400-4,000 cm^{-1} Wave numbers: 3,967-411.94 cm^{-1} 1.Alkanolamines (OH): 3,200-3,650 cm^{-1} (OH). 2. Alkanes (paraffins): 2,800-3,000 cm^{-1} (CH). 3. Alkenes (olefins): 1,600-1,680 cm^{-1} (C=C bond). 4. Aromatic compounds (benzene, toluene): 1,450-1,600 cm^{-1} (C=C). 5. Functional groups: Ketones (C=O): 1,700-1,750 cm^{-1}. Aldehydes (C=O): 1,700-1,750 cm^{-1}. Carboxyl groups (C=O): 1,600-1,700 cm^{-1}	Total peak: 23 Search area: 400-4,000 cm^{-1} Wave numbers: 3,362-871 cm^{-1} 1. Alkanes (paraffins): 2,800-3,000 cm^{-1} (CH). 2. Alkenes (olefins): 1,600-1,680 cm^{-1} (C=C). 3. Aromatic compounds (benzene, toluene): 1,450-1,600 cm^{-1} (C=C) 4. Functional groups: Ketones (C=O): 1,700-1,750 cm^{-1}. Aldehydes (C=O): 1,700-1,750 cm^{-1}. Carboxyl groups (C=O): 1,600-1,700 cm^{-1}.	Total peak: 16 Search area: 400-4,000 cm^{-1} Wave numbers: 3,373-872 cm$^{-1.}$ 1. Solid phases: (400-1,200 cm^{-1}) and alkynes (paraffins): C≡C (2,100-2,260 cm^{-1}). 2. Alkanes: CH (2,800-3,000 cm^{-1}) and water composition: OH (3,200-3,650 cm^{-1}). 3. Carbonaceous: C=O (1,600-1,700 cm^{-1}) and alkenes: C=C (1,600-1,680 cm^{-1}).
7	30% humate + N	Potassium	Total peak: 218 Search area: 400-4,000 cm^{-1} Wave numbers: 3,986-411.85 cm$^{-1.}$ 1 . Alkanolaminder (OH): 3,200-3,650 cm^{-1} (OH). Methyl groups (CH): 2,800-3,000 cm^{-1}. Ethyl groups (CH): 2,800-3,000 cm^{-1}. 3. Alkanes: CC 600-1,500 cm^{-1}.	Total peak: 16 Search area: 400-4,000 cm^{-1} Wave numbers: 3,365-679 cm^{-1} 1. Polar groups: 1,500-1,800 cm^{-1}: C=O 2. Organic acids and ethers: C=O groups in acid: 1,700-1,750 cm^{-1}. OC groups in ethers: 1,000-1,300 cm^{-1}. 3. Saturated and unsaturated hydrocarbons: CC and CH: 600-3,000 cm^{-1}.	Total peak: 14 Search area: 400-4,000 cm^{-1} Wave numbers: 3,379-418 cm^{-1}. 1. Phenolic groups: (C-OH) 3,200-3,600 cm^{-1} and aromatic compounds: C=C (1,450-1,600 cm^{-1}). 2. Alkanolamines: OH (3,200-3,650 cm^{-1}) and methyl groups: CH (2,800-3,000 cm^{-1}). 3. Nitric oxide (NO_x): 1,500-1,700 cm^{-1} N=O.
8	50% humate + N	Potassium	Total peak: 115 Search area: 400-4,000 cm^{-1} Wave numbers: 3,984-426.78 cm^{-1} 1. Phenolic groups (C-OH): 3,200-3,600 cm^{-1}. 2. Alkyne (acetylene): C≡C: 2,100-2,260 cm^{-1}. 3. Halogen-containing compounds: CX (where X is F, Cl, Br, I): 500-1,600 cm^{-1}. 4. OH-groups in water: 3,200-3,650 cm^{-1}. 5. Methoxyl groups ($O-CH_3$):2,800-3,000 cm^{-1}.	Total peak: 14 Search area: 400-4,000 cm^{-1} Wave numbers: 3,392-418 cm^{-1} 1. Methoxyl groups ($O-CH_3$): 2,800-3,000 cm^{-1}. 2. Alkylbenzene and other complex hydrocarbons: 600-1,500 cm^{-1}. 3. Acyclic aromatic hydrocarbons: cyclohexane: CH 2,800-3,000 cm^{-1}. 4. Solid phase and mineral components: Silicate resin, oxide sweat: 400-1,200 cm^{-1}.	Total peak: 13 Search area: 400-4,000 cm^{-1} Wave numbers: 3,373-872 cm$^{-1.}$ 1. Bitumen: 1,600-3,000 cm^{-1}, CH and C=C, OH may be present. 2. Alkanes: CH 2,800-3,000 cm^{-1}. 3. Nitric oxide (NO_x) 1,500-1,700 cm^{-1}, N=O.

9	1% Potassium humate +Fe	Total peak: 177 Search area: 400-4,000 cm^{-1} Wave numbers: 3,939-424 cm^{-1}: 1. Solid phases: 400-1,200 cm^{-1} and alkynes (paraffins): C≡C, 2,100-2,260 cm^{-1}. 2. Organic acids: C=O (1,700-1,750 cm^{-1}) and halogen-containing compounds: CX (500-1,600 cm^{-1}). 3. Aromatic compounds: C=C, (1,450-1,600 cm^{-1}) and functional groups : C=O, (1,600-1,750 cm^{-1}). 4. Methyl digroups: alkenes: (2,800-3,000 cm^{-1}) C=C	Total peak: 37 Search area: 400-4,000 cm-1 Wave numbers: 3,902-419 cm$^{-1.}$ 1. Alkanolamines: OH, (3,200-3,650 cm^{-1}) and alkyl bond: CC, (600-1,500 cm^{-1}). 2. Phenolic groups: (C-OH), 3,200-3,600 cm^{-1} and ketones: C=O, (1,700-1,750 cm^{-1}). 3. The composition of alkanolamines: OH, (3,200-3,650 cm^{-1}) and water: OH, (3,200-3,650 cm^{-1}). 4. Halogen-containing compounds: CX (500-1,600 cm^{-1}) and alkenes: C=C, (1,600-1,680 cm^{-1}).	Total peak: 13 Search area: 400-4,000 cm^{-1} Wave numbers: 3,394-668 cm$^{-1.}$ 1. Sulfates: 1,000-1,700 cm^{-1}, SO and S=O. 2. Thiophenes: 1,500-1,600 cm^{-1}, C=C. 3. Urea: OH 3,200-3,650 cm^{-1} and C=O 1,700-1,750 cm^{-1}.
10	10% Potassium humate + Fe	Total peak: 203 Search area: 400-4,000 cm^{-1} Wave numbers: 3,946-407 cm$^{-1.}$ 1. Alkanolaminder: OH (3,200-3,650 cm^{-1}). Alkyl: CC (600-1,500 cm^{-1}). 2. Phenolic groups: (C-OH) 3,200-3,600 cm^{-1} ketones: C=O (1,700-1,750 cm^{-1}). 3. Alkanolamines: OH (3,200-3,650 cm^{-1}). 4. Fe: 400-600 cm^{-1}, Fe ion.	Total peak: 13 Search area: 400-4,000 cm^{-1} Wave numbers: 3,360-871 cm^{-1} 1. Solid phases and alkanes: CC (600-1,500 cm^{-1}) 2. Methoxyl groups: O-CH3 (2,800-3,000 cm^{-1}) and aromatic compounds: C=C (1,450-1,600 cm^{-1}).	Total peak: 10 Search area: 400-4,000 cm^{-1} Wave numbers: 3,384-872 cm$^{-1.}$ 1. Aromatic compounds: C=C (1,450-1,600 cm^{-1}) and solid phases: (400-1,200 cm^{-1}). 2. Organic acids: C=O, (1,700-1,750 cm^{-1}) and halogen-containing compounds: CX, (500-1,600 cm^{-1}). 3. Methoxyl groups: O-CH_3 bond (2,800-3,000 cm^{-1}) and phenolic groups: (C-OH), 3,200-3,600 cm^{-1}.
11	30% Potassium humate + Fe	Total peak: 188 Search area: 400-4,000 cm^{-1} Wave numbers: 3,989-407 cm^{-1}: 1. Halogen-containing compounds: CX (500-1,600 cm^{-1}) and alkenes: C=C (1,600-1,680 cm^{-1}). 2. Solid phases and alkanes: CC (600-1,500 cm^{-1}) 3. Methoxyl groups: O-CH3 (2,800-3,000 cm^{-1}), aromatic compounds: C=C (1,450-1,600 cm^{-1}). 4. Fe: 400-600 cm^{-1}, Fe ion.	Total peak: 19 Search area: 400-4,000 cm^{-1} Wave numbers: 3,371-871 cm$^{-1.}$ 1. Alkyl mercaptans: 2,550-2,650 cm^{-1}, SH. 2. Strained alkenes: C=C, 1,600-1,680 cm^{-1}. 3. Nitric oxide: (NO_x) 1,500-1,700 cm^{-1}, N=O. 4. Polyethylenes: 600-3,000 cm^{-1}, bonds CH and C=C.	Total peak: 13 Search area: 400-4,000 cm^{-1} Wave numbers: 3,393-712 cm$^{-1.}$ 1. Solid phases: (400-1,200 cm^{-1}) Alkynes (paraffins): C≡C, (2,100-2,260 cm^{-1}) 2. Alkanes: CH, (2,800-3,000 cm^{-1}) and water composition: OH, (3,200-3,650 cm^{-1}). 3. Carboxylic groups: C=O (1,600-1,700 cm^{-1}) Alkenes: C=C, (1,600-1,680 cm^{-1}) 4. Phenolic groups: C-OH 3,200-3,600 cm^{-1} Aromatic compounds: C=C (1,450-1,600 cm^{-1})
12	50% Potassium humate + Fe	Total peak: 205 Search area: 400-4,000 cm^{-1} Wave numbers: 3,980-416 cm$^{-1.}$ 1. Aromatic compounds: C=C (1,450-1,600 cm^{-1}) solid phases: (400-1,200 cm^{-1}) 2. Organic acids: C=O (1,700-1,750 cm^{-1}) and halogen-containing compounds: CX (500-1,600 cm^{-1}). 3. Methoxyl groups: O-CH3 (2,800-3,000 cm^{-1}) and phenolic groups: (C-OH) 3,200-3,600 cm^{-1}. 4. Functional groups: C=O (1,600-1,750 cm^{-1}) and alkane: CH (2,800-3,000 cm^{-1}). 5. Fe: 400-600 cm Fe ions.	Total peak: 14 Search area: 400-4,000 cm^{-1} Wave numbers: 3,386-419 cm$^{-1.}$. S compounds: 1,000-1,200 cm^{-1}, SH and S=O. 2. Solid particles (asphaltenes): 600-1,600 cm^{-1}. 3. Pyrene: C=C, 1,450-1,600 cm^{-1}. 4. Ammonia (NH_3): 1,400-1,600 cm^{-1}, NH. 5. Fe: 400-600 cm^{-1}, Fe ion.	Total peak: 13 Search area: 400-4,000 cm^{-1} Wave numbers: 2,919-689 cm$^{-1.}$ 1. Functional groups: ketones (C=O) and aldehydes (C=O), (1,700-1,750 cm^{-1}) aromatic compounds: C=C, (1,450-1,600 cm^{-1}). 2. Alkynes (paraffins): C≡C, (2,100-2,260 cm^{-1}) and alkanes: CH, (2,800-3,000 cm^{-1}). 3. Phenolic groups: (C-OH) 3,200-3,600 cm^{-1} and functional groups: C=O in ketones (1,700-1,750 cm^{-1}).

13	1% Potassium humate + Si	Total peak: 61 Search area: 400-4,000 cm^{-1} Wave numbers: 3,679-423 cm^{-1} 1) Alkanes (paraffins): 2,800-3,000 cm^{-1} (CH bonds). 2) Alkenes (olefins): 1,600-1,680 cm^{-1} (C=C bond). 3) Aromatic compounds (benzene, toluene): 1,450-1,600 cm^{-1} (C=C in the aromatic ring). 4) Functional groups: Ketones (C=O): 1,700-1,750 cm^{-1}; aldehydes (C=O): 1,700-1,750 cm^{-1}; carboxylic groups (C=O): 1,600-1,700 cm^{-1}.	Total peak: 15 Search area: 400-4,000 cm^{-1} Wave numbers: 3,853-419 cm^{-1} 1) Solids 400-1,200 cm^{-1} Alkynes (paraffins): C≡C 2100-2260 cm^{-1} 2) C=O in organic acids (1,700-1,750 cm^{-1}) and CX in halogen-containing compounds (500-1,600 cm^{-1}). 3) Aromatic compounds and functional groups: C=C (1,450-1,600 cm^{-1}) and C=O (1,600-1,750 cm^{-1}).	Total peak: 12 Search area: 400-4,000 cm^{-1} Wave numbers: 2,920-711 cm^{-1} 1) Alkenes C=C (1,600-1,680 cm^{-1}); aromatic C=C (1,450-1,600 cm^{-1}) 2) Halogen-containing compounds CX (X: F, Cl, Br, I) (500-1,600 cm^{-1}); alkynes CH (2,800-3,000 cm^{-1}) 3) Functional groups C=O (1,600-1,750 cm^{-1}); methoxyl groups: O-CH_3 (2,800-3,000 cm^{-1})
14	10% Potassium humate + Si	Total peak: 181 Search area: 400-4,000 cm^{-1} Wave numbers: 3,943-427 cm^{-1}. 1) Acyclic aromatic hydrocarbons: cyclohexane: 2,800-3,000 cm^{-1} CH. 2) Silicates, oxides: 400-1,200 cm^{-1}. 3) C=O in acids: 1,700-1,750 cm^{-1}. OC in the ether: 1,000-1,300 cm^{-1}. 4) Aromatic compounds (benzene, toluene): 1,450-1,600 cm^{-1} C=C. 5) Silicates: Si-O 800-1,200 cm^{-1}.	Total peak: 15 Search area: 400-4,000 cm^{-1} Wave numbers: 3,385-711 cm^{-1}. 1) Methyl groups (2,800-3,000 cm^{-1}) and alkenes C=C (1,600-1,680 cm^{-1}) 2) Alkanolamines: OH (3,200-3,650 cm^{-1}) and CC alkyls (600-1,500 cm^{-1}). 3) Phenols 3,200-3,600 cm^{-1} (C-OH); ketones C=O (1,700-1,750 cm^{-1}). 4) Silicates: Si-O 800-1,200 cm^{-1}.	Total peak: 21 Search area: 400-4,000 cm^{-1} Wave numbers: 3,378-872 cm^{-1}. 1) Carboxyl groups: C=O (1,600-1,700 cm^{-1}) methyl groups (2,800-3,000 cm^{-1}) CH 2) Phenolic groups (C-OH) (3,200-3,600 cm^{-1}) alkanolamine groups (3,200-3,650 cm^{-1}) 3) Aromatic compounds: C=C (1,450-1,600 cm^{-1}) Halogen–containing compounds CX (where X is F, Cl, Br, I) (500-1,600 cm^{-1})
15	30% Potassium humate + Si	Total peak: 143 Search area: 400-4,000 cm^{-1} Wave numbers: 3,989-408 cm^{-1}. 1) Cyclohexane (acyclic aromatic hydrocarbon): 2,800-3,000 cm^{-1} CH. 2) Silicates (solid phases and mineral components): 400-1,200 cm^{-1}. 3) Carboxyl groups (C=O): 1,700-1,750 cm^{-1} 4) Alkanes: CH 2,800-3,000 cm^{-1}. 5) Phenolic groups (C-OH) in phenols and cresols: 3,200-3,600 cm^{-1}. 6) Silicates: Si-O 800-1,200 cm^{-1}.	Total peak: 14 Search area: 400-4,000 cm^{-1} Wave numbers: 3,384-419 cm^{-1}. 1) Alkanolamine groups: OH (3,200-3,650 cm^{-1}); OH groups in water (3,200-3,650 cm^{-1}) 2) halogen-containing CX compounds (500-1,600 cm^{-1}); alkenes C=C (1,600-1,680 cm^{-1}) 3) Solid phases in alkanes: C-C (600-1,500 cm^{-1}) 4) Silicates: Si-O 800-1,200 cm^{-1}.	Total peak: 17 Search area: 400-4,000 cm^{-1} Wave numbers: 3,371-871 cm^{-1} 1) Alkylbenzenes: 700-1,600 cm^{-1} CH 2) Polycyclic aromatic hydrocarbons: CH 800-1,600 cm^{-1} 3) Bitumen in oil: 1,600-3,000 cm^{-1} of CH and C=C bonds, OH groups. 4) Silicates: Si-O 800-1,200 cm^{-1}.
16	50% Potassium humate + Si	Total peak: 106 Search area: 3,691-405 cm^{-1}. 1) Methyl groups (CH) and ethyl groups (CH) 2,800-3,000 cm^{-1} 2) Aromatic compounds (benzene, toluene): C=C 1,450-1,600 cm^{-1}. 3) Functional groups (ketones, aldehydes, carboxyl groups): C=O 1,600-1,750 cm^{-1} 4) Alkenes (olefins): C=C 1,600-1,680 cm^{-1} 5) Halogen–containing compounds: CX (where X is F, Cl, Br, I) 500-1,600 cm^{-1} 6) Silicates: Si-O 800-1,200 cm^{-1}.	Total peak: 14 Search area: 400-4,000 cm^{-1} Wave numbers: 3,386-419 cm^{-1}. 1) Alkynes (paraffins): C≡C 2,100-2,260 cm^{-1}; solid phases and mineral components 400-1,200 cm^{-1} 2) Organic acids C=O (1,700-1,750 cm^{-1}); halogen compounds (500-1,600 cm^{-1}) CX 3) Aromatic compounds: peaks C=C (1,450-1,600 cm^{-1}); functional groups C=O (1,600-1,750 cm^{-1}) 4) Silicates: Si-O 800-1,200 cm^{-1}.	Total peak: 13 Search area: 400-4,000 cm^{-1} Wave numbers: 3,387-685 cm^{-1}. 1) Alkanes: 2,800-3,000 cm^{-1} CH. 2) S dioxide (SO_2): S=O 1,000-1,200 cm^{-1}. 3) Arene: 1,450-1,600 cm^{-1} C=C.

Table 6: Concentration of heavy metals in the soil before and after treatment with various solutions of humic preparations

Sample/Heavy metal	Cadmium (Cd)	Lead (Pb)	Chrome (Cr)	Zinc (Zn)	Copper (Cu)
Maximum permissible concentration (MPC) (mg/kg)	0.5-1	6.0	6.0	23.0	3.0
Original O-soil	0.4586	1.0757	0.2372	1.1997	0.4586
O-Soil + 1% Basic potassium humate solution	0.0010	0.0068	0.1402	0.2122	0.0082
O-Soil + 10% Basic potassium humate solution	0.0010	0.0052	0.0040	0.1422	0.0020
O-Soil + 30% Basic potassium humate solution	0.0016	0.0038	0.0021	0.0644	-0.0002
O-Soil + 50% Basic potassium humate solution	0.0000	0.0020	0.1604	0.1144	0.0081
O-Soil+ 1% Potassium humate-N solution	0.0020	0.0026	0.2088	1.2714	0.0808
O-Soil+ 10% Potassium humate-N solution	0.0044	0.0034	0.0051	0.1006	0.0072
O-Soil+ 30% Potassium humate-N solution	0.0080	0.0090	0.1605	0.1872	0.0139
O-Soil+ 50% Potassium humate-N solution	0.0031	0.0035	0.2670	0.1966	0.0245
O-Soil+ 1% Potassium humate-Fe solution	0.0028	0.0032	0.0116	0.2140	0.3387
O-Soil+ 10% Potassium humate-Fe solution	-0.0002	0.0049	0.3727	1.1576	0.0201
O-Soil+ 30% Potassium humate-Fe solution	0.0001	0.0010	0.0038	0.0276	0.0048
O-Soil+ 50% Potassium humate-Fe solution	-0.0004	0.0016	0.0046	0.1802	0.0082
O-Soil+ 1% Potassium humate-Si solution	0.0014	0.0036	0.0050	1.2292	0.0218
O-Soil+ 10% Potassium humate-Si solution	0.0017	0.0057	0.0074	1.2295	0.0353
O-Soil+ 30% Potassium humate-Si solution	0.0028	0.0068	0.1000	1.2440	0.0650
O-Soil+ 50% Potassium humate-Si solution	0.0075	0.0012	0.1000	1.2454	0.0662

DISCUSSION

The elemental analysis results of the original contaminated soil compared to the soil treated with humic preparations revealed only minor variations in the content of carbon (C), hydrogen (H), and nitrogen (N), relative to the control. Notably, S content exhibited a significant reduction. For instance, in the oil-contaminated soil treated with a 10% solution of basic potassium humate, the sulfur content decreased to 0.00%. This reduction is attributed to the high sorption capacity of humic substances, which effectively binds and removes S from the soil.

Different concentrations of humic preparation solutions had different effects on the pH of the control and treated soils. The original O-soil had a pH of 7.97. After applying the Basic humate-K solution at a concentration of 1%, the pH decreased to 7.39, and with an increase in concentration to 10, 30, and 50%, the pH equaled 7.29, 7.40, and 7.38, respectively. In the case of using the humic preparation potassium humate-N solution, a higher pH value was observed. For example, when 1% solution was used, the pH was 7.88, and when the concentration was increased to 50%, it equaled 7.73. The potassium humate-Fe solution also resulted in a slightly increased pH, especially at low concentrations. When 1% solution was used, the pH was 7.89, and at 50%, it was 7.75. When the potassium humate-Si solution was used, a decrease in pH was observed compared to the original soil. When 1% solution was added, the pH was 7.57, and when the concentration was increased to 30 and 50%, it equaled 7.68 and 7.70, respectively. The total range of pH values in the experiment ranged from 7.33 to 7.97.

The humus content in the original soil was 7.68%, and after various concentrations of solutions of basic potassium humate and modifications were applied, an increase in its value was observed. For example, when 1% basic humate-K solution was added to the soil, the humus content increased to 9.77%, and when the concentration was increased to 30%, the humus content went up to 11.31%. Potassium humate-N and potassium humate-Fe solutions also had a positive effect on the humus content in the soil. To determine the optimal composition of the solution and one of the modifications of humic preparations, further research is required, including an analysis of the mechanisms of interaction of various concentrations of solutions with the soil, as well as the study of their long-term effects (Bankole et al., 2024). Developments in this area will increase fertility and improve the ecological condition of the soil in conditions of oil pollution (Abdibattayeva et al., 2019).

The analysis of petroleum product content in the soil over the course of 5, 30, and 60 days following the application of biological preparations revealed that the most effective soil reclamation results were achieved at the final 60-day mark. Specifically, the degree of purification was highest with the humic preparation consisting of 50% Potassium Humate + Fe, achieving an 84.3% reduction in petroleum products. This was closely followed by a 30% Potassium Humate + Si preparation, which resulted in an 83.3% reduction, a 50% Potassium Humate + N preparation with an 83.1% reduction, and a 10% Basic Potassium Humate preparation, which achieved a 70% reduction.

IR spectroscopy showed the presence of aliphatic and aromatic alcohols, ethers, carboxylic acids, and conjugated double bonds in oil-contaminated soils. Such functional groups and acidic protons should provide humic acids with good sorption abilities in ion exchange and complex formation reactions (Mohamed et al., 2024). Humic preparations bind petroleum products well, which was demonstrated by the results (Doszhanov et al., 2024). In oil-contaminated soil treated with 50% potassium humate-Fe, the number of peaks on day 5 was 205, and on day 13 only 6.

In all soil samples treated with humic preparations, a downward trend was noted in the petroleum products content associated with high surface activity concerning model petroleum hydrocarbons of humic substances. Due to this, they can be used as washing surfactants, surfactant analogs, and biosurfactants. The studies demonstrated the increased emulsifying, petro-structuring, and recycling abilities of humic preparations concerning petroleum hydrocarbons (Al-Robai & Shaker, 2023).

The analysis of the effect of different concentrations of humic preparation solutions on the heavy metal content showed that the content of Cd and Pb was characteristic of the common form of the soil, while such metals as Cr, Zn, and Cu were more characteristic of the mobile form. This is important for determining a reclamation strategy since different types of soils require different approaches to cleaning and remediation (Kudaibergen et al., 2015).

Based on the data presented in Table 4, several conclusions can be drawn regarding the effectiveness of different treatments on heavy metal concentrations in soil. Cadmium (Cd) concentrations in the original soil and most treated samples, with the exception of those treated with silicon-containing solutions, remain within acceptable limits. However, lead (Pb) and zinc (Zn) concentrations exceed the maximum permissible concentrations (MPC) in both the original soil and the majority of treated samples. The concentrations of chromium (Cr) and copper (Cu) are generally within acceptable limits, although some exceptions exist. Solutions containing nitrogen (N) demonstrate significant effectiveness in reducing metal concentrations in the soil, while solutions with added iron (Fe) also show a positive effect but are less effective than those with nitrogen. On the other hand, potassium humate solutions with the addition of silicon (Si) are not consistently effective in reducing metal concentrations to MPC levels. To better understand the effectiveness of these various treatments and their impact on metal concentrations in soil, further research is needed. This should include extended observation periods and consideration of additional factors.

Humic preparations showed their effectiveness for the sanitation of contaminated soils and preventing the spread and localization of foci of new pollutants with simultaneous detoxification of oil and petroleum products. This type of treatment ensures effective sorption of hydrocarbons and activation of microbiological processes, resulting in accelerated degradation of petroleum products and soil purification. The basic agrochemical properties are improved, and soil fertility is increased. We established that when humic substances are introduced into the soil, the characteristic smell of petroleum products disappears, and a characteristic layer is formed that prevents the migration of oil and oil products down the soil profile, that is, surface localization and volume localization of the source of contamination occurs (Khokhlova et al., 2009).

Conclusion

Soil pollution with petroleum products, particularly in West Kazakhstan, presents a significant environmental challenge that demands attention and the development of effective reclamation strategies. This study demonstrated that the content of petroleum products and heavy metals varies across different O-soil samples, highlighting the need for tailored soil purification approaches. The results, corroborated by IR spectroscopy, indicate that humic preparations and their modifications with N, Fe, and Si at varying concentrations (1, 10, 30, 50%) effectively reduce petroleum products and heavy metals in contaminated soils, enhance the humus layer, and regulate soil pH. These findings suggest that humic preparations hold promise as a reclamation tool for O-soils and technologically disturbed lands.

Further research is needed to determine the optimal compositions and concentrations of humic preparation solutions and their effect on the ecological state of the soil. The obtained data can be used to develop practical recommendations and applications for cleaning contaminated soils and restoring their natural balance in West Kazakhstan and other areas.

The results confirm the effectiveness of humic preparations and their modifications in the reclamation of O-soils.

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