Use of Mineral Sorbents for the Purification of Natural Environments from Petroleum Products in the Kolsky Northern Region

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***Abstract* – The research was carried in order to study the effectiveness of using alumino-silicate vermiculite mineral of various modifications as a sorbent for the purification of environment from oil products. Thermally activated vermiculite with hydrophilic properties can be used to clean oil-contaminated areas, prevent hydrocarbon migration and improve the structural condition of polluted soils. Immobilization on the sorbent of bacteria cells-oil destructors of the genus Pseudomonas increases its efficiency and contributes to a more rapid recovery of the polluted environment. The treatment of thermally activated vermiculite with a water-repellent spirit makes it possible to obtain a sorbent with high water resistance properties. The use of a water-repellent sorbent in the purification of water from diesel fuel makes allows achieving a high degree of purification - up to 99.8%. Such a sorbent can be used for localization and collection of oil and petroleum products in coastal waters, as well as for cleaning oil-contaminated wastewater. The sorbent used in the cleaning process can be restored and reused.**

Keywords – subarctic region; bioremediation; mineral sorbents; hydrocarbon-oxidizing bacteria; oil pollution.

I. INTRODUCTION

The problem of pollution by oil and oil products of the natural environments of the Northern regions of Russia does is still relevant. The development of the oil and gas complex of the Euro-Arctic region has led to the need to develop ways to ensure environmental safety during transportation, transshipment and processing of oil and oil products in the Murmansk region.

Under natural conditions, the removal of oil and its components from polluted environment is determined by the combination of abiotic and biotic processes. The natural processes of self-purification and restoration of soils polluted by oil, proceed rather slowly, especially with high levels of pollution and low ability to self-purification, which is typical of the Northern regions.

Bioremediation using petro-destructive microorganisms and sorbents is an effective means of eliminating environmental pollution of oil and oil products [1-3]. For cleaning oil-polluted environment, both sorbents based on natural plant materials [4–9] and synthetic sorbents with higher oil capacity and low water absorption compared to sorbents based on plant and organic materials [10–12] are widely used.

For soil purification, it is important that the sorbent improves soil structure. It should be biodegradable and can serve as a source of mineral nutrition for hydrocarbon-oxidizing microorganisms [13, 14]. In order to clean the surface of water bodies, such properties of the sorbent as high hydrophobicity and oil capacity are used [15-17].

The purpose of this study is to assess the possibility of using mineral sorbent for the purification of water and soil from oil products and oil emulsion in laboratory experiments.

II. METHODS AND MATERIALS

In order to clean the water surface and soil from hydrocarbons, an aluminosilicate mineral – vermiculite was used as a sorbent. One of the largest deposits of vermiculite is located in the Murmansk region. Thermally activated sorbent based on vermiculite is characterized by a developed specific surface area, hydrophilicity, biostability, and chemical inertness. To obtain various modifications of the sorbent (Table 1), the thermally activated vermiculite was treated with a water-repellent agent, and the bacterial cells of hydrocarbon-oxidizing bacteria were immobilized.

For the immobilization on the surface of the sorbents 2 strains of bacteria belonging to the genus Pseudomonas were used, previously isolated from oil-contaminated soils of the Kola Peninsula and possessing hydrocarbon-oxidizing activity. The bacterial suspension with a density of 108 cells / ml was thoroughly mixed with the sorbent (suspension ratio: sorbent = 15: 1) for two hours using an electric stirrer. Then the sorbent was separated from the suspension and dried under an infrared lamp.

TABLE I. MODIFICATIONS OF VERMICULITE SORBENT

Variant	Sorbent processing method
T	Thermal activation
TH	Thermal activation + hydrophobization
TI	Thermal activation + immobilization of bacterial cells
THI	Thermal activation + hydrophobization + immobilization of bacterial cells

It was necessary to impart hydrophobic properties to the vermiculite sorbent for effective extraction of hydrocarbons from the water surface. In this article, the authors used a sorbent treated with a non-alkaline organosilicon compound – oligo-methy-lhydride-siloxane (the production name is “Penta-804”). As a result of the treatment, it was possible to obtain a hydrophobic sorbent, the oil capacity of which reached 6 g / g, the moisture capacity for three days did not exceed 0.5 weight %, and the ability to stay on the surface of the water was maintained for more than 10 days [18].

The determination of the content of petroleum products in water and in the sorbent was performed by IR-spectrometry on an AN-2 petroleum analyzer [19].

Water purification from oil and oil products. The water from the Barents Sea or model water was used, the salinity and density of which by adding sea salt corresponded to the average values for the Barents Sea (salinity 33, density 1.025 g / cm3). Commercial oil of Prirazlomnoye deposit and diesel fuel in the amount of 3.3 about % was used as pollutants. After contamination, modified vermiculite sorbents were applied to the water surface. The mass ratio of water: sorbent was 50: 1, the ratio of pollutant: sorbent - 2: 1.

The residence time of the sorbent in water was 3-7 days at a temperature of 15-20 ° C, after which the sorbent was removed and the residual content of oil products in water was determined.

Water purification from water-oil emulsion at low temperatures. The purification of water from emulsified oil is a more complex process than its collection from the surface. Water-oil emulsion was prepared from medium viscosity oil for 1 day on a special mixing device. The ambient temperature during the preparation of the emulsion and the experiment was 10 ° C. Hydrophobic heat-activated vermiculite was used as a sorbent. The residence time of the sorbent in water was 30-60 minutes with stirring.

Soil decontamination from oil. Cleaning the soil from oil and oil products, such properties of sorbents as their natural origin and lack of toxic effect are extremely important. For the research the authors used agro-soil Al-Fe-humus contaminated with commercial oil from the Prirazlomnoye field in an amount of 5 wt. %. The sorbent was introduced into the contaminated soil through in a day and thoroughly mixed. The ratio of soil and sorbent was 100:1, the ratio of oil and sorbent was 2: 1. The test was carried out at a temperature of 15-20 ° C for 90 days. The soil in the vessels was watered as it dried. After completion of the experiment, the oil product content in the soil and its phytotoxicity were determined by germination of wheat seeds.

III. RESULTS

Water purification from oil and oil products. Laboratory studies showed that thermally activated hydrophobic sorbent has the highest efficiency in the purification of water from diesel fuel (Table 2). In this case, the sorbent, together with diesel fuel, is localized on the surface of the water, which provides favorable conditions for the oxidation of hydrocarbons.

TABLE II. CONTENT OF HYDROCARBONS IN WATER AFTER 3 DAYS

Variant	The content of hydrocarbons in water, g/l	Cleaning degree, %
T	19.88±0.15	14
TH	0.05±0.01	99
TI	12.48±3.69	45
THI	0.05±0.01	99

Thermally activated sorbent (T), turned out to be ineffective for the purification of water from oil products due to its high hydrophilicity. The ability to bind hydrocarbons in hydrophobic (immobilized and non-immobilized) sorbents was the highest. At the same time, the presence of bacterial cells on the sorbent did not significantly affect the efficiency of water purification.

It is necessary to note that in the experiment in 7 days there was a tendency to the increase in the content of hydrocarbons in water, probably due to desorption (Table 3). Therefore, the use of sorbents for a long time is not advisable (Table 3).

TABLE III. CONTENT OF HYDROCARBONS IN WATER IN 3 AND 7 DAYS

Variant	The content of hydrocarbons in water, g/l	
	3 days	7 days
T	18.88±0.15	20.71±0.75
TH	0.05±0.01	0.03±0.01
TI	12.48±3.69	16.82±2.83
THI	0.05±0.01	2.36±0.5

Thus, based on the results obtained in further experiments on the purification of water from oil, thermally activated hydrophobic vermiculite sorbent was used.

The efficiency of a thermally activated hydrophobic sorbent was 95% with an initial oil content of 10 ml / l in laboratory experiments on the purification of water from oil. It was also found that during the experiment the amount of sorbent with oil deposited on the bottom of the vessel did not exceed 9%. Figure 1 shows the steps of water purification from oil.

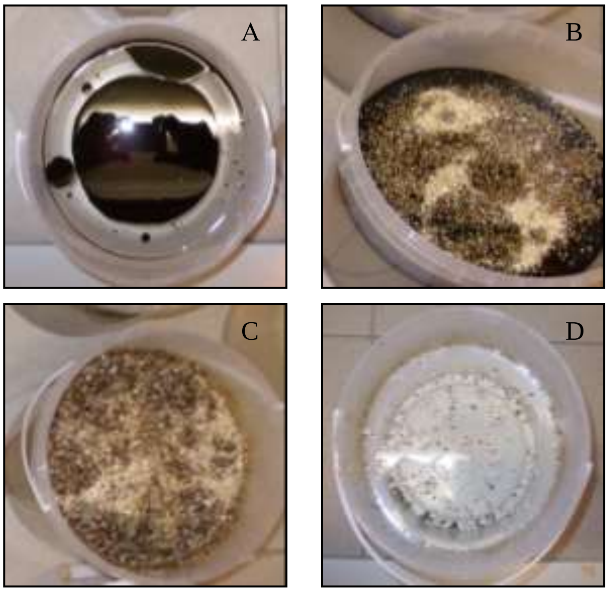

Fig. 1. Stages of water purification from oil: A - before applying the sorbent; B - in 1 hour after application of the sorbent; C - in 7 days after the application of the sorbent; D - after collecting the sorbent from the surface.

Laboratory experience in water purification from water-oil emulsion at low temperatures

The study of the ability of a thermally activated hydrophobic sorbent to purify seawater from an emulsion was carried out in several stages. At the first stage, the possibility of using a sorbent with high emulsion content with the formation of a film on the water surface was evaluated. In order to achieve it the emulsion was applied to the surface of the water. A different amount of sorbent — 1, 3, and 5 g — was applied to the surface of the emulsion on top. The contact time of the sorbent with water in a static state was 30 minutes, after which the glasses with water were placed on a laboratory rocking chair for another 30 minutes. After the set time, the emulsion with and without a sorbent was filtered and the residual content of hydrocarbons in water was determined. The obtained data are presented in Table 4.

TABLE IV. CONTENT OF HYDROCARBONS IN WATER (MG / L) AFTER CLEANING AFTER PURIFICATION

Variant	Amount of sorbent, g	The content of hydrocarbons in water, mg/l
Pure sea water	-	0.083±0.026
Contaminated sea water	-	4260±195
Water after mechanical cleaning (filtration)	-	45.2±3.8
Water after mechanical cleaning (filtration) with sorbent	1	3.35±0.16
	3	1.75±0.23
	5	1.70±0.47

The content of hydrocarbons in pure water is 0.083 ± 0.026 mg / l, which is close to the maximal permissible concentration of oil for water bodies of fisheries (0.05 mg / l), in polluted water without purification - 4260 ± 195 mg / l.

The use of sorbent made it possible to reduce the concentration of hydrocarbons in water by 25 compared with simple filtration. The addition of 1 g of sorbent was less effective, while there was no significant difference between the addition of 3 and 5 g of sorbent.

The second phase of the research was aimed at the assessment of the effectiveness of removing emulsified oil from the water column. In order o achieve this, a sorbent in the amount of 1 and 3 g was applied to the surface of polluted water (hydrocarbon concentration - 78 ± 17 mg / l), after which the glasses with water were placed on a laboratory rocking chair for 30 minutes. The effectiveness of the sorbent with vigorous stirring was also studied. For this, 1 g of the sorbent was placed in a column with contaminated water and vigorously stirred on a rotator for 30 minutes. After the set time, the sorbent was filtered, and the residual content of hydrocarbons in water was determined (Table 5).

TABLE V. CONTENT OF HYDROCARBONS IN WATER (MG / L) AFTER PURIFICATION

Variant	Amount of sorbent, g	The content of hydrocarbons in water, mg/l
Pure sea water	-	0.083±0,026
Contaminated sea water	-	78±17
Water after mechanical cleaning (filtration) with sorbent	1	5.00±0.95
	3	2.72±0.28
Water after mechanical cleaning (filtration) with sorbent and intensive mixing	1	1.77±0.31

The introduction of the sorbent reduces the hydrocarbon content in water by 16-28 times, and the intensive mixing of polluted water contributes to a more complete purification and decrease in the concentration of hydrocarbons by 44 times even with a minimum amount of sorbent.

At the final stage, the degree of desorption of hydrocarbons was evaluated. In order to do this, the contaminated sorbent used in the previous experiment was placed in clean water, and it was rocked for 30 minutes on a laboratory rocking chair, after which the concentration of hydrocarbons in water was determined (Table 6).

TABLE VI. CONTENT OF HYDROCARBONS IN WATER AFTER DESORPTION FROM THE SORBENT

Variant	Amount of sorbent, g	The content of hydrocarbons in water, mg/l
Pure sea water	-	0.091±0.026
Water after mixing with contaminated sorbent	1	0.28±0.11
	3	1.00±0.25

Thus, desorption of hydrocarbons from the sorbent in 30 minutes was 0.3-1.6%.

Purification of soil from oil. Laboratory experiments on the study of the effectiveness of purification of oil-polluted soil using sorbents of various modifications showed the following results. For 90 days, the content of hydrocarbons in the control due to physicochemical and biological oxidation processes decreased by 42%. The addition of hydrophilic sorbents (T and TI) led to the increase in soil purifying efficiency of about 20%. The use of hydrophobic sorbents significantly reduced the degree of soil purification (Table 7).

TABLE VII. CONTENT OF HYDROCARBONS IN THE SOIL AFTER PURIFICATION

Variant	The content of hydrocarbons in soil, g/kg		Cleaning degree, %
	1 day	90 days	
Control (without sorbent)	45.25±4.51	26.08±1.82	42
T	46.13±3.37	17.34±2.61	62
TH	39.7±0.72	33.14±2.42	17
TI	44.13±2.79	15.26±0.46	65

The sorbent treated with a water repellent has a high affinity with hydrocarbons, but at the same time prevents their active microbiological destruction. Such a sorbent must be removed from the soil after its complete saturation with oil products, which causes certain difficulties.

Hydrophilic sorbents can be left in the soil, because they serve as a matrix for the development of hydrocarbon-oxidizing microorganisms and improve the structure and water-air conditions of the soil.

The determination of soil phytotoxicity after the use of sorbents also showed that the hydrophobic sorbent has a negative impact on the development of wheat seeds (Fig. 2).

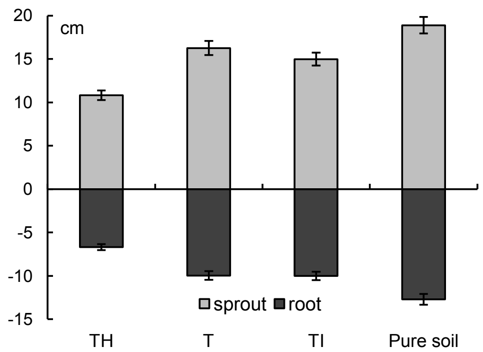

Fig. 2. Phytotoxicity of soil after use of sorbents

The height of the seedlings and the length of the roots of wheat in the variants with the use of a hydrophobic sorbent were the smallest. However, when using hydrophilic sorbents, the growth indicators of wheat did not reach the values characteristic of pure soil, which indicates the need for further purification.

IV. CONCLUSION

As a result of laboratory studies, it was found that thermally activated vermiculite, treated with water-repellent agent, effectively purifies water from oil and oil products. The research showed the effectiveness of this sorbent in the purification of oil-contaminated sea waters, especially with intensive mixing of polluted water with the sorbent. The concentration of hydrocarbons after using the sorbent is reduced tenfold. In this case, the desorption of oil products from the sorbent when transferring it to clean water does not exceed 0.3-1.6% in 30 minutes.

Hydrophobic vermiculite sorbent can be recommended for water purification after the demulsibility of oil collected during the elimination of an emergency oil spill, for the purification of contaminated ballast and industrial wastewater and the localization of oil stains during the purification of coastal waters.

Hydrophobic thermally activated sorbent is most effective for the purification of polluted aqueous media without prior immobilization with bacterial cells. According to the authors the treatment of the sorbent with a bacterial suspension should be carried out after its collection from the surface of the water in order to accelerate the biological oxidation of hydrocarbons and restore the sorbent for reuse.

The introduction of a hydrophobic thermally activated sorbent into contaminated soil prevents the migration of hydrocarbons in the soil profile and prevents contamination of surrounding environment. The use of such a sorbent is appropriate at the stage of localization of pollution. To purify for the restoration of contaminated soils in conditions where localization of pollutant is no longer required, it is more efficient to apply hydrophilic immobilized vermiculite, which showed a positive result in laboratory studies. This sorbent improves the structure and water-air regime of the soil, which contributes to the oxidation of hydrocarbons.

In general, the studies showed the possibility of using mineral sorbents based on thermally activated vermiculite for wastewater treatment, localization and collection of oil and oil products in water and land, as well as for measures to restore polluted natural environments.

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