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Efficiency of sorption-biological treatment of oil-polluted coastal areas in the Euro-Arctic region

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Abstract. A biotechnology based on sorption-biological treatment for the restoration of the Arctic coastal areas after oil spills was proposed. A hydrocarbon-oxidizing microbial preparation based on microfungi (Penicillium janthinellum, Penicillium simplicissimum) and bacteria (Pseudomonas fluorescens, Pseudomonas putida) was created. Granular activated carbon, thermoactivated vermiculite, and peat were used as sorbents. The sorbents are concentration centers for microorganisms, prevent the spread of hydrocarbons, and improve the condition of the polluted substrate by optimizing the water-air regime. After treatment, sorbents are not removed from the soil. As a result of laboratory studies at +10°C, the hydrocarbon content in the polluted coastal sand was reduced by 44-60%, and in the coastal soil by 25-68% after three months. This technology can be used at the final stage of coastal areas cleaning, as well as the only method of cleaning in highly sensitive areas. The use of aboriginal hydrocarbon-oxidizing microorganisms, typical of most coastal substrates of the Euro-Arctic region, excludes changes in the structure of the microbial community in these areas. The adaptation of these microorganisms to extreme climatic conditions allows biological treatment to be carried out with high efficiency in the Subarctic and Arctic.

1 Introduction

In recent years, the Arctic region has become the center of intersection of national interests of the Arctic states, which leads to the formation of a new system of global and regional security. Reserves of natural resources in the Arctic, primarily hydrocarbons of the continental shelf, cause competition for their development and exploitation, including control over the shelf zone of the Arctic seas [1,2].

At the same time, the Arctic is an area of valuable biodiversity. The growth and expansion of infrastructure, industrial activities and resource exploitation can damage vulnerable ecosystems of the Arctic [3]. The development of the Northern Sea Route is also a negative factor for oil pollution in coastal areas of the Arctic seas [4, 5].

Restoration of coastal ecosystems after oil cleanup can take a long time. A promising method of restoration of oil-polluted coastal areas is biotechnological, based on acceleration of natural processes in the environment [6-7], including the use of sorbents [8-9].

The purpose of this study is evaluation of the effectiveness of the sorption-biological method for cleaning and remediation of oil-polluted coastal areas in the Euro-Arctic region.

2 Materials and methods

2.1 Substrates

Coastal soil and sand from the coast of the Pechenga Bay of the Barents Sea were taken as substrates for laboratory studies (Figure 1).

Fig 1. Areas of substrate selection for laboratory experiments

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Table 1. Characteristics of the substrates for the laboratory experiment

Type of substrate	TOC (%)	pH	Dehydrogenase activity (mg TTC/10g)	Total petroleum hydrocarbon (mg/kg)	Description of the site
Soil	4.74	5.11	1.79	97	salt marsh: 0-2 cm – organogenic, deeper than 2 cm – medium loam
Sand	0.10	7.19	0.01	46	sandy beach

2.2 Oil-water emulsion

The oil-water emulsion was prepared from three types of oil: light, medium and heavy. The ratio of oil: water = 1 : 10. Before preparing the oil-water emulsion, volatile components were removed from the oil by heating it. After this treatment, the oil corresponded in its characteristics corresponded to the oil which had been on the water surface for 1-2 months. sea water of 22‰ salinity was used to prepare the oil-water emulsion.

2.3 Sorbents

We used as sorbents:
- granular activated carbon (GAC) with the size of 2-3 mm granule. GAC consists of 87-97% carbon; its sorption capacity of hydrocarbons is 200-980 g/kg.
- thermoactivated vermiculite (VER) is a mineral of hydromica group with a layered structure. When heated, vermiculite swells and increases in volume several times; it has a high absorption coefficient.
- Milled peat with a low degree of decomposition (no more than 35%).

2.4 Microbial preparation

On the basis of microorganisms isolated from seawater and soil of the Barents Sea coast, a microbial preparation of hydrocarbon-oxidizing action was developed, which includes strains of microscopic fungi (*Penicillium janthinellum, Penicillium simplicissimum*) and bacteria (*Pseudomonas fluorescens, Pseudomonas putida*).

2.5 Design of the laboratory experiment

oil-water emulsion of different types of oil was introduced into the substrates (soil and sand) and mixed. Polluted substrates were placed into containers in an amount of 200 g, and then microbial preparation, sorbents and mineral fertilizers were added (table 2). The studies were carried out at a constant temperature of +10°C. The soil and sand in the containers were periodically moistened and stirred 2 times a month. The experiment lasted for 3 months. Soil samples for analysis were taken once a month.

Table 2. Design of the laboratory experiment

Type of oil	Variant of treatment	Sorbents (g)			Mineral fertilizers	Microbial preparation
		Peat	GAC	VER		
All types (light, medium and heavy)	no treatment	-	-	-	-	-
	Peat	10	-	-	+	+
	GAC	-	2	-	+	+
	VER	-	-	1	+	+

2.6 Methods of analysis

The content of total petroleum hydrocarbons (TPH) in the soil was determined by infrared spectrometry using the AN-2 analyzer [10]. This method is based on extraction of TPH from soil by tetrachlorocarbon, separation of oil products from the polar hydrocarbons in a column filled with aluminum oxide, and further spectrophotometric identification of hydrocarbon content by the intensity of infrared radiation absorption.

The activity of soil dehydrogenase was determined by the colorimetric method (540 nm wavelength) based on the reduction of the colorless salt 2,3,5-triphenyltetrazolium chloride to red triphenylformazan [11].

2.7 Statistical processing

Statistical analysis of the data was carried out using Microsoft Excel 2007.

3 Results and discussion

3.1 Bioremediation of polluted sand

TPH content in the sand before its pollution with oil-water emulsion was 46 mg/kg, and after the pollution – from 2831 to 4677 mg/kg for different types of oil.

Three months after the start of bioremediation, the TPH content decreased by 44-60%. The maximum decrease was noted in the sand polluted with light oil. When polluted with medium and heavy oil emulsion of, the degree of oil products destruction was lower (Figure 2).

Type of oil	Variant of treatment	TPH (mg/kg)				Decrease of TPH (%)
		Initial	1 month	2 months	3 months	
Light	no treatment	4677	4494	4343	4080	13
	Peat		2091	2342	2293	51
	GAC		1903	2014	1881	**60**
	VER		2395	2305	2497	47
Medium	no treatment	2879	2585	2457	2213	23
	Peat		1540	1855	1416	**51**
	GAC		1742	1937	1408	**51**
	VER		1606	1736	1477	49
Heavy	no treatment	2831	2372	2313	2035	28
	Peat		1662	1823	1544	45
	GAC		1767	1781	1285	**55**
	VER		1837	1831	1595	44

Fig. 2. Dynamics of the TPH content in polluted sand

During the first month, biodegradation in variants with light oil proceeds more intensively than with heavier types of oil. There is a tendency of more intensive biodegradation of hydrocarbons with the use of GAC, but no statistically significant difference between types of sorbents was found.

In the first two months after the beginning of bioremediation, the greatest increase in the activity of soil dehydrogenase was noted in the variants with the addition of peat, but after three months the maximum activity was in the variants with the use of GAC (Figure 3). In general, the activity of the enzyme during the observation period increased by 10-12 times when using different sorbents, which indicates an increase in the processes of microbiological destruction of hydrocarbons.

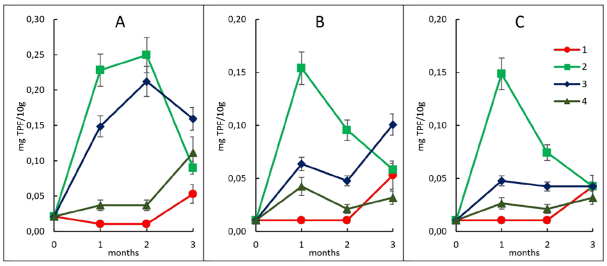

Fig. 3. dynamics of dehydrogenase activity in sand after pollution with light (A), medium (B) and heavy (C) oil emulsions. 1 - no treatment; 2 - peat; 3 - GAC; 4 - VER.

The most effective method proved to be sorption-biological treatment of sandy substrates using granular activated carbon. this method of treatment reduces the content of petroleum hydrocarbons, as well as high-molecular-weight polar organic compounds – products of hydrocarbon transformation.

3.2 Bioremediation of polluted soil

The TPH content in the sand before its pollution with oil-water emulsion was 97 mg/kg, and after the pollution it ranged from 2159 to 4981 mg/kg for different types of oil. The petroleum hydrocarbons predominate in the organic matter of polluted soil.

Three months after the beginning of bioremediation, the TPH content decreased by 25-68%. A significant decrease in the TPH content when using sorbents was noted only in variants with light oil emulsion. The use of granular activated carbon is the most effective among the sorbents (Fig. 4).

Type of oil	Variant of treatment	TPH (mg/kg)				Decrease of TPH (%)
		Initial	1 month	2 months	3 months	
Light	no treatment	4981	4544	4296	3690	26
	Peat		2122	2316	2137	57
	GAC		1684	2147	1601	**68**
	VER		1806	2467	2067	59
Medium	no treatment	2193	1921	1963	1390	37
	Peat		1548	1505	1362	38
	GAC		1548	1528	1438	34
	VER		1759	1776	1376	37
Heavy	no treatment	2159	1609	1690	1331	38
	Peat		1873	1526	1469	32
	GAC		1816	1855	1484	31
	VER		1862	1916	1610	25

Fig 4. The dynamic of the TPH content in polluted soil

Bioremediation with sorbents also reduced the content of high-molecular-weight polar organic compounds by 54-62% for variants with light oil and by 34-39% for variants with medium oil.

dehydrogenase activity increased immediately after contamination to 2.85-4.03 mg TPF/10g. three months later, the enzyme activity decreased 2-2.5 times to values comparable to uncontaminated soil. The use of sorbents with microbial preparation did not significantly effect on the activity of the enzyme (Figure 5).

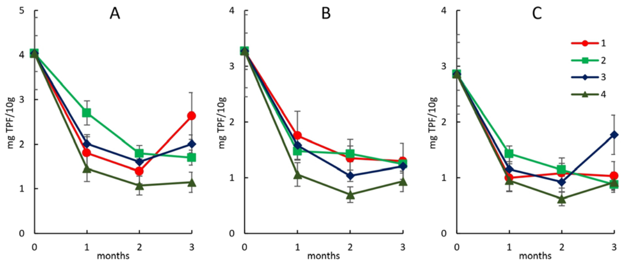

Fig.5. dynamics of dehydrogenase activity in soil after pollution with light (A), medium (B) and heavy (C) oil emulsions. 1 - no treatment; 2 - peat; 3 - GAC; 4 - VER.

An increase in dehydrogenase activity immediately after pollution of coastal soil indicates the presence of an active microbial pool in it, capable of using oil components as a source. As the available components for microbial oxidation decrease, dehydrogenase activity decreases.

3.3 Efficiency of remediation

Based on the results of the analysis of TPH content in the soil, we can calculate the time of their almost complete decomposition, i.e., at 99% (T99). The formulas for the calculation are as follows [12]:

$$T99 = \ln 100/k;$$

$$k = \ln(\frac{y0}{y})/t,$$

where k is the rate constant of hydrocarbon decomposition, y is the residual hydrocarbon content at the time t; y0 is the initial content of hydrocarbon.

The use of sorption-biological method accelerated the cleaning of coastal substrates (Figure 6).

Type of oil	Variant of treatment	The rate constant of hydrocarbon decomposition	T99 (days)
sand			
Light	no treatment	0.00152	3033
	Peat	0.00792	581
	GAC	0.01012	455
	VER	0.00697	660
Medium	no treatment	0.00292	1575
	Peat	0.00788	584
	GAC	0.00795	579
	VER	0.00742	621
Heavy	no treatment	0.00367	1256
	Peat	0.00673	684
	GAC	0.00877	525
	VER	0.00637	723
soil			
Light	no treatment	0.00333	1381
	Peat	0.00940	490
	GAC	0.01261	365
	VER	0.00977	471

Fig. 6. The time of almost complete decomposition (T99) of petroleum hydrocarbon

The sorption-biological method will reduce the cleaning time of sandy beaches by 2.0-5.5 times when polluted with different types of oil, and of coastal soils by 3.2 times when polluted with light oil. The obtained results confirm the conclusions about the effectiveness of the sorption-biological method of bioremediation of oil-polluted soils in the Subarctic that we made earlier on the basis of laboratory [13] and field [14] studies.

4 Conclusion

Studies have shown that the sorption-biological method of bioremediation can reduce the sand cleaning time by 2-5.5 times. Biodegradation in variants with light oil in the first month proceeds more intensively than heavier types of oil. The maximum decrease in the amount of hydrocarbons in the sand and the increase in the activity of dehydrogenase were noted when using GAC and peat (together with a microbial preparation and mineral fertilizers).

The efficiency of sorption-biological treatment of coastal soil was lower. The maximum effect was noted when GAC was added to the polluted soil. The use of this method is justified only when coastal soils are polluted with light oil. An increase in the activity of soil dehydrogenase immediately after pollution indicates the presence of a pool of microorganisms capable of utilizing oil components. Under these conditions, biostimulation, based on the application of mineral fertilizers to the polluted soil, will be an effective method of cleaning.

There is no significant difference between the sorbents used, therefore, each of them can be used depending on the availability and economic feasibility. The sorption-biological method of bioremediation allows cleaning with high efficiency in the Arctic and Subarctic.

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