Study of sorbents of oil and oil products for emergency oil spills response in the Arctic seas

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Abstract. The possibility of using sorbents with immobilized microorganisms to eliminate oil spills in the sea in the climatic conditions of the Arctic is investigated. Based on the research results, the appropriateness of using these sorbents was assessed. Studies have also been conducted on the effectiveness of using commercial sorbents for the elimination of oil spills and oil products on the surface of seawater at positive and negative ambient temperatures.

1. Introduction
The development of the oil and gas industry and plans for the development of the Arctic shelf is very likely to contaminate water resources, despite modern technologies and equipment for preventing accidental oil and oil product spills [1], [2], [3], [4].

Currently, there are many commercial sorbents for collecting oil and oil products from the water surface. However, the question remains of the actual effectiveness of the elimination of oil and oil product spills by these sorbents in the waters of the Arctic seas [5]. At the same time, a number of publications [6], [7] say that a promising direction in the development of sorption materials is the immobilization of hydrocarbon-oxidizing microorganisms on the surface of the sorbent.

A relevant area of research in this case is the study of the actual effectiveness of commercial sorbents and the effectiveness of sorbents with immobilized microorganisms in conditions of oil spill in the seas of the Arctic region.

2. Research methodology
The following sorbents were chosen as objects of study: the natural sorbent “Unisorb-extra” [8], the natural sorbent “SoNet-1” [9], the natural sorbent “Lessorb” [10], silicon carbide sorbent “TShR”, or “TShR”[11]. As a carrier of immobilized microflora, we selected: expanded clay (GOST 9757-90), grain size of 5–10 mm and natural sorbent “Lessorb”. The immobilization of microorganisms of excess activated sludge on the surface of expanded clay and the sorbent “Lessorb” was carried out according to the method described in the work [12].

Simulation of seawater pollution was carried out by introducing various samples of oil and oil products (OP) in seawater taken in the Kola Bay of the Barents Sea. The following products were selected as model pollutants: diesel fuel (density 820 kg / m³), motor oil (density 910 kg / m³) and oil (density 891 kg / m³). The choice of these pollutants is due to the most probable spills of each oil product as a result of emergency situations on ships in the sea area of the Kola Bay and the Barents Sea. To assess the effectiveness of using immobilized microorganisms to reduce pollution concentrations, petroleum products were introduced in a volume of 5 ml in a 4-liter container with a water surface area of 400 cm² filled with seawater from the Kola Bay. To determine the effectiveness of purification of oil-contaminated water using commercial sorbents, oil products were added in a
volume of 2 ml in a tank with a volume of 2 l, with a water surface area of 150 cm$^2$, filled with seawater of the Kola Bay. Simulating the conditions for the actual liquidation of a spill of oil products, taking into account the time the events started from the moment of the spill, the samples of contaminated water were stirred and aged for an hour before applying the sorbents to the surface of the water.

The sorption process was simulated as follows: the sorbent was evenly distributed over the surface of contaminated water. The sorption process continued for 30 minutes, and then the sorbent with adsorbed oil was removed from the water.

3. Methods and devices

The content of oil products in seawater was determined according to [13] using the standard fluorimetric method on the "Fluorat-02" liquid analyzer. Water samples were taken below the oil film.

4. Results and discussion

To determine the effective consumption of sorbents depending on the type of oil product, studies of the sorption capacity of materials were carried out according to [14]. The studies were carried out at a negative ambient temperature (minus 5°C (± 1°C)), simulating oil spill conditions in the winter, and at an ambient temperature plus 16°C (± 1°C), simulating oil spill conditions in the summer period. In addition, in order to take into account the water absorption of the sorbents during oil sorption on the water surface, the oil capacity of the sorbents on the water surface was determined.

Studies of the sorption capacity of materials for various petroleum products at a positive temperature are presented in table 1.

| Sample OP | Expanded clay + EAS* | “Lessorb” + EAS* | “Lessorb” | “Unisorb-extra” | “TShR” | “SoNet-1” |
|-----------|----------------------|------------------|-----------|-----------------|--------|-----------|
| Oil       | 0.150                | 3.69             | 4.02      | 1.638           | 6.61   | 1.48      |
| Diesel fuel | 0.108                | 2.65             | 3.19      | 1.608           | 6.76   | 1.108     |
| Engine oil | 0.145                | 3.08             | 3.56      | 1.66            | 7.30   | 1.33      |

* EAS - microorganisms of excess activated sludge

An analysis of the data showed that the sorption capacity of each material does not vary significantly with respect to the sorption of various types of oil products and significantly differs depending on the type of sorbent. It should be noted that the sorbent based on expanded clay with microorganisms immobilized on the surface was characterized by a low sorption capacity for diesel fuel, engine oil and crude oil: 0.108; 0.145; 0.150 g / g, respectively. Due to the low sorption capacity, it was decided not to use this sorbent in a further study. The sorption capacity of the sorbent based on peat of the Lessorb company with microorganisms immobilized on the surface turned out to be significantly higher than the previous indicators: 2.65; 3.08; 3.69 g / g, respectively. For comparison, the sorption capacity of the sorbent of the company “Lessorb” was determined without immobilization of microorganisms, which turned out to be 3.19; 3.57; 4.02 g / g, respectively. The decrease in the sorption capacity of the sorbent with microorganisms immobilized on the surface, most likely, is associated with partial clogging of the pores. The lowest indicators of sorption capacity for diesel fuel, engine oil and crude oil were shown by the sorbents Unisorb-extra and SoNet-1: 1.608; 1.660; 1.638 g / g and 1.108; 1.330; 1.480 g / g, respectively.

A comparative analysis of the sorption capacity of the sorbents obtained as a result of the present research work and the characteristics declared by the sorbent manufacturers [8-11] showed the following (table 2).

Table 2: Data on the sorption capacity of sorbents
Thus, the obtained data of the sorption capacity of Lessorb for oil and diesel fuel showed compliance with the indications of the sorption capacity declared by the manufacturer of the sorbent. The difference between the data obtained as a result of the study and the data from the manufacturer does not exceed 0.5% for the sorption capacity of oil and 2% for the sorption capacity of diesel fuel. The value of the sorption capacity of the Lessorb sorbent relative to the engine oil cannot be compared with the manufacturer's data due to the lack of such data in the public domain.

The values of the sorption capacity of "Unisorb-extra", presented by the manufacturer [8] in the open access, allow for a comparative analysis only for diesel fuel, since information about the sorption capacity for engine oil and oil is not published or does not exist. However, the values obtained in this study of the sorption capacity of the specified sorbent are significantly lower than those stated by the manufacturer. Thus, in the conditions of the study, the sorption capacity of this sorbent was 1.61 g/g, while the manufacturer indicated a value of 35 g/g. Thus, the difference between the claimed and actual data was 95.4%.

Analysis of the effectiveness of the sorbent "TShR" showed the following. The declared value "up to 9 g / g" specified in the manufacturer's characteristics cannot adequately and unambiguously reflect the effectiveness of the sorbent, since it includes the possibility of both a low and a sufficiently high sorption capacity of the sorbent from 0 to 9 g/g. Such uncertain information about the effectiveness can not suit the responsible contractor for the elimination of emergency spills of oil and petroleum products. On the other hand, in the course of research, the following values of the sorption capacity of the sorbent "TShR" were obtained for oil - 6.61 g/g; diesel fuel-6.76 g / g; engine oil - 7.3 g/g, which can be estimated in two ways. On the one hand, these values correspond to the wording "up to 9 g/g" and are quite large (in comparison with the previous studied sorbents), on the other hand, it does not meet the consumer's expectations for higher oil capacity values - mentioned "up to 9 g/g". The declared performance indicators of the sorbent for diesel fuel and engine oil are more unambiguous and range from 7.0 to 9.0 g/g and from 8.5 to 10.7 g/g, respectively. At the same time, the actual values of the sorption capacity obtained in the experiment do not correspond to the stated ranges, but to a lesser extent than in the case of the "Unisorb-extra" and "SoNet-1" sorbents. Thus, the difference in the sorption capacity of the TShR sorbent between the data obtained as a result of the study and the lower threshold of data from the manufacturer for diesel fuel was 3.43 %, for engine oil 14.12 %. This difference can be attributed to possible other conditions for testing sorbents, which is not possible to verify due to the lack of references to test methods.

Regarding the effectiveness of the sorbent "SoNet-1", the following should be noted. Due to the fact that the sorption capacity data for diesel fuel and engine oil are not freely available by the manufacturer of "SoNet-1" sorbent, it was possible to conduct a comparative analysis only with respect to the oil sorption efficiency. According to the results of the study, the difference between the values of the sorption capacity obtained as a result of experiments and those declared by the sorbent manufacturer was 63 %.

Thus, a comparison of the declared and actual values of the sorption capacity of four popular sorbents in Russia showed the following. Of the four studied sorbents, only in one case (Lessorb sorbent) the characteristics declared by the manufacturer were fully confirmed, and the actual value of the sorption capacity was within the limits of the experiment error. In other cases, the manufacturer's stated values exceeded the actual values by between 3.4 and 95.4 %.
The difference between the actual values of the sorption capacity and declared, however, can be attributed to different factors, among which we would like to highlight the following: possible breach of integrity of the package during transportation and long storage; study of the sorption capacity of sorbents manufacturer in conditions and at sites that differ from the conditions of this study in the absence of a currently installed standard techniques for determination of the studied indicator. However, the conditions and objects of research of the sorption capacity should not play a determining role, since the product characteristics declared by the manufacturer must correspond to the intended use, regardless of the change of contamination parameters and conditions for their determination. This requirement should ensure the effectiveness of measures to eliminate oil spills and preserve the unique and vulnerable Arctic environment.

The results of determining the sorption capacity of sorbents at a negative temperature (minus 5°C (± 1°C)) are presented in table 3.

**Table 3. Sorption capacity of sorbents at a negative temperature**

| Sample OP | Sorption capacity, g/g |
|-----------|------------------------|
|           | «Lessorb» | «Unisorb-extra» | «TShR» | «SoNet-1» |
| Oil       | 4.15      | 1.63           | 6.78   | 1.51      |
| Diesel fuel| 3.28      | 1.65           | 6.82   | 1.22      |
| Engine oil| 3.61      | 1.70           | 7.46   | 1.42      |

Comparison of the sorption capacity at negative and positive temperatures showed a slight change in the studied parameter, it should be noted that low temperature has a small but positive effect, increasing the sorption capacity of sorbents. Obviously, this is due to a decrease in the viscosity of oil products, which allows you to keep a larger amount of pollutant on the surface of the sorbents.

Taking into account the fact that the sorbents selected for the study do not have a selective effect on oil and oil products in the aquatic environment (sorbents are both oleophilic and hydrophilic), in the framework of the experiment, the sorption capacity of the sorbents was determined by the oil products used in the work on the water surface, taking into account the possible water absorption of the sorbents (table 4).

**Table 4. Sorption capacity of sorbents for oil and oil products in water**

| Sample OP | Sorption capacity, g/g |
|-----------|------------------------|
|           | «Lessorb» | «Unisorb-extra» | «TShR» | «SoNet-1» |
| Oil       | 4.09      | 1.65           | 6.67   | 1.50      |
| Diesel fuel| 3.87      | 1.63           | 7.59   | 1.24      |
| Engine oil| 3.72      | 1.68           | 7.45   | 1.34      |

An analysis of the data obtained showed that the sorbents “Lessorb”, “Unisorb-extra”, “TShR” and “SoNet-1” absorb the largest amount of water in addition to oil during sorption of spilled diesel fuel. Apparently, this is due to the low viscosity of diesel fuel compared to other oil products selected for the study, which provides more free access of the sorbent to the water surface. At the same time, the lowest percentage of water absorption is observed for the “Unisorb-extra” sorbent - 1.17%, however, this sorbent also has a rather low sorption capacity for oil products. Relatively small percentage of water absorption is possessed by TShR sorbents - 10.9% and SoNet-1 - 10.8%. The largest percentage of water absorption was shown by the sorbent "Lessorb" - 17.6%. Water absorption by sorbents during sorption of oil and motor oil does not exceed 2%.

Based on the data in Table 1, the effective consumption of sorbents for collecting oil products from the water surface was determined. Depending on the type of oil product (diesel fuel, motor oil, oil), the effective consumption of the Lessorb sorbent with immobilized microorganisms was 0.38,
respectively; 0.32; 0.27 g sorbent/1 ml OP and 0.31; 0.28; 0.25 g of sorbent/1 ml OP for the sorbent "Lessorb", on which the immobilization of microorganisms was not carried out. The results of the study of efficiency of use of selected sorption materials with immobilized microorganisms to reduce the concentration of oil products in oil spills on the water surface are given in Table 5.

Analysis of the dynamics of the OP content showed a significant decrease in the concentration of pollutants in the first day. Thus, the concentration of NP on the surface of the water during the spill of diesel fuel, engine oil and crude oil before the use of sorbents was 3.98, respectively; 5.2; 5.7 g / l, and after using the sorbent “Lessorb” with immobilized microorganisms, the concentration of OP in water decreased, respectively, to 0.275; 0.047; 0.108 g/l. After applying the Lessorb sorbent without immobilized microorganisms, the concentration of OP in water was 0.218, respectively; 0.038; 0.095 g/l.

An analysis of the subsequent reduction in residual pollution over the course of the week showed almost no dynamics. A decrease in the concentration of OPs on the 2nd – 3rd day after removal of sorbents from the surface of the water is most likely associated with the evaporation of light fractions of OPs, rather than with the action of microorganisms, since in both cases the results of a decrease in concentration are comparable. The values of OP concentrations on day 4-7 are practically unchanged.

As you know, oil products are capable of natural degradation under the influence of various natural factors [15], therefore, in order to take into account the contribution of the natural decomposition of oil products in the marine environment, we studied the dynamics of the content of OP in sea water without the use of sorbents (Figure 1-3). In addition, oil and petroleum products are subject to changes in their properties with temperature. The content of OP in sea water at negative temperatures can significantly differ from the content of OP at positive temperatures. In the framework of this work, the effect of low temperature (minus 5 °C (± 1 °C)) on the dissolution rate and the ingress of heavy fractions of oil and oil products into the water column during an emergency spill was studied (Figure 1-3).

**Table 5.** Indicators of a decrease in the concentration of oil products in samples of oil-contaminated water when using the studied sorbents

| Oil product | 0*  | 1** | 2*  | 3*  | 4*  | 5*  | 6*  | 7*  |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Diesel fuel, g/l | 3.98 | 0.275 | 0.218 | 0.225 | 0.210 | 0.213 | 0.208 | 0.207 | 0.204 | 0.205 | 0.204 | 0.202 | 0.204 | 0.200 |
| Engine oil, g/l | 5.20 | 0.047 | 0.038 | 0.047 | 0.035 | 0.046 | 0.035 | 0.046 | 0.035 | 0.046 | 0.035 | 0.033 | 0.045 | 0.033 |
| Oil, g/l | 5.70 | 0.108 | 0.095 | 0.087 | 0.078 | 0.075 | 0.070 | 0.070 | 0.062 | 0.070 | 0.060 | 0.067 | 0.067 | 0.060 |

* - Sorbent “Lessorb” with immobilized microorganisms
** - Sorbent “Lessorb”
1 – change in the concentration of oil products at a negative temperature;
2 – change in the concentration of oil products at a positive temperature

**Figure 1:** Change in the concentration of oil products during oil spills at negative and positive temperatures

1 - change in the concentration of oil products at a negative temperature;
2 - change in the concentration of oil products at a positive temperature

**Figure 2:** Change in the concentration of oil products during the spill of diesel fuel at negative and positive temperatures
1 - change in the concentration of oil products at a negative temperature;
2 - change in the concentration of oil products at a positive temperature

**Figure 3.** Change in the concentration of oil products during spill of engine oil at negative and positive temperatures

The results of the study showed the following. In the first 24 hours of the study in the absence of the operations for liquidation of spills of oil and oil products a rapid transition of oil has been seen in the water column. So, during an oil spill, the concentration of oil products in the first 24 hours increased from 0 to 5.44 mg/l. Subsequently, a decrease in the dynamics of the transition of oil products into the water column was noted. So, on the second day of the study the concentration of oil products amounted to 6.94 mg/l, and on the fourth day – 8.1 mg/l. Similar dynamics is observed for other types of pollutants – engine oil and diesel fuel, with the greatest increase in the concentration of oil-in-water marked diesel fuel from 0 to 17.16 mg/l. Based on the data obtained, the logarithmic dependence of the concentration of oil products in the water column on the spill time was established. The equation for describing the dependence of changes in the concentration of petroleum products during oil spill at a positive temperature (plus 16°C (+1°C)) is as follows.

\[ Y = 1,6668 \ln(x) + 0,888 \]  

The value of reliability approximation for the installed dependencies amounted to \( R^2=0.9511 \).

Also a logarithmic increase in the concentration of oil products in sea water from the time of the spill under the oil pollution at negative temperature (minus 17°C (-1°C)) has been found. The equation of dependence is as follows.

\[ Y = 0,3028 \ln(x) + 0,278 \]  

The value of reliability approximation for the installed dependencies amounted to \( R^2=0.9744 \).

Similarly, the dependence of the oil concentration in the water column from the time of the spill in the sea water pollution with diesel fuel at positive temperatures - the formula (3), negative temperature – the formula (4) and for spill of engine oil at positive temperatures - the formula (5), the negative temperature – the formula (6).

\[ Y = 3,1406 \ln(x) + 2,9124 \]  
\[ Y = 1,3837 \ln(x) + 1,9161 \]  
\[ Y = 0,1387 \ln(x) + 0,076 \]  
\[ Y = 0,0647 \ln(x) + 0,0571 \]  

The value of reliability approximation for the installed dependency was, respectively: \( R^2=0.9126, R^2=0.8808, R^2=0.8842, R^2=0.9493 \).

At the same time, there is a significant decrease in the dynamics of growth in the concentration of petroleum products (in contrast to the results of a similar study at a temperature of plus 16°C (+1°C) in seawater samples with the addition of oil. So, on day 4, the concentration of oil products in seawater samples at the oil spill turned out to be 1.68 mg/l, which is 4.8 times less than the concentration of oil products in water samples with the addition of oil on day 4 of the study at a positive ambient temperature. A less significant decrease in the rate of increase in the concentration of oil products was found in seawater samples supplemented with motor oil and diesel fuel. The oil content on the 4th day of the study in seawater samples at negative ambient temperature both in the case of adding engine oil and with the addition of diesel fuel was less than in a similar study at a positive temperature, 1.9 times.

5. **Conclusion**

As a result of the work carried out, it was found that the use of the method of immobilization of microorganisms of excess activated sludge on the surface of the selected sorbents under the simulated experimental conditions is ineffective for the elimination of oil spills.

Regarding the study of the effectiveness of popular commercial sorbents, the following should be noted. Screening of the characteristics of commercial sorbents, in particular, indicators of sorption capacity for oil products, showed that not all manufacturers provide adequate and unambiguous data. Overestimated or incorrect indicators of the sorption capacity of sorbents can adversely affect the efficiency of oil pollution removal and, thus, lead to unsatisfactory results of liquidation of emergency oil and oil spills, which in turn can lead to a negative impact on Arctic marine ecosystems.
According to the influence of negative ambient temperature on the effectiveness of oil and oil product spill response processes revealed the following. In general, within the framework of the study, a positive effect of a low ambient temperature on a decrease in the dissolution rate and the ingress of heavy fractions of oil and oil products into the water column during an accidental spill was observed. This fact may allow taking measures to eliminate accidental spills of oil and oil products in offshore areas in the harsh conditions of the Arctic climate without the risk of a significant increase in the concentration of oil products in a water body over time. In addition, an increase in the sorption capacity of sorbents for oil and oil products at a negative ambient temperature was noted, which can also increase the efficiency of liquidation of oil pollution in the Arctic marine areas.

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