

**SORBENTS AS A BIOPREPARATION FOR REMEDIATION
AND RECLAMATION OF OIL-CONTAMINATED SOILS
IN ABSHERON PENINSULA**

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Abstract

The aim of the study was to investigate the effectiveness of using various restorative complexes based on surfactants, and the effectiveness of soil cleaning for bioremediation of oil-contaminated peat soils. Carrying out remediation of oil-contaminated soil with the proposed composition, observing the processing technology and duration of exposure, shows a fairly high efficiency in reducing the oil content in the range of 69.7–87.6%, depending on the initial concentration. Peat and sorbent showed good results when combined with soil pH adjustment using lime and the addition of nitrogen-phosphorus fertilizers. The optimal exposure period for the recommended remediation composition was determined to be one month. Due to the loss of many coastal soils, studying the problem of cleaning up soil pollution is considered very important for Absheron Peninsula.

Key words: heavy metals, biogeoinidication, pollution, ash content, leaves

Introduction. Some pollutants, concentrating and accumulating in the soil, can negatively impact the environment through the food chain, a pressing environmental safety issue addressed by land reclamation. Remediation compositions

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include various mineral and organic sorbents, which significantly reduce the concentration of petroleum products [1, 2]. Modified, carbonized, or heat-treated peat (around 250–300 °C) can increase oil sorption capacity, with some reports showing efficiencies of 13.3–14.2 g of crude oil per gram of peat. The most vulnerable areas in this regard are those of the Absheron Peninsula, which have a low capacity for self-purification. One such region experiencing significant anthropogenic pressure is Surakhany. The use of sorbents as biopreparations transforms polluted soil into productive soil, which is consistent with the goals of ecological restoration and sustainable waste management [3, 4]. Biopreparations serve as the “active engine” in biological cleanup, moving beyond simple natural attenuation to a managed, high-speed recovery of the soil. Their role is divided into two distinct phases: the chemical cleanup and the biological restoration [5, 6]. The PH content in the organogenic soil horizon in background plots within the study area is 224 ± 39 mg/kg.

Methods. The method utilized a polymer sorbent and peat containing a specific strain of oil-degrading bacteria. One hundred grams of sand with various amounts of oil added were placed in plastic containers. The dynamics of changes in the oil product content in the sample were monitored for 2.5 months. Eleven soil samples were collected from the contaminated site using a soil sampler, from the surface layer of 0–10 cm, as well as from depths of 0–5, 5–10, and 10–20 cm ($40^{\circ}25'13''$; $50^{\circ}00'17''$). The soil samples were delivered to the laboratory, where they were air-dried. Low-decomposition high-moor peat neutralized with lime was used as a sorbent-structuring agent. The peat was crushed to a particle size of no more than 10 mm and then activated by adding a complex mineral fertilizer, NPK (N = 16%, P_2O_5 = 16%, K_2O = 16%), at a rate of 500 mg active ingredient/kg. The activated peat was left for a month to enhance the biodegradation properties of native microorganisms.

Contaminated soil samples were sifted through a 2 mm sieve, thoroughly mixed, and moistened to 60% of their full moisture capacity. Activated peat was added to the samples at a soil-to-peat ratio of 4:1 (for oil product content less than 20 000 mg/kg) and 2:1 (for oil product content greater than 20 000 mg/kg). The prepared soil was placed in equal weights into plastic containers. The soil containers were kept at room temperature (18–20 °C), and watered and stirred twice a week. Soil phytotoxicity was calculated based on the germination rate of seeds grown in the test soil relative to the control. To assess the toxicity of soil samples, seed germination parameters – germination rate and average seedling length – were determined in laboratory conditions [7, 8]. Soil dehydrogenase activity was determined colourimetrically based on the colour intensity of the solution after the reduction of TTC (triphenyltetrazolium chloride – $C_{19}H_{15}ClN_4$) to red TPF (triphenylformazan – $C_{19}H_{16}N_4$) compounds. The PH content in the soil, its toxicity, and dehydrogenase activity were assessed before and after reclamation. The results were processed mathematically using standard statistical software packages

(Microsoft Office Excel 2007). The significance of differences between samples (t) was assessed using the Student's t -test, and the correlation coefficient (r) was calculated using the Pearson method of squares at a significance level of 0.05 [9].

Results. The samples revealed that the HC content in the contaminated soil ranged from 2.864 ± 358 to 30.847 ± 3.856 mg/kg, which is 17–139 times higher than the background PH content. A study of the vertical distribution of contamination revealed high PH content throughout the profile (more than 26 cm from the surface), indicating the cessation of hydrocarbon transformation and accumulation. The cessation of PH biological oxidation in the soil is also evidenced by the activity level of soil dehydrogenase, an enzyme involved in hydrocarbon degradation processes. In the contaminated soil of the study site, dehydrogenase activity was 0.06 ± 0.01 mg TPP/10 g, which is assessed as very weak according to the comparative assessment scale of soil biological activity. Fifteen days after the introduction of activated peat into contaminated soil, the PH content in the test samples decreased by 22–47%. With this sample size, a reliable decrease in the amount of hydrocarbons was noted in samples with the highest (8 and 11) and lowest (7 and 10) initial PH content ($t = 2.93$ – 3.56 at $p = 0.05$, $df = 4$). In samples with initial PH content exceeding 20 000 mg/kg and a soil-to-peat ratio of 2:1, hydrocarbon content decreased by an average of 10 000 mg/kg (40%). In less contaminated samples with a soil-to-peat ratio of 4:1, the decrease averaged 3000 mg/kg (35%). Dehydrogenase activity in the soil after the experiment increased fivefold to 0.31 ± 0.16 mg TPF/10 g (weak activity), indicating the onset of microbiological degradation processes. The pH of the aqueous soil extract before the phytotests was within the optimal range for most plants – 5.7–6.1 which did not require additional liming. Sorrel seed germination averaged 7% of the control values, and in samples 5 and 11, where the PH content was the highest, complete seed death was observed. After reclamation, phytotests showed that test culture germination increased by 1.6–3.7 times. In samples with initial contamination levels of less than 20 000 mg/kg, the average germination rate was $21 \pm 2\%$, while in samples with high contamination levels (more than 20 000 mg/kg), it was $16 \pm 2\%$. In samples where complete seed death was initially observed, after peat addition, germination rates were 11–17%. The low germination rate in contaminated samples is due not only to the high PH content in the soil but also to the unfavourable water and nutrient conditions – the soil is predominantly sandy. Therefore, when peat is added to such soil, it acts both as a sorbent and as a component that improves the soil's physical properties. A significant strong negative correlation was established between the PH content and the germination of sorrel seeds in soil samples ($r = 0.07$ – 0.76 at $p = 0.05$, $n = 11$). When the PH content in the soil is less than 10 000 mg/kg, it is recommended to apply peat at a soil/peat ratio of 4:1, which is sufficient and effective. With higher PH content, it is recommended to increase the soil/peat ratio to 3:1 (10 000–20 000 mg/kg PH) and 2:1 (more than 20 000 mg/kg). Over a short period (15 days), it was

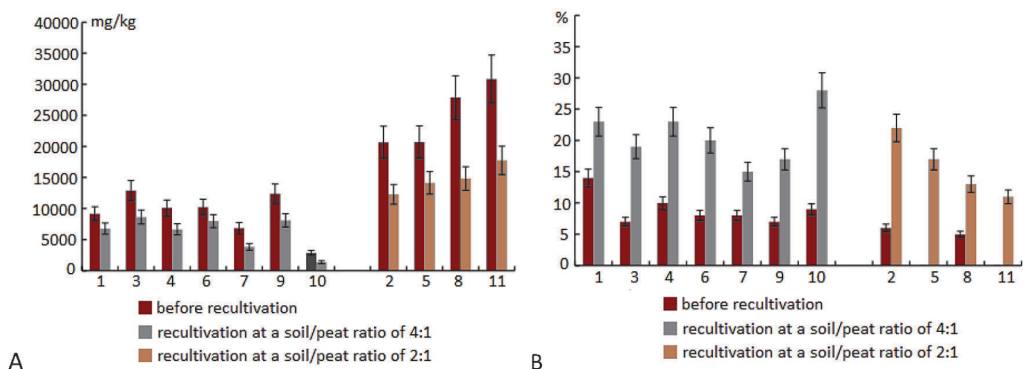


Fig. 1. Petroleum hydrocarbons (PH) content in contaminated soil samples (A) and sorrel seed germination in contaminated soil samples (B)

possible to reduce the PH content by 22–47%, while soil toxicity, as measured by test culture germination, decreased (Fig. 1A, B). The proposed method can be used to restore contaminated areas, including areas of accumulated environmental damage in Balakhany, Bibi-Eybet regions. The average PH content in the soil is 14.967 ± 675 mg/kg, and the contamination depth is 20 cm. Therefore, according to the studies, the soil-to-peat ratio should be 3:1. The amount of peat required for application to contaminated soil over an area of 0.07 hectares is 60.7 tons. This amount of sorbent requires the application of 33.4 kg of mineral fertilizer, calculated as the active ingredient.

An analysis of the experimental data for an initial oil content of 50 g/kg (Fig. 2A) revealed an intense reduction in the oil content over the first two weeks, amounting to 54% and 56%, respectively. Subsequently, from the period of 4 to 10 weeks, biodegradation was less intense, with an increase of 8.5%. The final oil degradation effect at the end of 10 weeks was 69.7% (Fig. 2A). The results obtained for an initial oil content of 300 g/kg (Fig. 2B) showed that over the first 15 days, the oil content reduction dynamics were less intense, with an effect of 49.25%.

In a laboratory experiment using activated peat, it was possible to reduce the PH content in contaminated soil by 22–47% over two weeks. A 5-fold increase in

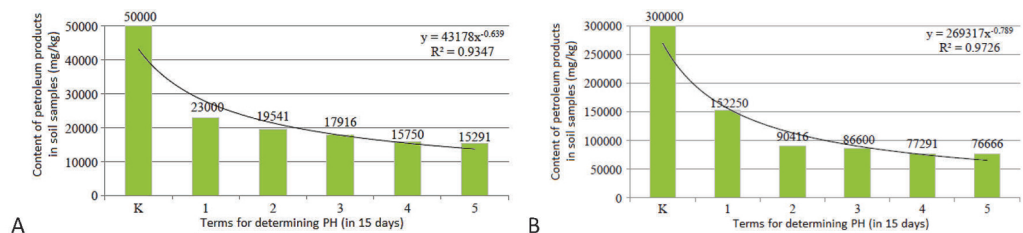


Fig. 2. Dynamics of changes in the content of petroleum products in a soil sample at a mass concentration of sorbent of 1% (A) and 10% (B) with a treatment duration of 1.5 months

soil dehydrogenase activity was also observed, indirectly indicating increased microbiological oxidation of hydrocarbons. The optimal amount of peat required for application to contaminated sandy soil was determined, depending on the degree of contamination. For PH content in soil below 10 000 mg/kg, peat application is recommended at a soil-to-peat ratio of 4:1. For higher PH content, it is recommended to increase the soil-to-peat ratio to 3:1 (10 000–20 000 mg/kg PH) and 2:1 (more than 20 000 mg/kg). After reclamation, the germination rate of the test crop seeds increased by 1.6–3.7 times. In samples where complete seed loss was initially observed, germination rates after reclamation were 11–17%.

Conclusion. The study demonstrated the effectiveness of the proposed method for the remediation of contaminated sites consisting of heavily polluted sandy soil with low biogenic activity and a small area. Based on the study, work continues on processing the experimental data using innovative design methods to obtain a mathematical model that allows for determining the optimal sorbent dose depending on the initial concentration of oil contaminants. Remediation of oil-contaminated soil using the proposed formulation, in compliance with the treatment technology and exposure duration, demonstrates a high degree of effectiveness in reducing oil content in the range of 69.7–87.6%, depending on the initial concentration.

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