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# Carbonized Sorbents of Shungite and Rice Husk for Purification of Petroleum Contaminated Soils

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## ABSTRACT

Contamination of soil and water with petroleum during its extraction, collection, transportation, storage and preparation occurs frequently, and purification of oil spills is one of the pressing environmental problems of oil producing organizations. There are a large number of methods for utilization oil spills. The sorption method in combination with bioremediation is capable of effectively purification of petroleum contaminated soils. The paper shows the possibility of using a carbonized mixture of shungite from the Koksu deposit (Kazakhstan) with rice husk as a sorbent and carrier of microorganism strains. The physicochemical properties and elemental composition, as well as the microstructure of carbonized samples were established. The maximum sorption capacity of carbonized sorbents when purifying the soil samples from oil from the Karazhanbas field was 1.86 g/g after 60 days. The carbonized samples with microorganism strains immobilized on them showed a degree of oil destruction reaching 90%.

**Keywords:** shungite, rice husk, carbonization, sorbent, petroleum contaminated soils, purification, bioremediation.

## INTRODUCTION

Oil is one of the main sources of energy. Oil spills occurring during production, collection, transportation, storage and preparation of oil, and repair work on wells are an urgent environmental problem. When oil is present on the surface of soil and water, it negatively affects their composition, as well as the organisms and plants living in it. In this regard, it becomes necessary to develop a technology for cleaning soil and water contaminated with oil and oil products.

Treatment of oil pollution includes the stages of localization, separation and destruction, which are carried out by biological, chemical, physicochemical, thermal, electrical, electromagnetic, acoustic and ultrasonic methods [Ossai et al., 2019]. Bioremediation, phytoremediation, photocatalysis, and other methods are also used for the disposal of oil pollution and soil restoration. The choice of remediation method depends on the hazard of exposure to the pollutant.

One of the potential methods of oil spill response is sorption, which is due to the high sorption capacity, selectivity, chemical inertness and the possibility of secondary processing of sorbents. The work [Al-Jammal and Juzsakova, 2016] emphasizes the importance of removing oil from contaminated areas by adsorption and presents natural organic, inorganic and synthetic sorbents for cleaning oil-polluted water, showing their effectiveness and limitations.

The sorbents based on carbon materials have a large surface area, low density, excellent mechanical properties, good chemical stability, environmental friendliness and large pore volume. Activated carbon has been widely used as an adsorbent for the past several decades.

The possibilities of employing the activated carbon obtained from coconut shells for processing oil-contaminated soil with varying amounts of pollutants, adsorbent and time were studied [Ibrahim et al., 2016]. There was a decrease in total petroleum hydrocarbons from 28.92 to 2.83 mg/l at a ratio of oil to activated carbon of 1:1.5, while the degree of remediation was 90.22%.

The spent mud with drill cuttings was cleaned with activated carbon based on coal or coconut shells [Orng et al., 2020]. The optimal washing conditions were a liquid to solid adsorbent ratio of 10 ml/g, a washing time of 20 minutes, a stirring speed of 100 rpm, while the degree of removal of total petroleum hydrocarbons was 87.6%.

Carbon materials based on pine sawdust, obtained at a temperature of 300°C for 8–10 minutes, showed a buoyancy of 97–100% [Rogovskii et al., 2020]. It was established that in the process of low-temperature one-stage carbonization of plant raw materials, the surface of the sorbent is hydrophobized. The highest sorption rate was demonstrated by a mixture of carbonized pine sawdust and expanded graphite in a 50:50 ratio, which is explained by the developed porous structure and surface chemistry of the materials.

During water purification, pecan shells showed the highest adsorption capacity in relation to petroleum products [Chukaeva et al., 2021]. As a result of the temperature treatment of the sorbent, it was possible to increase the adsorption capacity twice and the adsorption activity by 13 times, without reducing the strength characteristics. It was found that it is advisable to carry out carbonation at a temperature of 400°C.

Currently, carbon aerogels, sponges coated with graphene or carbon nanotubes, graphene foams or sponges, carbon coatings, activated carbon, porous carbon nanoparticles, and carbon fibers are widely studied to clean up oil and wastewater spills [Gupta and Tai, 2016]. The high sorption capacity of carbon nanomaterials in relation to hydrophobic organic pollutants is due to their large surface area and high hydrophobicity. The nature of the physicochemical properties of soil and carbon nanomaterials is considered to determine their behavior and interaction with pollutants and soil microflora [Riding et al., 2015]. It was shown that it is necessary to assess the stability and toxicity of sorbed contaminants and carbon nanomaterials prior to sorption.

Nanomaterials have unique physicochemical properties, and therefore attract a lot of attention from researchers in various fields of science. They can also be used for the bioremediation process due to their low toxic effect on microorganisms. Bioremediation is one of the main methods of soil rehabilitation due to ease of use, absence of secondary pollution and low cost [Sui et al., 2021]. The article [Rizwan et al., 2014] presents the main types of nanomaterials that were used for bioremediation of waste and toxic materials. They are noted to improve the microbial activity of waste and toxic materials, which reduces the overall time and cost. Correlation studies on the use of nanomaterials for the restoration of contaminated soils provide a theoretical basis for the rational and efficient use of land resources [Sun et al., 2021].

In combination with the adsorption method, photocatalysis was used to assess the efficiency of oil decomposition in soils [Mambwe et al., 2021]. Photocatalytic nanostructured adsorbents not only play a bifunctional role in the adsorption of pollutants, but are also capable of degrading organic pollutants using sunlight [Kennedy et al., 2018].

Recently, much attention has been paid to the use of agricultural waste for the production of activated carbon. Rice hulls are a waste from rice production and have good adsorption properties. Rice husk is a cheap and readily available material that can be processed into activated carbon for a variety of purposes. Various pollutants such as textile dyes, organic pollutants, inorganic anions, pesticides and heavy metals can be effectively removed using the activated carbon obtained from rice hulls [Kenes et al., 2012], [Alam et al., 2020].

Carbonized rice hulls have been used to purify oil-contaminated seawater and study the optimal adsorption conditions [Cui et al., 2014]; 70% of oil was removed with an optimal sorbent content of 13.33 g/l, the oil concentration decreased from 1.35 mg/l to 0.39 mg/l. The oil removal rate of 71% was achieved after adsorption for 3 hours. The adsorption capacity of rice hulls is due to the high silicon content.

The use of carbonized rice husk for water purification was investigated [Viana et al., 2016]. The carbonization process is carried out by the pyrolysis of rice husks in an inert atmosphere. The results showed the constancy of sodium ions $Na^+$ in activated carbon.

Shungite rocks, natural composite materials, are promising carbon-containing raw materials for multipurpose use. The basis of shungite is carbon, which is fullerene-like, as well as aluminosilicates, oxides of alkali metals, which suggests good adsorption properties in it [Moshnikov and Kovalevski, 2018]. It is a good sorption material, which allows it to be used for water purification from oil, heavy metal salts [Polunina et al., 2017]. However, the use of shungite rocks as sorbents for cleaning soils from oil pollution is practically not studied, which is associated with their high mechanical strength and complex morphology of carbon inclusion in the silicate matrix.

In this regard, in this work, carbonized nanomaterials of mixtures of shungite with rice husk were obtained and tested for purification of model samples of petroleum contaminated soils. The possibility of using the obtained materials for the immobilization of strains of microorganisms – biodegradants of oil hydrocarbons of the soil – is also shown. The aim of this work was to obtain and test carbonized nanomaterials based on shungite and rice husk for use as a sorbent for purification of petroleum contaminated soils.

## MATERIALS AND METHODS

The objects of study in this work were shungite samples from the Koksu deposit with a dispersion of 1 mm. The samples of shungite mixed with rice husk were subjected to a carbonization process. The ratio of shungite (Sh) and rice husk (RH) was 1:1.7; 1:4; 6:1. The carbonization process was carried out at a temperature of 600°C in an inert argon atmosphere for 1 hour.

Specific surface area, specific volume and pore size of carbonized samples were determined with an automatic analyzer 3H-2000PS1. The specific surface area is measured by the single-point and multi-point BET method, as well as by using the Langmuir method. The elemental composition of the samples was determined by energy dispersive spectroscopy on an EDAX ametek instrument. Electron microscopic images were taken on a SEM FEI Quanta 3D 200i scanning electron microscope.

To test the samples as sorbents, model samples of oil-contaminated soils were prepared. For their preparation, the oils from the Karazhanbas and Tengiz fields (Kazakhstan) were selected. The oil from the Karazhanbas or Tengiz field with a weight of 5 g was introduced into the soil with a mass of 50 g, which makes the oil contamination of the soil 10%. Then, the samples of carbonized sorbents weighing 2 g were introduced into the soil. Subsequently, after a certain time (from 5 to 60 days), the sorption capacity of the sorbents and the degree of oil destruction under static conditions were determined. The sorption capacity was calculated by the ratio of the mass of oil absorbed by the sorbent to the mass of the sorbent itself. The degree of destruction of oil in the soil was determined by their residual content using the gravimetric method.

The physical and chemical characteristics of the oils from the Karazhanbas and Tengiz fields are shown in Table 1. The selection of oils from these fields is due to the fact that the oil from the Karazhanbas field is heavy and highly viscous, while the oil from Tengiz field is light and waxy.

As can be seen from the tabular data, the oil from the Karazhanbas field is characterized by high density, viscosity and coking properties. High values of viscosity-density indicators are predetermined by high resin content (24.5%) of oil and low content of light hydrocarbons. Oil has high asphaltene content (5.7%). A distinctive feature of oil is a high content of sulfur compounds (2.1%).

The oil from the Tengiz field is characterized by low density (790.4 kg/m$^3$), viscosity and coking properties. The oil is paraffinic (5.5 wt. %) and contains a high yield of light fractions. It is characterized by a low content of resins (0.9 wt. %) and asphaltenes (1.1 wt. %).

The number of different groups of soil microorganisms was determined by using the method of successive dilutions of the soil suspension on solid nutrient media. Determination of the number of cells was carried out with the Koch method. The essence of the method consists in sowing a certain volume of the studied suspension of microorganisms on a solid medium in Petri dishes and counting the colonies that have grown after incubation. Sowing is carried out on agar medium in Petri dishes. To determine the total number of microorganisms, the mesopatamia agar is used. Cultivation of crops was carried out in a thermostat at 28°C for several days, depending on the type of microorganisms. After incubation of the inoculations, the grown colonies were quantified and the number of colony-forming units (CFU) in 1 g of soil was determined.

Obtaining pure cultures was carried out by mechanical separation on the surface of a dense nutrient medium (method of streaking with firing a loop). Individual colonies were checked for purity by microscopy and plated on nutrient agar slants for cultivation.

**Table 1.** Physical and chemical characteristics of crude oils from the Karazhanbas and Tengiz fields

| Indicator | Oil fields | |
|---|---|---|
| | Karazhanbas | Tengiz |
| Density at 20°C, kg/m$^3$ | 931.6 | 790.4 |
| Viscosity at 50°C, mm$^2$/s | 97.5 | 1.35 |
| Pour point, °C | -18.0 | -15.0 |
| Paraffin content, wt. % | 0.8 | 5.5 |
| Resin content, wt. % | 24.5 | 0.9 |
| Asphaltene content, wt. % | 5.7 | 1.1 |
| Sulfur content, wt. % | 2.1 | 0.52 |
| Coking capacity, wt. % | 7.0 | 0.21 |
| Fractional composition, wt. %<br>b.p.–200°C<br>200–350°C<br>350–500°C | <br>3.8<br>24.4<br>52.1 | <br>41.0<br>63.0<br>71.0 |

Sorption immobilization of cells was carried out as follows: 100 ml of cell suspension in isotonic sodium chloride solution was incubated in the presence of carriers at the rate of 1 g per 100 ml of medium in an Erlenmeyer flask for 48 hours at room temperature, shaking on a laboratory shaker at a stirring speed of 220 rpm. Then, the carrier with immobilized cells was washed from weakly attached cells with isotonic solution and the number of desorbed cells was determined.

To assess the degree of sorption and desorption of cells, the concentration of cells in the solution was measured by the optical density of the suspension using a KFK-2MPA photocolorimeter in standard cuvettes with an optical path length of 1 cm at a wavelength of 540 nm. To determine the relationship between the number of cells and optical density, a calibration curve was constructed.

The number of adhered cells was calculated based on the difference between the initial and final values of the optical density of the samples. The percentage of adsorbed cells was determined by using the Nikovskii method.

Microcultural analysis was used to determine the viability of microbial cells immobilized on carbonized carriers. For this, cells attached to a carrier were ground in a mortar and diluted with phosphate buffer. The resulting suspension was added with a sterile pipette to the wort-agar culture medium on a glass slide. After 6–8 hours of incubation at 28°C, the preparations were viewed under a phase-contrast light microscope, and in each of them the number of cells that formed microcolonies was counted.

## RESULTS AND DISCUSSION

The efficiency of the sorption method is primarily determined by the properties of the sorbent used in it, including its porous structure and surface characteristics, which make it possible to achieve a high degree of purification and repeated use of the adsorbent. Table 2 shows the physicochemical characteristics of the shungite and carbonized samples of a mixture of shungite and rice husk. As it can be seen from the tabular data, the specific surface area of the shungite is low and amounts to 20.4–21.8 m$^2$/g. After carbonization with rice husk, an increase in the specific surface area of shungite samples is observed. Carbonization led to an increase in the specific surface area with a ratio of shungite and rice husk 6:1 3 times up to 54.21 m$^2$/g, with a ratio of 1:1.7 - up to 148.25 m$^2$/g, with a ratio of 1:4 - up to 133.41 m$^2$/g. The same increase in specific surface area is observed after the measurements performed by using the one-point BET method and the Langmuir method.

The specific pore volume of carbonized samples also increases, for shungite its value was 0.0107 cm$^3$/g, after carbonization it increased to

**Table 2.** Physicochemical characteristics of shungite and carbonized samples

| Sample | BET specific surface, m$^2$/g multipoint / singlepoint | Langmuir specific surface, m$^2$/g | Specific pore volume, cm$^3$/g | Pore size, nm |
|---|---|---|---|---|
| Shungite | 21.81/20.40 | 35.19 | 0.0107 | 0.8107 |
| Product of carbonization of a mixture of shungite and rice husk at a ratio of 6:1 | 54.21/62.71 | 83.00 | 0.0277 | 0.7882 |
| Product of carbonization of a mixture of shungite and rice husk at a ratio of 1:1.7 | 148.25/183.28 | 226.81 | 0.0774 | 0.7378 |
| Product of carbonization of a mixture of shungite and rice husk at a ratio of 1:4 | 133.41/162.55 | 204.39 | 0.0695 | 0.7554 |

0.0774 $cm^3/g$ in the case of the ratio of shungite and rice husk 1:1.7.

Carbonized samples are characterized by slightly underestimated values of the pore size, the pore size of shungite is 0.8107 nm, the pore size of carbonized samples is 0.7378–0.7882 nm, which is 0.02–0.07 nm less than the samples in shungite.

Thus, after carbonization of shungite together with rice husk, an improvement in the physicochemical characteristics of the shungite samples is observed. It has led to a significant increase in the specific surface area and specific pore volume of the samples. These data make it possible to use carbonized samples as sorbents.

Further, the obtained samples were tested to determine the sorption properties in relation to oil in the soil. Table 3 shows the results of sorption by sorbents of oil from the Karazhanbas field from the samples of oil-contaminated soils. The results of the sorption of oil from the soils with oil contamination of 10% showed that the sorbents show the maximum values of the sorption capacity after 60 days of testing. In the case of using the shungite, the sorption capacity turned out to be low and amounted to only 0.25–0.38 g/g. The degree of oil destruction did not exceed 11.4%. The carbonization of shungite with rice hulls led to an improvement in the sorption capacity. The carbonization product of a mixture of shungite and rice husk in a ratio of 1:1.7 showed a maximum sorption capacity equal to 1.86 g/g, while the degree of destruction was 55.8% in 60 days. For comparison, the product of rice husk carbonization was tested without the addition of shungite, its sorption activity was lower than that of carbonization products with the addition of shungite, the sorption capacity was 0.47 g/g after 60 days of testing with a degree of oil destruction of 14%.

The study of the sorption of the oil from the Tengiz field from the soil samples with oil contamination of 10% showed relatively low values of the sorption capacity of sorbents and the degree of oil destruction in comparison with the oil from the Karazhanbas field. As it can be seen from the data shown in Table 4, here also the maximum sorption capacity of 1 g/g was shown

**Table 3.** Results of sorption of oil from the Karazhanbas field from soil samples

| Sorbent | Sorption time, days | Sorption capacity, g/g | Degree of oil destruction,% |
|---|---|---|---|
| Shungite | 5 | 0.25 | 7.5 |
| | 10 | 0.30 | 9.0 |
| | 20 | 0.30 | 9.0 |
| | 30 | 0.31 | 9.3 |
| | 60 | 0.38 | 11.4 |
| Product of carbonization of a mixture of shungite and rice husk at a ratio of 6:1 | 5 | 0.48 | 14.4 |
| | 10 | 1.25 | 37.5 |
| | 20 | 1.32 | 39.6 |
| | 30 | 1.46 | 43.8 |
| | 60 | 1.75 | 52.5 |
| Product of carbonization of a mixture of shungite and rice husk at a ratio of 1:1.7 | 5 | 0.83 | 24.9 |
| | 10 | 0.92 | 27.6 |
| | 20 | 1.07 | 32.1 |
| | 30 | 1.33 | 39.9 |
| | 60 | 1.86 | 55.8 |
| Product of carbonization of a mixture of shungite and rice husk at a ratio of 1:4 | 5 | 0.91 | 27.3 |
| | 10 | 0.94 | 28.2 |
| | 20 | 1.07 | 32.1 |
| | 30 | 1.33 | 39.9 |
| | 60 | 1.35 | 40.5 |
| Rice husk carbonization product | 5 | 0.12 | 3.6 |
| | 10 | 0.24 | 7.2 |
| | 20 | 0.31 | 9.3 |
| | 30 | 0.40 | 12.0 |
| | 60 | 0.47 | 14.1 |

by the product of carbonization of shungite and rice husk at a ratio of 1:1.7, while the degree of oil destruction was 30%. With other ratios of shungite and rice husk, the sorption capacity of the sorbents and the degree of oil destruction turned out to be lower.

To explain the results of oil sorption by the tested sorbents, their elemental composition was determined, which is shown in Table 5. As it can be seen from the table, shungite is represented mainly by carbon, oxygen and silicon. It also contains a small amount of aluminum, iron, potassium, calcium and magnesium. Carbonized rice husk is represented by carbon with a mass fraction of 88.69%, oxygen content – 9.59%, calcium – 0.38%.

Carbonization of shungite with rice husk at different ratios led to an increase in the silicon content; the carbon and oxygen contents in the samples are very different. The carbonization product of shungite and rice husk at a ratio of 1:1.7, which showed the maximum sorption capacity and the degree of oil destruction, has a higher carbon content of 50.71% compared to other samples where the amount of carbon does not exceed 30%. This sorbent contains 14.7% silicon, which is almost three times lesser than other sorbents, but greater than pure shungite. Compared to shungite, the contents of potassium and iron in carbonization products decrease. Thus, in order to increase the sorption activity of the samples as a result of carbonization, it is desirable that the average content

**Table 4.** Results of sorption of oil from Tengiz field from soil samples

| Sorbent | Sorption time, days | Sorption capacity, g/g | Degree of oil destruction,% |
|---|---|---|---|
| Shungite | 5 | 0.06 | 1.8 |
| | 10 | 0.07 | 2.1 |
| | 20 | 0.08 | 2.4 |
| | 30 | 0.18 | 5.4 |
| | 60 | 0.21 | 6.3 |
| Product of carbonization of a mixture of shungite and rice husk at a ratio of 6:1 | 5 | 0.17 | 5.1 |
| | 10 | 0.21 | 6.3 |
| | 20 | 0.34 | 10.2 |
| | 30 | 0.50 | 15.0 |
| | 60 | 0.95 | 28.5 |
| Product of carbonization of a mixture of shungite and rice husk at a ratio of 1:1.7 | 5 | 0.20 | 6.0 |
| | 10 | 0.39 | 11.7 |
| | 20 | 0.42 | 12.6 |
| | 30 | 0.61 | 18.3 |
| | 60 | 1.00 | 30.0 |
| Product of carbonization of a mixture of shungite and rice husk at a ratio of 1:4 | 5 | 0.06 | 1.8 |
| | 10 | 0.18 | 5.4 |
| | 20 | 0.48 | 14.4 |
| | 30 | 0.49 | 14.7 |
| | 60 | 0.50 | 15.0 |

**Table 5.** Elemental composition of shungite and carbonized samples

| Sample | Content, wt. % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C | O | Si | Mg | Al | K | Ca | Fe |
| Shungite | 43.20 | 31.88 | 11.67 | 0.59 | 5.77 | 2.13 | 0.58 | 3.02 |
| Rice husk carbonization product | 88.69 | 9.59 | – | – | – | – | 0.38 | – |
| Product of carbonization of a mixture of shungite and rice husk at a ratio 6:1 | 23.36 | 36.97 | 34.4 | 0.29 | 0.83 | 1.52 | 0.81 | 1.81 |
| Product of carbonization of a mixture of shungite and rice husk at a ratio 1:1.7 | 50.71 | 30.68 | 14.70 | 0.26 | – | 1.77 | – | 0.75 |
| Product of carbonization of a mixture of shungite and rice husk at a ratio 1:4 | 30.69 | 16.09 | 42.98 | – | – | 8.20 | 2.04 | – |

of carbon in the sorbents be 50%, oxygen 30%, and silicon 15%.

Figure 1 shows electron microscopic images of the studied samples: shungite (a), carbonization products of a mixture of shungite and rice husk in a ratio of 6:1 (b), 1:1.7 (c), 1:4 (d). The main structural element of the samples corresponds to globules, which are spherical or ellipsoidal carbon formations, within which the presence of voids, interglobular voids or pores was established. As it can be seen from the figure, in the samples after carbonization of a mixture of shungite and rice husk in a ratio of 1:1.7, one can note the appearance of particles with a size of 43.3; 46.1; 47.1 nm, which confirms the receipt of nanostructured samples. This leads to the statement that these samples, due to such a structure, exhibit a higher sorption activity and the degree of oil destruction.

The ability to assimilate oil hydrocarbons is inherent in microorganisms of various systematic groups - micromycetes, yeasts and bacteria, etc. Their use as biological products for bioremediation of soils and water bodies contaminated with oil and oil products is based on this ability.

It is known that immobilization affects the physiological activity of cells in different ways, and therefore one of the most important aspects is its preservation. Immobilization, depending on the method and conditions of its implementation, has a different effect, and the morphology of cells and their physiology undergo changes. Immobilization also affects enzymatic activity, reproduction rate, and the intensity of biochemical

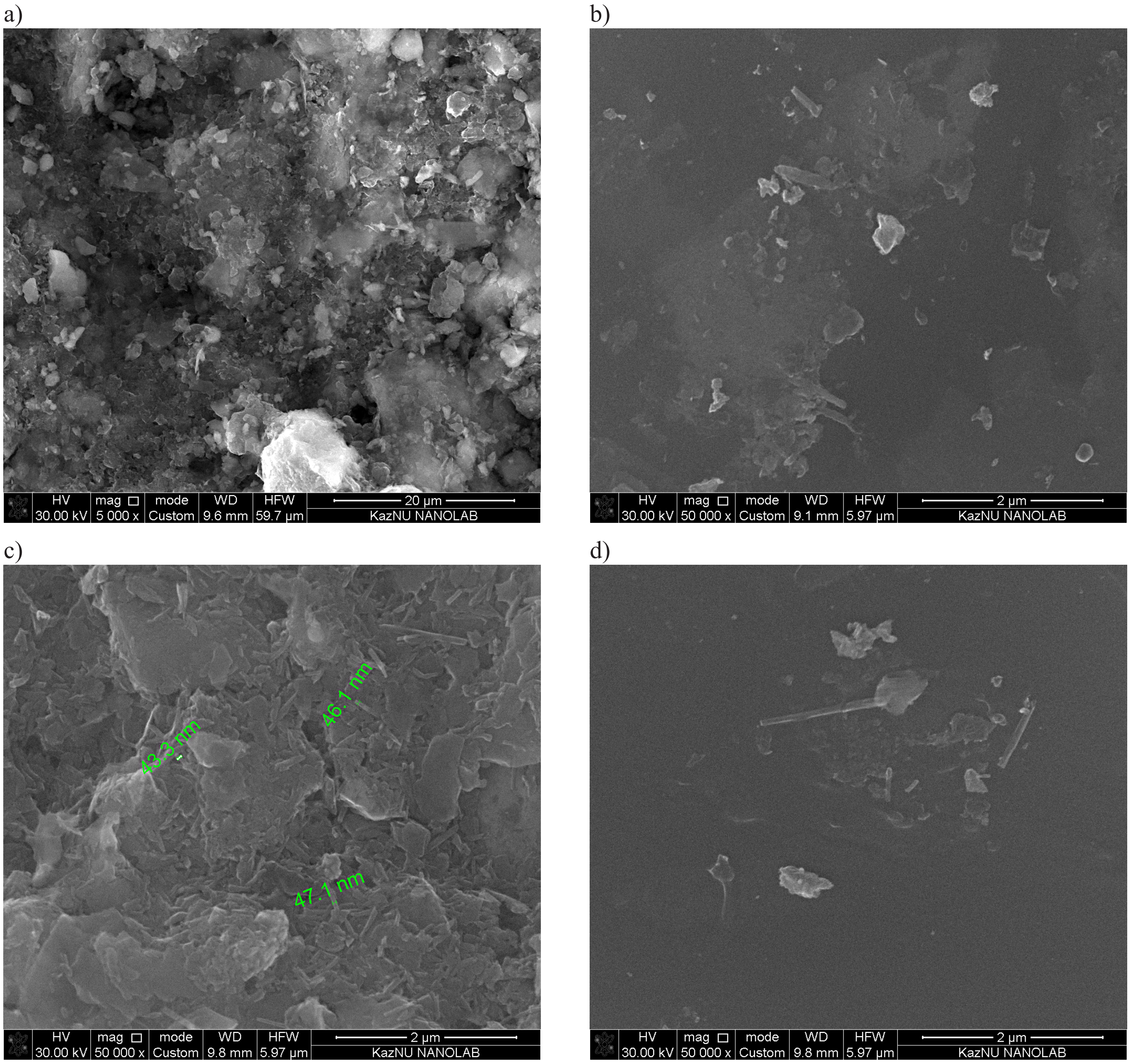


**Figure 1.** Electron microscopic images of samples: shungite (a), after carbonization of a mixture of shungite and rice husk in a ratio of 6:1 (b), 1:1.7 (c), 1:4 (d)

processes. In this regard, the viability of cells of microorganisms after immobilization on sorbents was studied.

As can be seen from Table 6, the viability of the cells attached to the carriers is very high. This means that the sorbents are not toxic to microbial cells and, after immobilization, do not inhibit metabolic processes in the cells of microorganisms. Thus, the maximum number of viable cells of strain B1 immobilized on the carbonized sample of a mixture of shungite with rice husk at a ratio of 1:1.7 is 96%. The maximum viability of strains B2 and B3 attached to carbonized samples was 92–95%. The viability of the B4 strain was found to be low in comparison with other strains. All strains immobilized on a carbonized sample of a mixture of shungite and rice husk at a ratio of 6:1 showed a low viability value from 73 to 79%.

Thus, it was found that the used sorbents based on shungite and rice husk do not affect the physiological activity of cells and the viability of immobilized cells. From the studied samples of sorbents, carbonized samples with a ratio of shungite and rice husk of 1:1.7 and 1:4 were selected as an effective sorbent for immobilizing microorganisms.

Further, the degree of destruction of oil hydrocarbons with strains of microorganisms immobilized on these samples was studied. From Table 7 it can be seen that in the carbonized sample with a ratio of shungite and rice husk of 1:1.7, the concentration of the substrate compared with the original was noticeably different. At the beginning of the experiment, the initial concentration of oil in the medium was 2 g/l, after 7 days in the presence of strain B2, its value decreased to 0.19 g/l. At the same time, the concentration of cells of the strains-destructors ranged from $3.7 \cdot 10^7$ to $5.6 \cdot 10^8$ CFU/ml.

According to the results of studying the degree of oil destruction by immobilized microorganisms on the carbonized sample of shungite and rice husk at a ratio of 1:4, as shown in Table 8, due to the oil-destructive activity of the B2 strain, the oil concentration

**Table 6.** Viability of cells of microorganism strains after immobilization on carbonized samples

| Strains | Cell viability immobilized on carbonized carriers of shungite (Sh) and rice husk (RH),% | | |
|---|---|---|---|
| | Ratio Sh:RH = 6:1 | Ratio Sh:RH = 1:1.7 | Ratio Sh:RH = 1:4 |
| B1 | 79±1.3 | 96±1.9 | 93±1.8 |
| B2 | 75±1.3 | 92±1.8 | 95±1.9 |
| B3 | 76±1.3 | 93±1.8 | 92±1.8 |
| B4 | 73±1.2 | 85±1.7 | 87±1.7 |

**Table 7.** The degree of oil destruction by immobilized microorganisms on a carbonized sample of shungite and rice husk at a ratio of 1:1.7

| Strains | Concentration | | | | Degree of destruction, % |
|---|---|---|---|---|---|
| | Cells/ml | | Substrate, g/l | | |
| | Initial | Ultimate | Initial | Ultimate | |
| B1 | $2.2 \times 10^9$ | $5.6 \times 10^8$ | 2 | 0.25±0.010 | 87.5±3.5 |
| B2 | $1.8 \times 10^9$ | $4.8 \times 10^8$ | 2 | 0.19±0.008 | 90.5±3.6 |
| B3 | $1.2 \times 10^9$ | $3.2 \times 10^8$ | 2 | 0.81±0.024 | 60.0±2.4 |
| B4 | $1.4 \times 10^9$ | $3.7 \times 10^7$ | 2 | 1.3±0.052 | 35.0±1.4 |

**Table 8.** The degree of oil destruction by immobilized microorganisms on a carbonized sample of shungite and rice husk at a ratio of 1:4

| Strains | Concentration | | | | Degree of destruction,% |
|---|---|---|---|---|---|
| | Cells/ml | | Cells/ml | | |
| | Initial | Initial | Initial | Initial | |
| B1 | $2.3 \times 10^9$ | $6.1 \times 10^8$ | 2 | 0.34±0.014 | 83.0±3.32 |
| B2 | $2.1 \times 10^9$ | $5.7 \times 10^8$ | 2 | 0.29±0.012 | 85.5±3.42 |
| B3 | $2.0 \times 10^9$ | $3.8 \times 10^8$ | 2 | 0.86±0.034 | 57.0±2.28 |
| B4 | $1.8 \times 10^9$ | $4.1 \times 10^7$ | 2 | 1.2±0.048 | 41.0±1.64 |

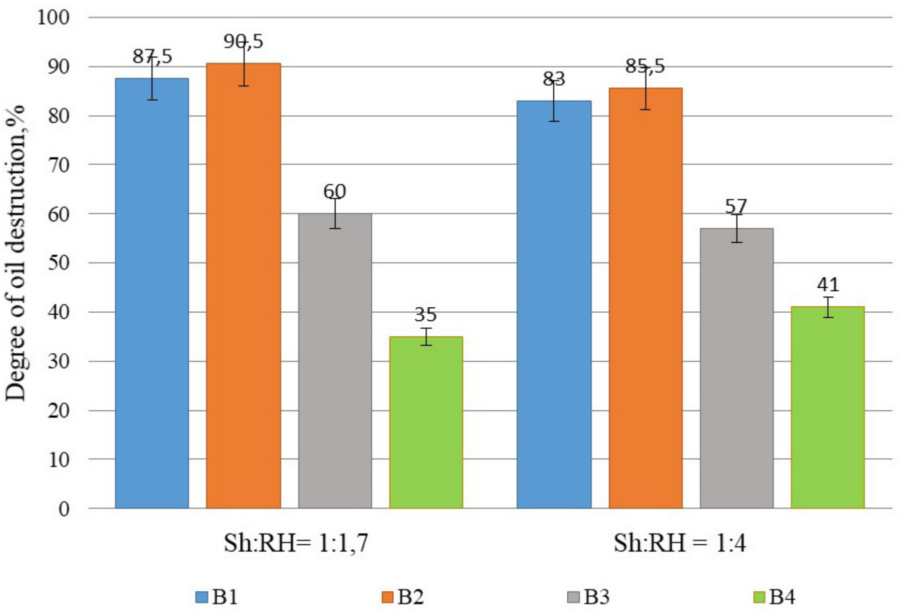


**Figure 2.** The degree of oil destruction by immobilized strains of microorganisms

decreased from the initial 2 g/l to 0.29 g/l. The concentration of cells of destructive strains in the presence of oil ranged from $4.1 \cdot 10^7$ to $6.1 \cdot 10^8$ CFU/ml. This indicates that the concentration of oil does not have a toxic effect on the growth of microorganisms. Therefore, the increase in the biomass of culture cells in the presence of oil does not greatly decrease.

As can be seen from Figure 2, a high degree of oil degradation was demonstrated by strains immobilized on a carbonized sample of a mixture of shungite and rice husk at a ratio of 1:1.7, the degree of oil degradation reached 87.5% for B1 and 90.5% for B2. The oil-destructive activity of the B4 strain was low and amounted to 35%. According to the results of the degree of oil degradation immobilized on carbonized samples of a mixture of shungite and rice husk at a ratio of 1:4, strains B1 and B2 showed high destructive activity in relation to oil and the degree of degradation was within 83–85.5%. The degree of degradation of strains B3 and B4 was 41% and 57%, respectively.

Thus, according to the results of studying the degree of oil degradation from all studied cultures, strains B1 and B2 showed high oil-destructive activity. This selective ability of strains to destroy various organic compounds is determined by the activity of the corresponding enzymes. In this regard, these cultures were selected to identify strains to species. Since the degree of biodegradation of oil by microorganisms is determined by the multicomponent and heterogeneity of their constituent substances, when creating biological products – oil destructors – it is necessary to take into account both the ecological and metabolic characteristics of each strain.

## CONCLUSIONS

In this work, carbonized materials were obtained from the shungite from the Koksu deposit in a mixture with rice husks at various ratios. Their physical and chemical characteristics for use as sorbents have been determined. The carbonized samples were tested for cleaning the model soil samples contaminated with the oil from the Karazhanbas and Tengiz fields. The maximum sorption capacity of 1.86 g/g was shown by a sorbent based on the carbonization product of shungite with rice husk at a ratio of 1:1.7, while the degree of oil destruction was 55.8% in the case of cleaning a soil sample contaminated with 10% oil from the Karazhanbas field in within 60 days. The viability of cells and the degree of destruction of oil strains of microorganisms immobilized in carbonized materials were studied. A high degree of destruction in relation to oil was demonstrated by the strains immobilized on the product of carbonization of shungite and rice husk at a ratio of 1:1.7, the maximum degree of destruction was reached in strain B2 – 90.5%.

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