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Sorption of oil by mechanochemically activated shungite

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Abstract

In this paper, the sorption capacity of shungite rocks of Koksu Field (Kazakhstan) in relation to the oil from the Karazhanbas and Tengiz fields (Kazakhstan) were studied. Oil spills occurring during production, gathering, transportation, storage and refining, and repair work on wells are an urgent environmental problem. There are effective methods of soil purification, including particular interests addressed to sorption process. The aim of this research is to study oil sorption by shungite rocks of the Koksu deposit after mechanochemical activation. The mechanochemical activation of shungite rock samples was carried out in a planetary ball mill at different speeds of rotation and ratios of ball mass to the sample. The developed sorbents based on shungite rocks of the Koksu deposit were tested for cleaning samples of oil-contaminated soils and their sorption capacities under dynamic and static conditions were determined. For the sorption of oil, the sorbent based on shungite of shale grade (TS) after mechanochemical activation is recommended, whose sorption capacity under dynamic conditions is 2.57-2.85 g/g. Sorption of oil from 10% of oil contaminated soil samples with the sorbents based on shungite after mechanochemical activation showed sorption capacities of 0.44-0.45 g/g in 60 days under static conditions. The practical significance of the research lies in the prospects of using shungite rocks to clean up oil spills.

Keywords:

shungite; oil; sorption; mechanochemical activation; sorption capacity

1. Introduction

Oil spills occurring during production, gathering, transportation, storage and refining, and repair work on wells are an urgent environmental problem. Oil belongs to one of the most dangerous groups of substances that pollute the environment. The negative effects of spilled oil on the surface of soil are regarding its composition, which is harmful to the organisms and plants (**Kenes et al., 2012**).

The movement of spilled oil in soil includes the processes of migration, adsorption and decomposition. The migration capacity of oil in soil is very weak, and oil is mainly absorbed and concentrated in the surface layers of the soil (**Hu, 2020**). Oil pollution on the soil surface can self-purify by volatilization. At high pollution intensity and oil with high content of small hydrocarbon molecules, the mentioned molecules can migrate into the underground aquifer. The sorption capacity of soils was controlled by the content of organic carbon and practically did not depend on the content of clay. The effect of soil composition and temperature on the sorption and desorption of naphthalene and benzene was studied (**Shi et al., 2020**). The sorption of naphthalene increased with a decrease in temperature, while the temperature had almost no effect on the sorption of benzene.

Oil pollution affects the physical properties of soil. It causes clogging of the soil pores, reducing soil aeration and water infiltration, and increases bulk density. Heavy oil can reduce and limit soil permeability. As a result, it subsequently affects plant growth. According to **Klamerus-Iwan et al. (2015)**, oil has a negative impact on the activity of enzymes in soil. Understanding hydrophobic compounds in the soil matrix and their interaction with soil moisture under the influence of hydrocarbon contamination of soil is essential in order to better plan and implement remediation processes (**Hewelke et al., 2018**).

Nowadays, most of the known methods for cleaning soil from oil and oil products are expensive, difficult to implement, and require scarce reagents. Physical and

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chemical soil cleaning methods can quickly and effectively remove oil pollution, but they have disadvantages associated with high cost, secondary pollution, and destruction of soil structure (**Wanga et al., 2017**). Bioremediation has many advantages, but in practice it is vulnerable to natural environmental conditions, resulting in unstable treatment efficiency. In addition, microbes cannot decompose all contaminants in soil (**Ali et al., 2020**).

In this regard, particular interests are addressed to the sorption process that is one of the inexpensive and effective methods of soil purification. The advantages of the sorption method are the following: the ability to remove contaminants from many forms of nature polluted by residual concentration, regardless of their chemical stability, the absence of secondary contamination and controllability of the process.

Recently, natural sorbents have been widely used in industry. Wide distribution in nature, low cost, and simple technology of their application along with rather high sorption properties makes it promising to use these minerals and natural raw materials in various industries (**Bandura et al., 2017**). The sorption capacity of clay minerals for oil and oil products was studied (**Zadvernyuk H., 2012; Pijarowski and Tic, 2014**). It is shown that the amount of sorbed oil and oil products depend on the oil film thickness and the nature of the sorbent. It has been determined that the larger the particle size and the smaller specific surface area of clay minerals, the greater amount of oil and oil products will be absorbed. It is noted that the clay minerals adsorb more crude oil than diesel fuel (**Zadvernyuk H., 2012**).

Synthesis and absorption properties of porous sorbent materials for oil spill response are considered (**Moses et al., 2003**). Silica, zeolites, organoclays and other natural sorbents have shown excellent oil absorption properties. Zeolite has high potential as an adsorbent for crude oil, and the highest oil sorption is achieved at a zeolite/oil ratio of 1:1 with 86.3% adsorbed oil. Enrichment of the zeolite with *Bacillus subtilis* improved the absorption of oil into the mineral (**Kalbuadi et al., 2019**).

Shungite rocks as natural composite materials are promising carbon-containing raw materials for multipurpose use. Due to the unique structure and content of mineral and carbon substances, the shungite mineral has a wide range of interesting properties (**Kovalevski and Shchiptsov, 2019**). This allows for the hope of the discovery of new areas of application of this mineral and requires a deeper study of its structure and properties using modern methods.

Shungite rocks are natural composite, which consists of highly ordered carbonaceous matter, silica and metal oxides such as aluminum oxide and calcium oxide. These components give good adsorption properties to the rocks (**Fujita et al., 2021**).

In the article by **Mel'nik et al. (2017)**, it is shown that shungite is able to efficiently adsorb impurities from aqueous-alcoholic solutions with the formation of sufficiently strong adsorption systems. Heat treatment at 180°C in a vacuum led to almost complete decomposition of adsorption systems, which ensures the extraction and a small increase in the specific surface area and sorption volume of shungite. It is shown that the parameters of shungite adsorption in relation to organic compounds dissociating anionically suggest that the mineral can be used as a filtering material with a sorption effect for water purification (**Bondarenko et al., 2008**).

The ability of shungite to adsorb zinc ions was studied in **Fischer et al. (2018)** and proposed as an alternative to activated carbon, since both substances showed the same adsorption capacity. However, in the study of **Baimatova et al. (2016)**, adsorbents based on shungite are not recommended for removing benzene, toluene, ethylbenzene and xylene (BTEX) from air because of the much higher efficiency of classic adsorbents with activated carbon.

To increase the efficiency of sorbents, their surface is modified. It is known that the defining property of sorbents is their dispersion, expressed in terms of particle size and their specific surface area. The more dispersed the sample, the higher the level of sorption properties of the sorbent. The presence of a complex of hydrophilic and hydrophobic, acidic and alkali structures in the composition of shungite, facilitates the processes of its physical and chemical modification.

An increase in powder dispersion is possible with the use of intensive and energy-intensive crushing technologies (**Kajdas, 2015**). Currently, mechanochemical activation is widely used as a method for obtaining new highly dispersed materials (**Tole et al., 2019**). The review paper of **Hu and Zhang (2021)** summarizes recent advances in the mechanochemical production of mineral-based adsorbent and its effective ability to treat wastewater containing toxic substances. In a study conducted by **Obijole et al. (2019)**, clay soils rich in aluminosilicates were prepared through mechanochemical activation and found to have a maximum adsorption capacity of 1.87 mg/g at 32% fluorine removal.

The application of this method in relation to shungite rocks has not been studied enough, which is probably due to shungite's high mechanical strength and complex morphology of carbon inclusion in the silicate matrix (**Moiseevskaya et al., 2015**). It has been shown that mechanical activation and thermal activation enable the increase of shungite surface by 10-35 times and obtain samples with high dispersion (**Petukhova and Kulkova, 2021**). Nanodispersed mechanical activated shungite reduced the formaldehyde emission from wood composite materials to 0.040 mg/m^3, which is two times lower than the norm of formaldehyde (0.124 mg/m^3) in the air.

The authors of the article (**Wu et al., 2021**) established the effects of the formation of products of mechanochemical transformations due to the occurrence of physicochemical processes of interphase interactions at the site of active centers of the combined components.

Figure 1: Map of Kazakhstan oil fields (from **http://www.kmgep.kz/eng/about_kazakhstan/key_facts**)

The effect of thermo- and mechanochemical modification of the mineral shungite from Karelia (Russia) on its chemical composition and physicochemical properties has been studied (**Polunina et al., 2017**). A method of mechanochemical modification of shungite has been proposed, which makes it possible to obtain a finely dispersed sorbent with a specific surface area of 70.6 m^2/g, a total pore volume of 0.336 cm^3/g, and a carbon concentration of more than 75 % (**Polunina et al., 2017**).

The possibility of obtaining a dispersed modifier from shungite for the production of various building materials has been studied. The composition of dispersed carbon-containing modifiers obtained in the processes of "dry" and "wet" grinding of shungite has been investigated (**Yusupova et al., 2020**).

The article (**Obradovic et al., 2019**) presents the results of the effect of mechanical activation of shungite on its sintering ability and the production of pure silicon carbide (SiC) ceramics. The authors of the article (**Gubernat et al., 2017**) also used shungite as a raw material for the synthesis of silicon carbide. The resulting products are recommended as abrasive and polishing powders.

Nanostructured fillers obtained by heat treatment of shungite rocks and containing carbon nanosized shells and SiC fibers are also of particular interest (**Moshnikov and Kovalevski, 2018**). It was shown that a small addition (2.5%) of nanostructured shungite filler can replace more than 40% of fillers with increased shielding efficiency of the composite material.

It was found that carbon materials with a more developed and ordered surface structure and increased porosity can be obtained as a result of the flotation enrichment of shungite and its subsequent thermal activation (**Kazankapova et al., 2019**). It was established by the Brunauer-Emmett-Teller (BET) method that thermal and vapor-gas activation of shungite leads to a significant increase in the specific surface of the sample and the specific pore volume, as well as to the decrease in the average pore size (**Kazankapova et al., 2019**).

Metal-carbon sorbents based on highly dispersed porous shungite modified with silver have been synthesized and their sorption properties to phenol have been studied (**Goncharova et al., 2018**). The modification of shungite with silver contributed to an increase in the dispersion of its aqueous suspensions as a result of enhancing the hydrophilic properties of shungite.

Mechanochemical activation of mineral shungite, increasing its dispersion and porosity, and changing the structure of the organomineral matrix will improve its sorption properties and obtain new sorbents for use in various industries. In this research, the possibility of increasing oil sorption capacity of shungite samples from the Koksu deposit (Kazakhstan) by mechanochemical activation were studied.

Karazhanbas and Tengiz crude oil (Kazakhstan) (see **Figure 1**) were selected due to their various characteristics. Karazhanbas is large oil and gas field in the northwestern margin of the South Buzachi Trough of the Turan Platform in the Mangystau region (**Petroleum encyclopedia of Kazakhstan, 2005**). Karazhanbas reservoirs are made of sandstones with a porosity of 27-29%, a permeability of (0.0136-0.351) $\times 10^{-12}$ m^2, and oil saturation factors which vary from 0.63 to 0.73. Also, the Karazhanbas oil is characterized as low paraffinic (0.7-1.4%) and highly sulfurous (1.6-2.2%).

Tengiz is a giant oil field located in the subsalt complex of deposits in the south-southeastern margin zone of the Caspian Depression in the Atyrau region. Tengiz reservoirs are fissured with an open porosity of 0.1-24% and a permeability of (1-30) $\times 10^{-12}$ m^2, and a saturation factor of 0.82. Tengiz oil is sulphurous (0.5-0.7%), paraffinic (3.6-6.0%) and low-pitched (1.14%).

2. Methods

Due to their physicochemical properties, shungite rocks are of practical value in the purification of water and soil from oil pollution (**Jurgelane and Locs, 2021**). The prospect of using amorphous non-crystallized fullerene-like carbon containing shungite and zeolite as an adsorbent in water treatment and other industries has been shown (**Ignatov and Mosin, 2014; Ignatov et al., 2016**). The efficiency of using biosorbents based on a shungite substrate in water treatment for removal of heavy metals and oil has been studied (**Efremova, 2006**). The bioremediation of oil-contaminated wastewater by microorganisms immobilized on shungite sorbents has been studied and it has been shown that they provide effective adsorptive and biological treatment of wastewater from oil (**Kazankapova et al., 2013**).

Koksu deposit of shungite rocks discovered in 1986, is located 250 km from Almaty city (Kazakhstan). It has been commercially developed since 2002. The rocks of the Koksu deposit are natural composite represented by shale taurite (TS) and carbonate taurite (TC), consisting of quartz, muscovite, carbonaceous matter and calcium carbonate (**Mussina and Samonin, 2013**). The ecological potential of Koksu shungite rocks is presented by **Mussina (2014)**: shungite is non-radioactive, does not contain toxic impurities, and is effective in the purification of drinking and waste water, soil, and screening of low-radioactive waste.

Sorption properties of shungite from the Koksu deposit, modified with polyethylenepolyamine and epoxy resin were determined depending on the pH of the medium, contact time, and solution concentration (**Kambarova et al., 2020**). The sorption capacity to the lead-(II) ion (Pb^{2+}) under static conditions was 0.45 mg/g. Metals and polyethylene glycol were synthesized by pyrolysis of nanocomposites based on Koksu shungite at 600°C and 1000°C. The size of the obtained nanoparticles was 5-40 nm (**Serikbaev et al., 2009**).

2.1 Objects of the study

Reserves of the Koksu deposit of shungite rocks in the Almaty region of the Republic of Kazakhstan are estimated at more than 620 million tons (**Moiseevskaya et al., 2015**). The Taurite brand of shungite is produced by the Koksu mining company. It is a kind of natural mineral of the cluster type, which has both organic and mineral parts, unlike the already known carbonaceous fossil minerals. Two samples of the brand "Taurite" were selected as the following: carbonate TC and shale TS with a fraction size of 1 mm.

Samples of shungite brands TC and TS are in an irregular geometric shape of grains and dust from dark gray to black. As shown in **Table 1**, the samples differ in mass fraction of carbon and silicon oxide (SiO_2). In carbonate samples, the carbon content is 12 mass %, which is 2 times more than in the shale rock samples (5.6 mass %). The mass fraction of silicon oxide in the shale rocks samples is 76.1%, whereas in the carbonate rocks samples it is 48.1%. The content of water-soluble substances in the samples is not more than 1.0%. Mass fraction of moisture in the carbonate samples is 1.0%, and in the shale samples - 3.5%. The pH value of the aqueous suspension of both samples is in the range of 8.2-8.8. The specific surface area of the original carbonate rocks (10.37 m^2/g) is almost 2 times less than shale rocks (21.81 m^2/g). The pore size in the carbonate samples (1.0942 nm) is larger than in the shale samples (0.8107

Table 1: Qualitative indicators of the shungite samples

Indicator	Carbonate TC	Shale TS
Mass fraction of carbon, %	12.0	5.6
Mass fraction of SiO_2, %	48.1	76.1
Content of water-soluble substances, %	0.72	0.91
Moisture content, %	1.0	3.5
pH of aqueous suspension	8.8	8.2
Size, mm	0-1	0-1
BET specific surface area, m^2/g	10.37	21.81
Langmuir specific surface, m^2/g	16.28	35.19
Specific pore volume, cm^3/g	0.0051	0.0107
Pore size, nm	1.0942	0.8107

Table 2: Physical and chemical characteristics of oil from the Karazhanbas and Tengiz fields

Index	Oil	
	Karazhanbas	**Tengiz**
Density at 20°C, kg/m^3	931.6	790.4
Viscosity at 50°C, mm^2/s	97.5	1.3
Pour point, °C	-18.0	-15.0
Paraffin content, mass %	0.8	5.5
Resin content, mass %	24.5	0.9
Asphaltene content, mass %	5.7	1.1
Sulfur content, mass %	2.1	0.5
Coking capacity, mass %	7.0	0.2
Fractional composition, mass % boiling start-200°C 200-350°C 350-500°C	 3.8 24.4 71.8	 22.0 41.0 37.0

nm). Whereas the same pattern is observed in the values of the specific pore volume in both samples.

For the preparation of samples of oil-contaminated soils, the crude oil from the Karazhanbas and Tengiz fields (Kazakhstan) were selected. The physical and chemical characteristics of oils are shown in **Table 2**. As it can be seen from the tabular data, 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 of oil and low content of light hydrocarbons. The content of resins in the Karazhanbas oil is 24.5% and content of asphaltenes is 5.7%. A distinctive feature of the oil is a high content of sulfur compounds (2.1%).

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

2.2 Methods of mechanochemical activation and analysis

The specific surface area, specific volume and pore size of the shungite samples were determined by automatic analyzer 3H-2000PS1. The specific surface area was measured through the single-point BET and Langmuir methods for the low-temperature adsorption of liquid nitrogen.

Mechanochemical activation (MA) of shungite rock samples was carried out on a Pulverisette 6 planetary ball mill (see **Figure 2**) in the following parameters: grinding speed - 250-500 rpm, activation time - 20 min, sample weight - 70-350g, ball weight - 70-170g. The mill allows grinding solid samples to particle sizes of 20 µm.

To determine the sorption capacity of sorption materials under dynamic conditions, the sorbent was weighed on an analytical balance. Sorption material with a certain

Figure 2: Photograph of Pulverisette 6 planetary ball mill

mass of 3g was placed in a glass column (length 15cm, diameter 3cm), and a certain volume of oil (3-5ml) was poured through the funnel. The experiment continued until oil droplets formed after passing through the layer of sorption material. The dynamic sorption capacity was determined by the difference in the masses of the spent sorption material with oil and the initial sorbent as in **Equation 1**:

$$a = \frac{m_{abs} - m_{sorp}}{m_{sorp}} \quad (1)$$

Where:

a – dynamic sorption capacity [g/g],

m_{abs} – mass of the sorption material with absorbed oil [g],

m_{sorp} – mass of the sorption material [g].

The sorption capacity under static conditions was calculated by the ratio of the mass of oil absorbed by the sorbent to the mass of the initial sorbent, according to the **Equation 2**:

$$A = \frac{m_{oil}}{m_{sorbent}} \quad (2)$$

Where:

A – sorption capacity under static conditions [g/g],

m_{oil} – mass of absorbed oil by sorbent [g],

$m_{sorbent}$ – mass of the initial sorbent [g].

3. Results and discussion

The results of the sorption of oil from the Tengiz Field under dynamic conditions showed that the initial shung-

Table 3: Results of sorption of oil from the Tengiz Field by the sorbents based on shungite rocks under dynamic conditions

Shungite grade	Grinding speed	Sample-to-ball ratio	Sorbent weight, g	Absorbed oil mass, g	Sorption capacity, g/g
TS	-	-	2.95	1.71	0.58
	250 rpm	1:2	1.05	2.70	2.57
	350 rpm	1:2	1.35	1.72	1.27
TC	-	-	3.61	1.70	0.47
	400 rpm	1:1	2.74	3.27	1.19
	400 rpm	1:3	1.59	1.65	1.04
	500 rpm	1:2	3.22	4.01	1.24

Table 4: Results of sorption of oil from the Karazhanbas Field by sorbents based on shungite rocks under dynamic conditions

Shungite grade	Grinding speed	Sample-to-ball ratio	Sorbent weight, g	Absorbed oil mass, g	Sorption capacity, g/g
TS		-	1.6	2.64	1.65
	250 rpm	1:2	0.68	1.94	2.85
	350 rpm	1:2	0.63	1.55	2.46
TC		-	2.72	1.23	0.45
	400 rpm	1:1	1.64	3.59	2.19
	400 rpm	1:3	0.59	1.35	2.29
	500 rpm	1:2	2.29	2.53	1.10

ite rocks as sorbents have low values of the sorption capacity in the range of 0.47 and 0.58 g/g. Testing of sorbents based on shungite after mechanochemical activation led to an improvement in sorption capacity. The maximum oil sorption capacity, equal to 2.57 g/g, was shown by the TS brand shungite sorbent after mechanochemical activation with a grinding speed of 250 rpm and a ratio of the sample and mill balls of 1:2. An increase in the grinding speed to 350 rpm led to a decrease in the sorption capacity of the TS brand shungite sorbent to 1.27 g/g. **Table 3** shows the results of determining the sorption capacity of the sorbents for oil from the Tengiz Field under dynamic conditions.

Shungite of carbonate origin TC has a higher strength than the shale one, and a relatively high grinding speed of 400-500 rpm was used to grind it. Testing samples of shungite of carbonate origin grade TC showed lower values of sorption capacity than shungite of shale origin. In this case, an increase in the ratio of the sample and balls from 1:1 to 1:3 leads to a decrease in the value of the sorption capacity.

The same experiments under dynamic conditions were carried out for the sorption of oil from the Karazhanbas Field (see **Table 4**). This oil is more heavy, viscous, and resinous than oil from the Tengiz Field, and the sorption capacity of sorbents changed to relatively higher than Tengiz oil. In this case, the sorbents based on the shungite of shale origin, TS grade, have the highest indicator of sorption capacity. The maximum sorption capacity of 2.85 g/g is observed when testing the sorbent based on shungite grade TS after mechanochemical activation at a rate of 250 rpm and a ratio of the sample and mill balls of 1:2.

To test the developed sorbents, samples of oil-contaminated soils were prepared. Karazhanbas or Tengiz crude oil (5.0g) were added to the soil (50.0g), then 10% oil-contaminated soil were prepared. Further, 2.0g of sorbent samples based on mechanochemical activated (grinding speed of 250 rpm and a ratio of the sample and mill balls of 1:2) shungite rocks in various origins, were introduced into the samples. Then, after a certain time (from 5 to 60 days), the sorption capacities of the sorbents under static conditions were determined.

Figure 3 shows the sorption results of oil from the Karazhanbas Field gained from samples of oil-contaminated soils by sorbents. The results of the sorption of oil from the Karazhanbas Field from soil samples showed that all sorbents show the maximum values of the sorption capacity after 60 days of testing. In the case of using the shungite rocks of shale origin, the maximum sorption capacity of 0.44 g/g was shown by the samples after mechanochemical activation. The shungite of carbonate origin (TC) after mechanochemical activation as a sorbent also has a higher sorption capacity (0.42 g/g).

To test the sorption of oil from the Tengiz Field, a brand of shungite of shale origin TS was used before and after mechanochemical activation. The results of the Tengiz oil sorption in **Figure 4** show that the sorption capacity of the shungite sample of the TS grade, is lower than in case of the Karazhanbas oil. However, after mechanochemical activation, the sorption capacity of the sorbent increased to 0.45 g/g.

Further, for testing the sorbents, samples of oil-contaminated soils with an increase in oil content and sorbent weight were prepared. Karazhanbas or Tengiz crude oil (7.5g) were added to the soil (50.0g), then 15% of

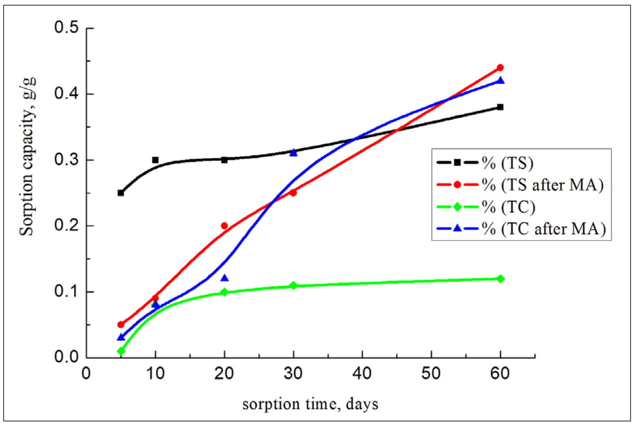

Figure 3: Results of the sorption of oil from Karazhanbas Field from soil samples with oil contamination of 10% by sorbents based on shungite rocks

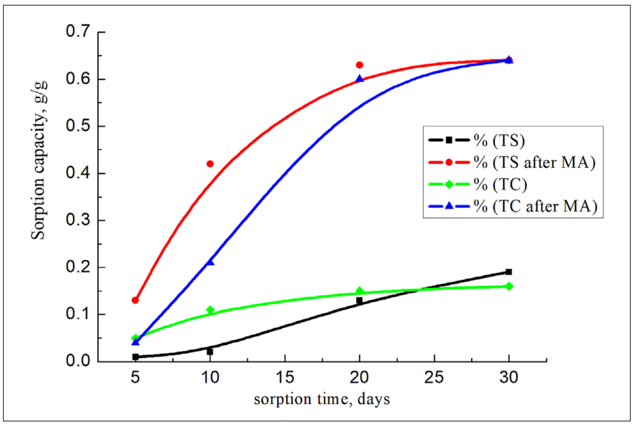

Figure 5: Results of the sorption of oil from Karazhanbas Field from soil samples with 15% oil contamination with sorbents based on shungite rocks

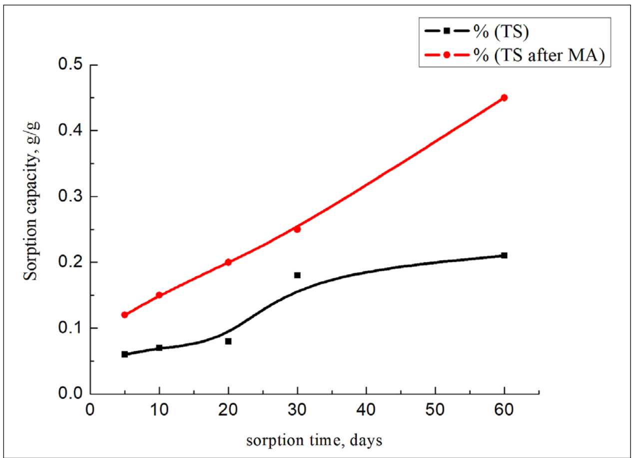

Figure 4: Results of the sorption of oil from Tengiz Field from soil samples with oil contamination of 10% by sorbents based on shungite rocks

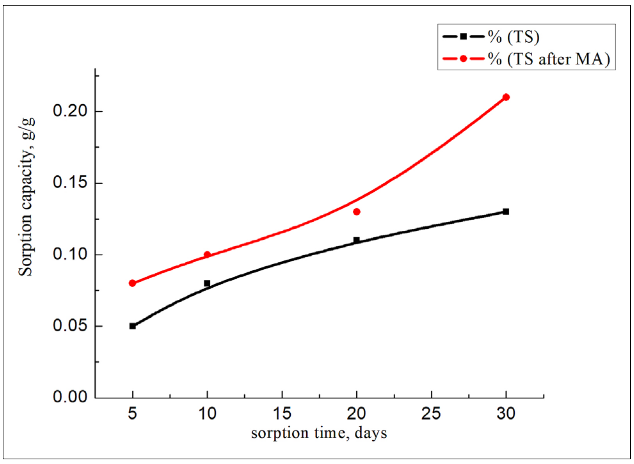

Figure 6: Results of the sorption of oil from Tengiz Field from soil samples with oil contamination of 15% by sorbents based on shungite rocks

oil-contaminated soil was prepared. Further, 5.0g of the sorbent sample based on mechanochemical activated (parameter is the same as the previous model) shungite rocks were introduced into the prepared soil samples. Then, during 5 to 30 days, the sorption capacity of the sorbents and the degree of oil destruction under static conditions were determined.

Figure 5 shows the results of the Karazhanbas oil sorption from oil-contaminated soils samples by sorbents. As it can be seen from the tabular data, with an increase in the degree of oil contamination of the soil to 15% and the mass of sorbents, the sorption capacity of the sorbents increases to 0.64 g/g. The maximum sorption capacity in relation to oil from the Karazhanbas Field was shown by the sorbents based on the shungite of the TS and TC grades after mechanochemical treatment. In this case, the optimal values of the sorption capacity of the sorbents are achieved after 30 days of testing the samples.

The results of the Tengiz oil sorption in **Figure 6** show low values of the sorption capacity of the tested sorbents based on shungite grade TS. The maximum sorption capacity of 0.21 g/g had been achieved after 30 days when using the sorbent based on shungite after mechanochemical activation.

The test results showed that in the case of 15% oil contamination of the soil, the sorbents based on shungite after mechanochemical activation have higher values of the sorption capacity. This data is consistent with the values of the specific surface area, volume and pore size of shungite, which increase after the mechanochemical treatment (**Baigulbayeva et al., 2021**).

The sorbents based on shungite of carbonate origin of TC grade also have relatively lower sorption characteristics than the shungite of TS grade. In this case, mechanochemical activation also leads to the increase in sorption parameters. The improvement in the sorption properties of the sorbents is explained by the formation of nanostructured powders as a result of mechanochemical activation (**Baigulbayeva et al., 2021**). A feature of finely dispersed shungite samples is low structure and high functionality of the surface. The peculiarity of the structure of shungite consists of active carbon with silica forming an interpenetrating network with a common highly developed surface. During mechanochemical activation, shungite crushing proceeds along carbon veins, which is due to the high hardness (a measure of the connectivity of the atomic structure of the substance) of quartz (SiO_2).

Thus, as a result of mechanochemical activation, a change in the sorption properties of shungite rocks is observed and shungite rocks appear to be promising as an adsorbent for purifying soil from oil pollution.

5. Conclusion

For the sorption of oil from Tengiz Field under dynamic conditions, the sorbent based on shungite from Koksu Field of TS grade after mechanochemical activation with a grinding speed of 250 rpm and a ratio of sample and balls of 1:2 is recommended. Its sorption capacity was 2.57 g/g. For the sorption of oil from Karazhanbas Field, the sorbent based on shungite from Koksu Field of TS grade after mechanochemical activation with a grinding speed of 250 rpm and a ratio of sample and balls of 1:2 is also recommended. This is because it has a sorption capacity of 2.85 g/g.

Sorption capacity of the oil sorbents during the purification of samples of oil-contaminated soils under static conditions were investigated. For the sorption of high-viscosity oil of Karazhanbas Field from 10% of oil contaminated soil samples, the sorbent based on shungite of the TS brand after mechanochemical activation is recommended because it showed a sorption capacity of 0.44 g/g in 60 days of treatment. For the sorption of light oil of Tengiz Field from 10% of oil contaminated soil samples, the sorbent based on TC shungite after mechanochemical activation is recommended. Its sorption capacity was 0.45 g/g in 60 days of treatment. According to the increased degree of oil contamination of the soils to 15%, the sorption capacity of the sorbent based on shungite after mechanochemical activation increased to 0.64 g/g.

Thus, the shungite samples from the Koksu deposit after mechanochemical activation showed the possibility of sorption of Karazhanbas and Tengiz oil from soil under dynamic and static conditions. The research was carried out with soils that were previously contaminated with oil. In the future, research regarding sorption capacity of shungite samples for cleaning real oil-contaminated soils, as well as with the immobilization of strains of microorganisms isolated from soil are planned.

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SAŽETAK

Sorpcija nafte mehanokemijski aktiviranim šungitom

U radu je proučavan sorpcijski kapacitet šungitnih stijena polja Koksu (Kazahstan) u odnosu na naftu s polja Karazhanbas i Tengiz (Kazahstan). Izlijevanje nafte tijekom proizvodnje, sabiranja, transporta, skladištenja i rafiniranja te remontnih radova na bušotinama predstavlja velik ekološki problem. Postoje učinkovite metode pročišćavanja tla, u okviru kojih je poseban interes usmjeren na proces sorpcije. Cilj je ovoga istraživanja proučavanje sorpcije nafte šungitnim stijenama ležišta Koksu nakon njihove mehanokemijske aktivacije. Mehanokemijska aktivacija uzoraka šungitnih stijena provedena je u planetarnome kugličnom mlincu pri različitim brzinama rotacije i različitim omjerima mase kugle prema uzorku. Razvijeni sorbensi na bazi šungitnih stijena ležišta Koksu ispitani su za čišćenje uzoraka tla zagađenih naftom, pri čemu je utvrđena njihova sorpcijska sposobnost u dinamičkim i statičkim uvjetima. Za sorpciju nafte preporučuje se mehanokemijski aktiviran sorbens na bazi šungita, niskoga stupnja metamorfoze, čiji sorpcijski kapacitet u dinamičkim uvjetima iznosi 2,57 – 2,85 g/g. Sorpcija nafte iz naftom zagađenih uzoraka tla (10 % zagađenje) sorbensima na bazi šungita nakon mehanokemijske aktivacije pokazala je sorpcijski kapacitet od 0,44 – 0,45 g/g u 60 dana u statičkim uvjetima. Praktična važnost provedenoga istraživanja leži u perspektivi korištenja šungitnih stijena za čišćenje naftnih izljeva.

Ključne riječi:
šungit, nafta, sorpcija, mehanokemijska aktivacija, sorpcijski kapacitet

Author’s contribution

Yerdos Ongarbayev (professor, doctor of chemical sciences) analyzed the research results and their discussion, wrote and designed the manuscript. **Moldir Baigulbayeva** (PhD student) prepared sorbents and conducted sorption experiments. **Yerbol Tileuberdi** (PhD, associate professor) determined the properties of oils. **Kairat Zhumakhan** (PhD student) conducted experiments on the mechanochemical activation of shungite.