Glauconite-Based Sorbents for Skimming Oil and Oil Products

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Voronezh State University of Engineering Technologies,
19 Revolyutsii prospect, Voronezh 394036, Russian Federation

Abstract

Natural glauconite-based sorbents were obtained for skimming oil and oil products from different surfaces. Glauconite is an aluminosilicate mineral and is widely used for cleaning various pollutants from water and soil. The classification allowed selecting a glauconite fraction with a particle size of 0.045-0.1 mm, which is the most effective for the sorption of oil products. For this, the sorbent was thermally activated and modified using organic compounds. The glauconite samples were thermally treated at temperatures of 100, 600, and 1000 °C. To provide glauconite with hydrophobic properties, it was modified with stearic acid.

When the sorbents came into contact with water (duration 92 hours), it was found that with the mass fraction of stearic acid of 5 wt% the lowest weight loss was observed in all the three samples. The contact angle of wetting for sorbents is greater than 90°, which led to a change in the state of its surface. The obtained samples were not wetted with water and could remain on its surface for a long time. The interaction of oil and a hydrophobic sorbent showed that after seven minutes the particles of the sorbent penetrated the oil that also has a hydrophobic surface and can sorb a surfactant applied on the sorbent, which indicates the affinity of stearic acid to oil. A granular sorbent, thermally activated at a temperature of 1000 °C and modified with a cellulose-containing component, sorbed the oil for 2 minutes. The use of this modifier increased the sorbent porosity, which affected the sorption rate.

Keywords: glauconite, sorbent modification methods, hydrophobicity, oil spill clean-up.

1. Introduction

Oil production, transportation, and refining are sometimes accompanied by emergency situations. To eliminate the spills of oil products on water or soil, natural sorbents (mineral and organic), as well as waste from various industries and waste composition are used [1–4].

A sawdust-based sorbent was treated with ethanol, sodium hydroxide, and hydrochloric acid to increase the efficiency of oil absorption. It was shown that the treated sawdust had a higher sorption capacity, even after 90 minutes of sorption with four-fold recurrence [5].

The effectiveness of wetting and sorption of oil by natural fibres (kapok, cattail, cotton), which possess natural hydrophobicity and oleophilicity, was evaluated and compared. Water on the surface of the fibres forms contact angles of wetting between 120 and 145°. A drop of oil was quickly absorbed by the surface of the fibres within several seconds. Kapok fibre has the highest sorption and oil retention ability as compared with other samples [6].

Artificial organic sorbents based on glycerol propoxylate were obtained for oil sorption by volume polymerisation method with various amounts of a cross-linking agent. The synthesised gels were used as absorbents...
for various organic solvents, petroleum, and oils [7].

A sorbent with high hydrophobic and oleophilic properties for the separation of oil-water mixtures and oil-water emulsions was obtained based on kapoka fibre with a ZnO nano-needle coating. For this, a one-stage hydrothermal method followed by hydrophobic modification with dodecanol was used [8].

An effective sorbent with high oil sorption was obtained by the inclusion of crushed rice straw into a polyurethane matrix. The oil absorption rate was high in the first 15–30 minutes, then it decreased, and a complete saturation of the sorbent was observed after 2 hours [9].

Sorbents based on natural minerals are widely used in sorption technologies, for example, samples with high mesoporosity (oxides of silicon, aluminium, zirconium, carbon materials, aluminosilicates) are recommended for clean-up of oil spills on land [10]. Capillary condensation is observed in materials with pores of this size (2–50 nm).

Good sorption results for petroleum products are typical for diatomites, sepiolite, and zeolites obtained from ash. Adsorption of petroleum substances on the porous surface of such minerals proceeds according to the capillary mechanism associated with the filling of existing pores and the formation of a layer of oil products on the outer surface of the adsorbent particles. Oil substances cannot penetrate into narrow micropores of the mineral; there is a correlation between the viscosity and density of the oil: viscous and thick oils were adsorbed by the same material in larger amounts than light oils.

Hydrophobic silica aerogels, zeolites, organoclay, and other natural minerals demonstrated high oil absorption [11].

The modification of silica clay results in the increase of hydrophobicity, specific surface area, and porosity of the sorbent, as well as its ability to absorb oil. It was established that the modified silicate clay is a highly effective sorbent with respect to emulsified oil products. The optimal sorption parameters were determined that allow achieving a degree of oily wastewater treatment of more than 99 % [12].

A group of sorbents based on cellulose-containing materials is also of interest [13–15].

A new physicochemical method for obtaining a sorbent based on cellulose was proposed that includes foaming, plasma treatment, and modification with a hydrophobic agent [15].

Aerogels based on nanocellulose can be obtained that combine such properties as high porosity, large surface area, low density, high sorption, biodegradability, and easy surface modification [16].

A sorbent in the form of a hydrophobic nanostructured aerogel was obtained based on cotton cellulose, which had high oil absorption and retention ability, excellent selectivity with respect to oil and water, good mechanical strength, and recycling ability [17].

Using biological delignification, cellulose was extracted from raw rice husk and acetylated to make it hydrophobic. The obtained sorbents showed a high oil absorption rate, and saturation capacity was achieved after 5 minutes of contact with oil [18].

Nanofibrillation and hydrophobic modification of spent cellulose fibres allowed obtaining nanofibre sponges with ultra-low density and high porosity. They demonstrated excellent absorption characteristics for various oils and organic solvents and can be reused multiple times. Nanofibre aerogels showed selectivity in the absorption of marine diesel fuel from a water-oil mixture [19].

Hydrophobic sponge materials, in particular melamine sponges, can be used as potential oil sorbents [20, 21, 22]. Fluorinated kaolin was used to transfer the sponge from a hydrophilic to a hydrophobic state, which increased the adsorption capacity for various oils and organic solvents [20]. Hydrophobic sponges based on commercial melamine sponges can also be obtained through the adsorption of silica nanoparticles and coating silanization [21] or by N-acylation with fatty acid derivatives [22].

It seems relevant to use glauconite, a widespread natural eco-friendly aluminosilicate, as a sorbent of oil products. Its important property is the ability to improve sorption properties as a result of applying various activation and modification methods.

Almost all sorbents based on natural minerals are hydrophilic; therefore, to reduce water absorption and wettability of the mineral sorbent
surface, they are modified with hydrophobic agents [23, 24, 25].

A hydrophobic modification of the sodium alginate foam was obtained by simple freeze-drying and subsequent cross-linking with zirconium ions. They showed excellent adsorption capacity for various oils and organic solvents [26].

When treating vermiculite, an aluminosilicate mineral, with a hydrophobic agent, a sorbent was obtained that has high water resistance values and can remain on water surface for a long time. The immobilisation of bacterial cells of oil degraders of the genus Pseudomonas on the surface of a hydrophobic sorbent allows intensifying metabolic processes and achieving a high degree of purifying water from oil products [27].

Various forms of sorbents, including powdered, granular, briquetted, fibrous, canvas, etc., are used for oil sorption [28–32]. It is more convenient to use different types of sorbents for different purposes, such as skimming oil from a water surface, from a solid surface, or for treating wastewater containing oil products. These sorbents should be different in their operational properties.

Sorbent oil-spill booms are used to contain the spread of oil and minimise the effects of oil spills [33].

The reviewed technologies and materials used to create sorbents for oil and oil products are sometimes expensive. In some cases, unsustainable substances are used. Most of the proposed sorbents are combustible and require specific storage conditions. Therefore, developing inexpensive, effective, and eco-friendly sorbent materials for oil and its derivatives remains an important task. This problem can be solved by using natural aluminosilicate mineral materials.

The aim of this work was to obtain powdered hydrophobic and granular oil sorbents based on an eco-friendly mineral glauconite.

2. Experimental

The chemical, oxide, and phase compositions of glauconite from the Karinsky deposit in the Chelyabinsk Region are well-known [34]. It was found that the best results for the sorption of oil products were shown by the glauconite fraction with a particle size of 0.045–0.1 mm. It was chosen as the basis for creating the oil sorbents.

The technique for obtaining hydrophobic sorbents was implemented as follows. The first glauconite sample was heated in an electric furnace at 100 °C, the second and the third ones were heated at 600 and 1000 °C, respectively. They were thermally treated for 2 hours. The second and the third samples were cooled to 90–100 °C. All the three sorbents were transferred to a laboratory mixer and mixed with the added crystalline stearic acid (melting temperature above 69.6 °C). During this process, the glauconite particles were coated with stearic acid. The hydrophobic agent was added in an amount of 2, 3, 4, and 5 wt% to determine the effect of its amount on the buoyancy of sorbents.

The preparation of granular sorbents was different from the hydrophobic ones, as instead of stearic acid, 5 wt% of cellulose-containing component was added at 25 °C and mixed in a mixer. Then, a small amount of distilled water was added to the obtained sorbents and mixed thoroughly. The mixture was extruded through a spinneret with a hole diameter of 3 mm. The obtained granules with a length of 0.5–1.0 mm were dried in air for 24 hours.

The buoyancy of the sorbents was determined as follows. A weighed portion of the sorbent weighing 3 g was placed in a glass with a volume of 50 ml that was half-filled with water. The contact time of the sorbent with water was: series 1 – 6 hours; series 2 – 12 hours; series 3 – 24 hours; series 4 – 56 hours; series 5 – 48 hours; series 6 – 92 hours. After this, the sorbent remaining afloat was removed, dried to a constant mass, and the amount of the drowned sorbent was determined by the difference in the weights.

Oil absorption (A, %) was calculated by the formula:

\[ A = \left( \frac{P_T - P_0}{P_0} \right) \times 100\% \]

where \( P_T \) is the weight of the sorbent after its immersion in oil, g; \( P_0 \) is the initial weight of the sorbent, g.
3. Results and discussion

The results of the study for the buoyancy of the obtained hydrophobic sorbents after 92 hours of contact with water are presented in Fig. 1.

An increase in the fraction of hydrophobic agent contributes to an increase in the buoyancy of sorbents in the following series: glauconite at 100 °C < glauconite, thermally activated at 1000 °C < glauconite, treated at a temperature of 600 °C. The smallest weight loss was observed for all three hydrophobic sorbents with a mass fraction of the hydrophobic agent of 5 %. This value of 5% produced the best buoyancy for the sorbent that was thermally activated at 600 °C.

Using the Statistica Neural Networks programme, a three-dimensional graph of the dependence of the buoyancy of glauconite-based sorbents on the mass fraction of the hydrophobisator and temperature was constructed (Fig. 2).

It is clear that with an increase in the mass fraction of stearic acid from 2 to 5 %, the buoyancy increases. The activation temperature of glauconite does not greatly affect the buoyancy. When stearic acid is added to glauconite in an amount of more than 4 %, a sorbent with the buoyancy of more than 90 % can be obtained in the entire range of burning temperatures.

To determine the hydrophobicity, the sorbents modified with a 5 wt% stearic acid with maximum buoyancy were chosen. When a drop of water is applied to the surface of the obtained sorbents, the liquid does not spread over the surface and retains the shape of a drop (Fig. 3).

The contact angle of wetting is a characteristic of the ability of water to wet a solid surface. The sorbent surface, on which the water forms an obtuse contact angle, is hydrophobic, and the water on such surface is in the form of balls. The images show that the contact angle for all sorbents is greater than 90°. This prevents the interaction of water molecules with the sorbent surface. A change in the state of surface due to the modification with a hydrophobic agent provides sorbents with such new properties as water non-wettability, the ability to remain on the water surface for a long time, and a change in the mechanism of interaction with oil compared to the initial mineral.

The first stage of the study involved testing the interaction of oil with the surface of sorbents. Fig. 4 presents images of the interaction of a hydrophobic sorbent with oil on a solid surface (as exemplified by glauconite treated at a temperature of 1000 °C).

Hydrophobic powdered sorbents were placed on glass plates, and a drop of oil was applied to them, which did not spread as compared to the initial mineral. After 2 minutes, the shape of the drop of oil changed; it became flat, and after 7 minutes it turned into a film containing a hydrophobic sorbent. Oil particles also have a hydrophobic surface on which they can sorb a surfactant deposited on the sorbent. This indicates the affinity of stearic acid to oil.

The obtained sorbents were tested for the absorption of oil and oil products from a solid
The sorption capacity of powdered sorbents after hydrophobisation decreases by an average of 40% due to the changes in the state of the glauconite surface. The sorbent pores are sealed with a layer of hydrophobisator, which leads to a decrease in sorption (Fig. 5).

The results of sorption for oil and oil products by granular sorbents are presented in Fig. 6.

According to the presented diagrams, the modification of glauconite-based sorbents with a cellulose-containing component increases their sorption capacity. For the initial glauconite, the sorption capacity for oil and oil products increases by 1.2–1.3 times, for the glauconite thermally activated at a temperature of 1000 °C by 1.3–1.5 times, and for the glauconite treated at a temperature of 600 °C by 1.0–1.2 times. The best values of sorption for oil and oil products were shown by a sorbent thermally activated at a temperature of 1000 °C. This is due to the fact that the activation results in the formation of a large number of defects on the glauconite surface in the form of pores and cracks [34]. When glauconite is modified, a cellulose-containing component gets into these defects, and it absorbs and retains oil.
Fig. 5. The effect of a hydrophobic agent on the sorption capacity of sorbents: a) glauconite at 100 °C; b) glauconite, thermally activated at a temperature of 600 °C; c) glauconite, thermally activated at a temperature of 1000 °C

Fig. 6. Absorption of oil and oil products by granular sorbents: a) glauconite; b) glauconite, thermally activated at a temperature of 600 °C; c) glauconite treated at a temperature of 1000 °C
and oil products in a larger amount than other samples.

Let us determine the time of oil absorption by a granular sorbent treated at a temperature of 1000 °C. After applying a drop of oil to the sorbent, it is completely absorbed within 2 minutes with stirring (Fig. 7), while for a hydrophobic sorbent, the interaction time with the oil is 7 minutes.

The studies of the obtained sorbents based on glauconite (hydrophobic powdered and granular) showed a decrease and an increase in the sorption of oil and oil products on a solid surface, respectively. A granular sorbent absorbs oil 3.5 times faster than a hydrophobic one, which indicates different sorption mechanisms. The modification with a cellulose-containing component had a positive effect due to obtaining a more porous structure of the sorbent in comparison with the initial glauconite. Taking into account the short time of oil absorption, it can be used to eliminate oil spills on solid surfaces and for the treatment of oily wastewater.

4. Conclusions

To prepare the sorbents for oil and oil products, a natural eco-friendly mineral was used. A hydrophobic powdered glauconite-based sorbent is characterised by low sorption of oil and oil products, but it can remain on the water surface for a long time and has affinity to oil. While distributing in the oil phase, this sorbent aggregates and thickens it, forming dense conglomerates. This prevents the oil from spreading and increases its viscosity, which will increase the degree of extraction of the formation-bound oil. Therefore, it can be used to remove oil films from water surfaces.

The granular glauconite sorbent showed its effectiveness as it absorbs oil 3.5 times faster. Timely use of this sorbent in case of emergency spills of oil and its derivatives can minimise hazardous effects on the human environment.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References


Fig. 7. The interaction of petroleum with a granular sorbent, thermally activated at a temperature of 1000 °C
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Information about the authors
Yurii S. Peregudov, PhD in Chemistry, Associate Professor at the Department of Inorganic Chemistry and Chemical Technology, Voronezh State University of Engineering Technologies, Voronezh, Russian Federation; e-mail: inorganic_033@mail.ru. ORCID id: https://orcid.org/0000-0003-2129-3191.

Rami Mejri, Postgraduate Student at the Department of Inorganic Chemistry and Chemical Technology, Voronezh State University of Engineering Technologies, Voronezh, Russian Federation, e-mail: mezhr@inbox.ru. ORCID id: https://orcid.org/0000-0002-4165-687X.

Elena M. Gorbunova, PhD in Chemistry, Associate Professor at the Department of Inorganic Chemistry and Chemical Technology, Voronezh State University of Engineering Technologies, Voronezh, Russian Federation; e-mail: lobanova8686@gmail.com. ORCID id: https://orcid.org/0000-0002-3550-0115.

Sabukhi I. Niitaliev, DSc in Chemistry, Professor, Head of Department of Inorganic Chemistry and Chemical Technology, Voronezh State University of Engineering Technologies, Voronezh, Russian Federation; e-mail: sabukhi@gmail.com. ORCID id: https://orcid.org/0000-0002-3550-0115.

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