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Stanislav Hrynyshyn,
Zenovii Znak

STUDY OF LYOPHILIC PROPERTIES OF NATURAL CLINOPTILOLITE AS A SORBENT OF OIL AND OIL PRODUCTS

The object of research is natural clinoptilolite as a potential sorbent in the processes of water and soil purification from oil, petroleum products (A-95 gasoline, kerosene), industrial oil, benzene, toluene, hexane, water-gasoline emulsions, as well as water-organic condensate. It is known that this material has a high adsorption capacity for various organic media. Therefore, the lyophilic properties of different fractions of clinoptilolite in relation to the specified environments were investigated.

The lyophilic properties of clinoptilolite were studied using the lying drop method to measure the marginal wetting angle of different zeolite fractions using the specified media. The data obtained determined the suitability of clinoptilolite for cleaning soils and waters from these liquids.

The dependence of the wetting of clinoptilolite on the dispersion of clinoptilolite was established. All clinoptilolite fractions are characterized by high lyophilicity in all media except oil. The wettability of clinoptilolite with oil and the corresponding work of adhesion significantly depends on its dispersion. It was established that with an increase in the size of clinoptilolite particles from 0.1 to 2.5–3.0 mm, the work of adhesion increases from $13.5 \cdot 10^{-3}$ to $51.2 \cdot 10^{-3}$ J/m^2. The influence of the surface morphology of clinoptilolite may cause this. An increase in temperature in the clinoptilolite-oil system contributes to the wetting of small fractions of zeolite with oil.

The obtained experimental data show that natural clinoptilolite with a wide fractional composition can be used to purify natural and wastewater waters and soils from the indicated organic and water-organic environments. At the same time, only clinoptilolite fractions over 1 mm are suitable for oil sorption.

Keywords: *zeolite, clinoptilolite, oil, oil products, natural and wastewater treatment, lyophilic properties, marginal wetting angle.*

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1. Introduction

One of the most common pollutants that contaminate surface waters are oil and oil products. They most often enter reservoirs with wastewater from industrial enterprises for oil production and processing, as a result of accidents of wheeled and pipe transport [1]. After the beginning of the full-scale invasion of Russia, the problem of pollution of natural surface water bodies in the southern and eastern regions of Ukraine sharply worsened. This is a result of the destruction of military equipment in nearby areas, often directly within reservoirs, as well as the damage to utility infrastructure, oil refineries, oil product storage facilities, and pipeline transport systems.

Compounds of the arene and alkene series as components of oil and oil products have high bioresistance and are toxic to aquatic biota. They are also able to accumulate in water and aquatic biota. In addition, oil and oil products form thin films on the surface of water bodies, which significantly impair gas exchange between the water and air environments. As a result, there is a lack of oxygen in the water, and therefore anaerobic conditions begin to prevail. As a result, compounds such as sulfates, nitrates, and phosphates that enter the water environment with fertilizers are transformed into highly toxic ones, such as hydrogen sulfide, ammonia, and phosphine. Oxygen deficiency and the accumulation of these compounds have a negative effect on natural aquatic ecosystems, in particular, on fish diseases. In addition, the quality of water used in industry and the communal economy is deteriorating sharply. In particular, aromatic compounds, such as benzene and its homologues, harm the immune system and cause cancer. Alkenes have a general toxic and mutagenic effect.

Spills of oil and oil products on industrial sites, on the territories of motor vehicle enterprises and military units, etc., can become sources of ignition and spread of fires.

Therefore, addressing oil spills and cleaning natural waters of oil is becoming increasingly urgent.

Among the various methods of cleaning hard surfaces and water, adsorption is the most appropriate. As a rule, they do not cause secondary pollution. Materials of various origins are used as sorbents. Sorbents based on natural raw materials have the lowest cost. These include, in particular, sunflower husks [2], alumino-silicates (clays, perlite, kaolinite, zeolites [3–5]), activated carbon, cotton, etc. Synthetic materials include materials based on polymers, for example, polystyrene foam, polyimide, and polyurethane foam. Their cost is significantly higher than natural ones. Therefore, to increase technical and economic indicators of cleaning processes, these sorbents are preliminarily hydrophobized [6]. This approach enhances the sorption capacity of hydrophobized sorbents by 30 to 90 times. Additionally, synthetic sorbents can be regenerated, enabling their long-term use in cyclic processes [7–11]. Consequently, they are well-suited as filter materials. However, their application is not economically viable for addressing oil spills, cleaning soils, or purifying natural water bodies.

Using waste from other industries as sorbents, such as pyrocarbon, is economically appealing. Pyrocarbon is produced through the pyrolysis of worn car tires or polymer-based products [12]. Research has shown that pyrocarbon is hydrophobic, making it selective as a sorbent for oil and oil products. However, this property renders it unsuitable for cleaning aqueous emulsions of oil products [13]. Furthermore, its low density and mechanical strength pose challenges for its use in cleaning soils or natural water bodies, as its particles are easily dispersed by wind.

Therefore, the use of natural clinoptilolite as a potential sorbent for oil and oil products, significant deposits of which are concentrated in the Sokyrnytsky deposit (Transcarpathian region, Ukraine), is of interest.

The suitability of clinoptilolite of different fractions for the sorption of oil and oil products can be determined by its lyophilicity. The main feature of lyophilicity is the marginal wetting angle (θ), which depends on the surface tension of the phases. Depending on the value of θ, three types of wetting are distinguished [14, 15]: complete wetting ($\theta \to 0°$, the liquid spreads over the surface); wetting ($0° < \theta < 90°$), non-wetting ($90° < \theta < 180°$).

Among the simplest yet sufficiently accurate techniques for determining the marginal wetting angle are direct methods, such as photographing the droplet profile. These methods include direct measurement of the contact angle of a liquid droplet on the surface of a solid using optical systems and angular scales (e. g., photographing the droplet profile or projecting it onto a screen).

The aim of this research was to investigate the lyophilic properties of clinoptilolite as a potential sorbent for oil and oil products, depending on its dispersion. This research seeks to enable the use of clinoptilolite, an inexpensive natural sorbent, for cleaning natural and wastewater as well as soils contaminated with oil and various organic or water-organic substances.

2. Materials and Methods

Determination of the marginal angle of wetting was carried out by a direct method – the lying drop method with photofixation of its profile.

The research used natural clinoptilolite of the following fractional composition, mm: <0.1; 0.1–0.25; 0.25–0.5; 0.5–1.0; 1.0–1.5; 1.5–2.0; 2.0–2.5; 2.5–3.0; as well as pieces of zeolite with flat surfaces, which were obtained by grinding some pieces with others, with dimensions of 5 mm and more. Zeolite fractions were obtained by sieving using a standard set of sieves of pre-crushed clinoptilolite. The use of these fractions of clinoptilolite is due to their use in various processes: sorption of oil and oil products from hard flat surfaces (asphalt, concrete), and soils, as well as water purification using filter loading or the method of applying dispersed zeolite to the surface of a reservoir. In addition, it is known that the sorption capacity of many materials depends on their dispersion.

Crude oil from the Boryslavsky field, gasoline A-95 were used in the research; benzene and hexane as typical components of gasoline, industrial oil, tap water, emulsions of oil, gasoline, and kerosene in water, as well as water-organic condensate formed during tire pyrolysis. Stable emulsions were obtained by processing a mixture of water and petroleum products (oil, kerosene, gasoline A-95) using an ultrasonic emitter "Ultrasonic Disintegrator" UD-20 (Poland); frequency – 20 kHz, radiation power – 11.2 W. The maximum content of gasoline at which the emulsion was stable for 2 hours was equal to 17±2 % by volume.

Determination of the value of the edge angle in the systems "clinoptilolite – oil, oil products, water, aqueous emulsions of oil and oil products" makes it possible to establish the suitability of this zeolite for cleaning water environments and soils from the specified liquids.

Determination of the value of θ in the indicated systems was carried out under isothermal conditions. Before the research, the specified liquids and clinoptilolite of different dispersions, as well as the tips of the "Variable Volume Pipette" dispenser, were kept at the specified temperature in the TS-80M-2 thermostat (Ukraine). After thermostating with the help of a dispenser, drops of liquids were applied to clinoptilolite. Research in isothermal conditions at a temperature of 20–40 °C was carried out in a TS-80M-2 thermostat, and for research in the range of 5–15 °C a thermostated chamber was used, in which the coolant was supplied with a given temperature from a water ultra-thermostat UTU-4 (Germany).

The image of the profile of the drops or their plan view was obtained by photographing. Further, the photographic images were processed using the capabilities of the Microsoft 365 software complex. The value of the marginal wetting angle was determined by the tangent method, analyzing at least two photographic images for each of the studied systems.

3. Results and Discussion

It was established that the behavior of oil on the surface of clinoptilolite of different dispersions is significantly different from the behavior of oil products and water emulsions. The behavior of organic substances on the surface of pyrocarbon of different fractions is significantly different. In particular, drops of gasoline A-95, benzene, and hexane, industrial oil, tap water, emulsions of oil, gasoline, and kerosene in water, as well as water-organic condensate formed during tire pyrolysis, spread over the surface of clinoptilolite regardless of its dispersion and at the same time they absorbed on it. That is, the marginal wetting angle was practically equal to 180°. However, these processes took place at different speeds. For example, gasoline A-95, benzene, toluene, hexane, and water spread over the surface and were simultaneously absorbed by it (Fig. 1). Therefore, a clear image of the drop on the surface of the clinoptilolite was not obtained. Industrial oil and kerosene are sorbed by clinoptilolite more slowly, so the corresponding replicas have time to form on the surface (Fig. 2).

The blurred edges of the "drops" indicate the absorption of oil and kerosene.

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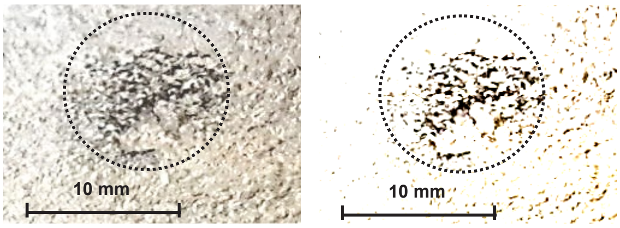
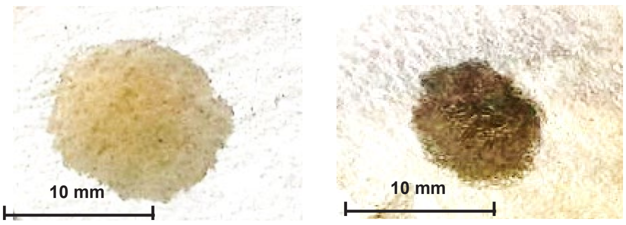


a *b*

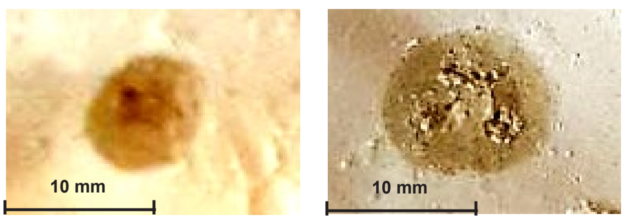
Fig. 1. Photo of the trace of a drop of gasoline A-95 on the flat surface of clinoptilolite ~1 s after application: *a* – original image; *b* – processed



a *b*

Fig. 2. Photo of the trail of drops: *a* – industrial oil; *b* – kerosene on the flat surface of clinoptilolite ~3 s after application

In the case of using highly dispersed clinoptilolite (fraction – 100 μm), the sorption of oil products occurs more slowly, although complete wetting of the zeolite takes place (Fig. 3).



a *b*

Fig. 3. Photo of traces of: *a* – kerosene; *b* – toluene droplets on the surface of clinoptilolite (fraction – 100 μm) ~3 s after application

Water completely wets the surface of clinoptilolite and is very quickly absorbed at any dispersion. Aqueous-organic systems (15 % emulsion of gasoline A-95, kerosene, benzene, as well as aqueous-organic condensate from tire pyrolysis) are absorbed more slowly. For emulsions of A-95 gasoline and kerosene, the value of the marginal wetting angle is about 170° (Fig. 4, *a*). In addition, there is a breakdown of the emulsion in the peripheral regions of the drop, as a result of which the contour of the drop is created by water, which is quickly sorbed. For about 10 s the emulsion drop is almost completely absorbed by clinoptilolite. Water-organic condensate of tire pyrolysis completely wets the surface of clinoptilolite (Fig. 4, *b*). This is due to the fact that it contains polar organic compounds that form stable systems with water. Therefore, organic compounds and water are sorbed simultaneously.

a *b*

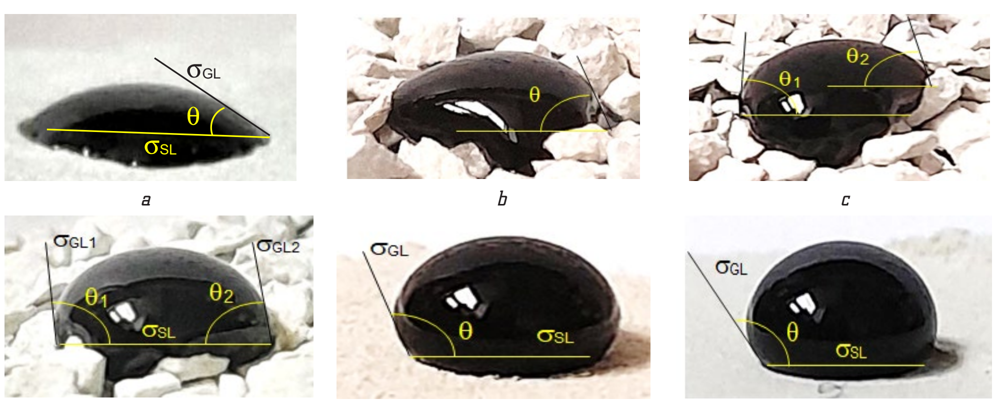
Fig 4. Photo of the trail of drops: *a* – aqueous emulsion of gasoline A-95; *b* – water-organic condensate of tire pyrolysis on the flat surface of clinoptilolite ~3 s after application

Similar results regarding the wetting of clinoptilolite with petroleum products and water-organic emulsions were obtained for all zeolite fractions. Therefore, based on the conducted research, it can be stated that clinoptilolite is characterized by high lyophilicity in relation to the indicated environments and water. At the same time, it should be noted that this mineral does not have selectivity of action with respect to the specified organic compounds in the presence of water.

It was established that the lyophilic properties of clinoptilolite in relation to crude oil depend significantly on its dispersion. Thus, oil drops wet the flat surface well, that is, if the area of the projection of the drop is not less than the area of the zeolite surface (Fig. 5). The marginal angle of wetting is 33–35°, and after 3–5 s even the spreading of drops is observed.

In the case of using crushed clinoptilolite, the value of the marginal wetting angle increases with an increase in the dispersion of the zeolite. So, for clinoptilolite fractions (mm) 2.0–2.5; 1.5–2.0; 1.0–1.5; 0.25–0.5; 0.1–0.25; 0.063–0.1 the value of the edge angle is respectively equal to 65°, 71–87° (average value 79°), 78–98° (average value 88°), 112°, 117°, 127°.

Based on the analysis of the dependence of the limiting angle of wetting on the fractional composition (Fig. 6) or the equivalent diameter of clinoptilolite particles (Fig. 7), obtained by us, it was concluded that for the removal of oil from the surface of water or soil it is necessary to use clinoptilolite with a fraction of more than 1 mm, and the optimal dispersion is about 3 mm.



a *b* *c* *d* *e* *f*

Fig 5. Photo of the side projection of crude oil drops on clinoptilolite particles: *a* – flat surface (>5 mm, the area of spreading is marked with a circle); zeolite fractions, mm: *b* – 2.0–2.5; *c* – 1.5–2.0; *d* – 1.0–1.5; *e* – 0.25–0.5; *f* – 0.063–0.1

The equilibrium work of adhesion (W_a) of oil on the surface of clinoptilolite was calculated based on the value of the marginal wetting angle using the Dupre-Young equation:

$$W_a=\sigma_{LG}(1+\cos\theta),$$

where σ_{LG} – the value of surface tension of oil at the liquid-gas (air) interface, J/m^2 (σ_{LG}=0.028 J/m^2); θ – the value of the marginal wetting angle, deg.

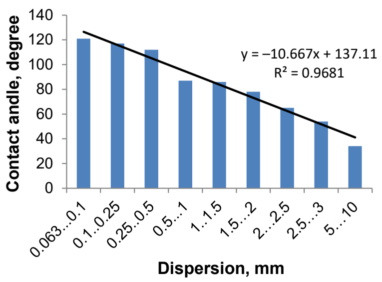


Fig. 6. Dependence of the marginal wetting angle value for oil on the fractional composition of clinoptilolite

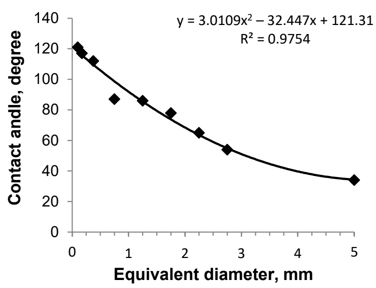


Fig. 7. Dependence of the value of the marginal wetting angle for oil on the equivalent diameter of clinoptilolite particles

For the clinoptilolite-oil system, the equilibrium work of adhesion for zeolite with a dispersion of <0.1; 0.1–0.25; 0.25–0.5; 0.5–1.0; 1.0–1.5; 1.5–2.0; 2.0–2.5; 2.5–3.0 and of a flat surface at a temperature of 20 °C, respectively, is equal to (W_a·10^3, J/m^2) 13.5; 15.2; 17.5; 29.4; 29.9; 33.8; 39.8; 44.4 and 51.2.

By differentiating the dependence of the work of adhesion on the equivalent diameter of clinoptilolite particles (Fig. 8), it was established that the optimal dispersion of clinoptilolite for oil removal is 2.5 mm, at which the value of the work of adhesion is about 40·10^3 J/m^2.

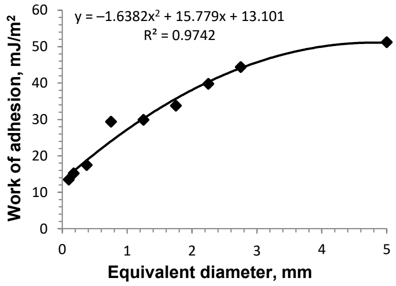


Fig. 8. Dependence of oil adhesion work on the equivalent diameter of clinoptilolite particles

A decrease in temperature to 5 °C practically does not affect the wettability of clinoptilolite with A-95 gasoline; benzene, hexane, toluene, industrial oil, water, aqueous emulsions of gasoline, and kerosene, as well as water-organic condensate. Therefore, the study of the wettability of the specified liquids at a higher temperature was not carried out.

With a decrease in temperature from 20 to 5 °C, wetting of clinoptilolite with oil worsens. Thus, for the 1.5–2.0 mm fraction, the value of the edge angle increases from 78° to 102°, that is, these particles are practically not wetted by oil. As the temperature increases from 20 to 40 °C, the particles of the fraction 0.25–0.5 mm become lyophilic in relation to oil: the value of the marginal wetting angle decreases from 112° to 76°.

Limitation of the study: In order to implement the research results in practice, it is necessary to develop a technology for obtaining granular materials using the obtained powder-like adsorbents, which will significantly increase their manufacturability. But, at the same time, on the one hand, the separation of the spent adsorbent from the solution is significantly simplified, and on the other hand, the adsorption capacity of the granules decreases due to the reduction of the specific surface area.

Impact of martial law conditions: The study was also influenced by the conditions of martial law in Ukraine, namely: due to power outages, the operation of the thermostat and ultrasonic emitter may be suspended. In the absence of an uninterrupted power supply, the experiment may be interrupted.

Prospects for further research: In further research, it is necessary to focus attention on improving the structural and sorption characteristics of granular materials and the selectivity of the obtained adsorbents. In addition, it is important to investigate the features of removing heavy metal ions from real industrial wastewater, which contains a complex mixture of pollutants, and to study the possibility of regenerating the spent material for its reuse.

4. Conclusions

The study shows that all fractions of clinoptilolite used in research are characterized by high lyophilicity with respect to polar and non-polar liquids (gasoline A-95, kerosene, industrial oil, benzene, toluene, hexane, water, and water-gasoline emulsions, as well as water-organic condensate), except for crude oil. Almost complete wetting of the clinoptilolite surface is characteristic of all these liquid-phase environments, regardless of its dispersion.

The lyophilicity of water and organic media, except for oil, is practically the same, so clinoptilolite does not have sorption selectivity.

Based on the data on the wettability of clinoptilolite with oil, the work of oil adhesion was calculated depending on its fractional composition; for fractions (mm) <0.1; 0.1–0.25; 0.25–0.5; 0.5–1.0; 1.0–1.5; 1.5–2.0; 2.0–2.5; 2.5–3.0 and for a flat surface at a temperature of 20 °C, it is correspondingly equal to (W_a·10^3, J/m^2) 13.5; 15.2; 17.5; 29.4; 29.9; 33.8; 39.8; 44.4 and 51.2.

As the temperature increases from 20 to 40 °C, the lyophilicity of smaller fractions increases. For example, for the fraction of 0.25–0.5 mm, the value of the marginal angle of wetting decreases from 112° to 76°, that is, they acquire the ability to get wet, and therefore, absorb oil.

Based on the obtained results, it is possible to recommend the use of natural clinoptilolite, in particular, with particle sizes over 1 mm, for cleaning natural and wastewater from oil and oil products.

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Conflict of interest

The authors declare that they have no conflict of interest in relation to this study, including financial, personal, authorship, or any other, that could affect the study and its results presented in this article.

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Data availability

The manuscript has no associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating this work.

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✉***Zenovii Znak,*** *Doctor of Technical Sciences, Professor, Department of Chemistry and Technology of Inorganic Substances, Lviv Polytechnic National University, Lviv, Ukraine, ORCID: https://orcid.org/0000-0002-3871-4063, e-mail: zenovii.o.znak@lpnu.ua*

Stanislav Hrynyshyn, *PhD Student, Department of Chemistry and Technology of Inorganic Substances, Lviv Polytechnic National University, Lviv, Ukraine, ORCID: https://orcid.org/0009-0007-8645-2532*

✉*Corresponding author*