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FUNDAMENTALS OF OIL SPILL CLEAN-UP TECHNOLOGY USING NATURAL CLINOPTYLOLITE

ОСНОВИ ТЕХНОЛОГІЇ ЛІКВІДАЦІЇ РОЗЛИВІВ НАФТИ ЗА ДОПОМОГОЮ ПРИРОДНОГО КЛИНОПТИЛОЛІТУ

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Abstract*. The paper examines the ability of natural clinoptilolite to sorb oil in the event of its spill on solid surfaces. It is shown that oil sorption begins, in most cases, immediately after contact with clinoptilolite particles. The regularities of oil sorption by different fractions of natural clinoptilolite are established, in particular, the dependence of the mass of sorbed oil and the sorption capacity of zeolite on time. The effect of selective sorption of different fractions of oil during the process is revealed. If the height of the clinoptilolite layer is significant, then the value of the dynamic capacity of clinoptilolite decreases due to an increase in the height of the working layer of zeolite.*

Keywords: *clinoptilolite, sorbent, sorption, sorption capacity, oil, petroleum products, surface cleaning, soil cleaning.*

Oil is one of the most dangerous environmental pollutants, as it contains many individual substances that are characterized by high toxicity. These include, in particular, aromatic compounds. During extraction, transportation and storage, there are many cases of oil entering the environment [1]. The problem of environmental pollution by oil has become acute after the full-scale aggression of russia, when many infrastructure elements of the oil production and oil refining industries were damaged and destroyed. Previous studies have shown that natural clinoptilolite from the Sokyrnytsia deposit (Transcarpathian region, Ukraine) is inherently lyophilic with respect to oil [2]. The influence of the fractional composition on the lyophilic characteristics, for example, limited wettability of small clinoptilolite fractions, was due to a spatial factor, namely, the placement of an oil droplet on a surface formed by clinoptilolite particles of a certain fraction. However, in the end, almost all zeolite fractions showed good oil wettability. This formed the basis for studying the regularities of oil sorption by natural clinoptilolite. Taking into account the technological features of using clinoptilolite as a potential sorbent and the technical and economic indicators of the oil purification process, the zeolite was not pre-enriched.

The study was conducted using a setup in which zeolite of different fractions was placed in glass tubes (for visual observation of oil movement through a clinoptilolite layer (Figure 1). The height of the sorbent layer was 150±3 mm.

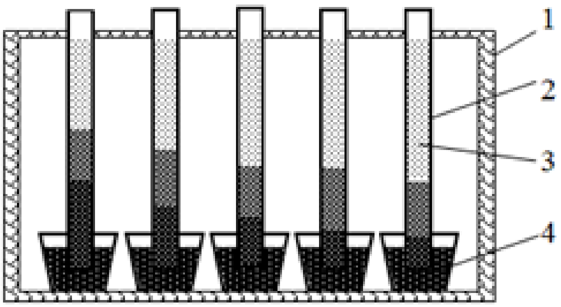

Figure 1 – Diagram of a laboratory setup for oil sorption studies

1 *– cartridge;* ***2*** *– oil tanks;* ***3*** *– tripod*

Cartridges (2) were simultaneously immersed in tanks (4) with oil from the Boryslav field (Lviv region). Periodically, the cartridges were photographed to determine the height of oil rise in each of them. Also, the cartridges were periodically removed from the oil and, after removing it from the cartridge surface, weighed to determine the mass of sorbed oil. Almost immediately, the oil moved up the zeolite layer in all cartridges. That is, oil sorption began immediately. In this case, there was no induction period of sorption in the case of fractions with high dispersion, which could be expected after studying the lyophilicity of clinoptilolite of different fractions [3]. In particular, it was found that oil sorption is preceded by an induction period. However, in these studies, the spatial arrangement of zeolite-oil was diametrically opposite. In addition, the mass of the clinoptilolite layer was about 17 g. This provided a certain pressure on the oil layer, which contributed to the manifestation of capillary phenomena and, as a result, its sorption with clinoptilolite.

The sorption capacity of clinoptilolite was calculated using the formula

$$SC = \frac{m_{oil}}{m_{klin}} = \frac{m_{oil}}{\frac{\pi}{4} \cdot d^2 \cdot h \cdot \rho},$$

where m_{oil} – the mass of sorbed oil, g; m_{klin} – the mass of clinoptilolite in the colored layer, g; d – the diameter of the cartridge, cm; h – the height of the colored clinoptilolite layer, cm; ρ – the average bulk density of clinoptilolite of a certain fraction, g/cm^3.

The oil sorption front moved upwards, as evidenced by the color of clinoptilolite particles (Figure 2).

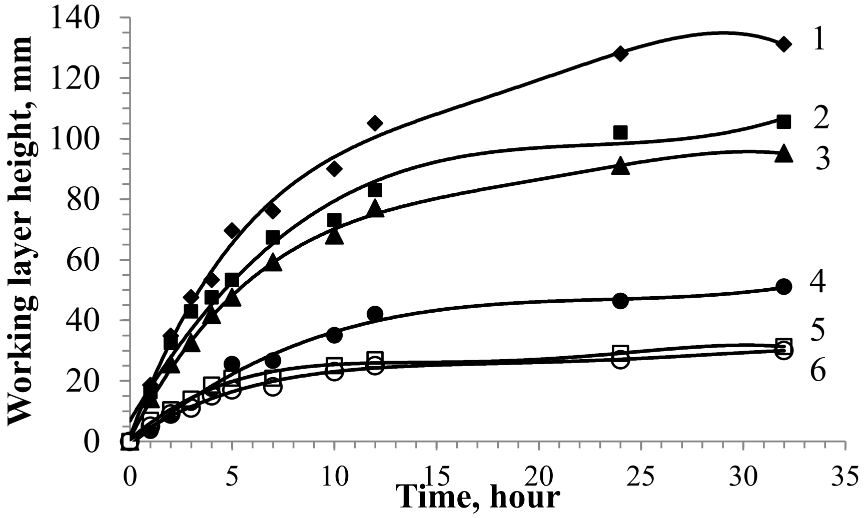

Figure 2 – Dependence of the length of the working zeolite layer on time for fractions, mm: ***1*** *– 0.1…0.25;* ***2*** *– 0.25…0.5;* ***3*** *– 0.5…1.0;* ***4*** *– 1.0…1.5;* ***5*** *– 1.5…2.0;* ***6*** *– 2.0…3.0.*

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There was no clear boundary of the sorption front, especially for fractions over 1.5 mm. This is due to the inhomogeneity of the particle surface, their shape, the presence of impurities, etc. As can be seen, approximately the same speed of movement of the adsorption front is observed during the first 5…8 hours. At the same time, it was noted that for fractions of 0.125-0.25 and 0.25-0.5 mm, a different color of the working layer is visually observed after 5…6 hours of the process. The lower layer has a dark color, like oil, and a layer of much lighter color was formed above it. This phenomenon is due to the fact that oil is a polyfractional substance, which consists of components with different molecular weights and which belong to different classes of organic compounds (saturated, unsaturated, aromatic, etc.). The formation of a lighter layer is caused by the sorption of low-molecular-weight oil components.

The more intensive movement of oil components in the layer of a more dispersed sorbent is explained by the larger particle contact area. It is obvious that the oil sorption process is heterogeneous, therefore the phase contact area plays a significant role in this process. However, a clear dependence of the length of the working layer on the dispersion of clinoptilolite particles was not found. For example, Figure 3 shows the dependence of the length of the working layer of clinoptilolite of different fractions (average size) for several time intervals.

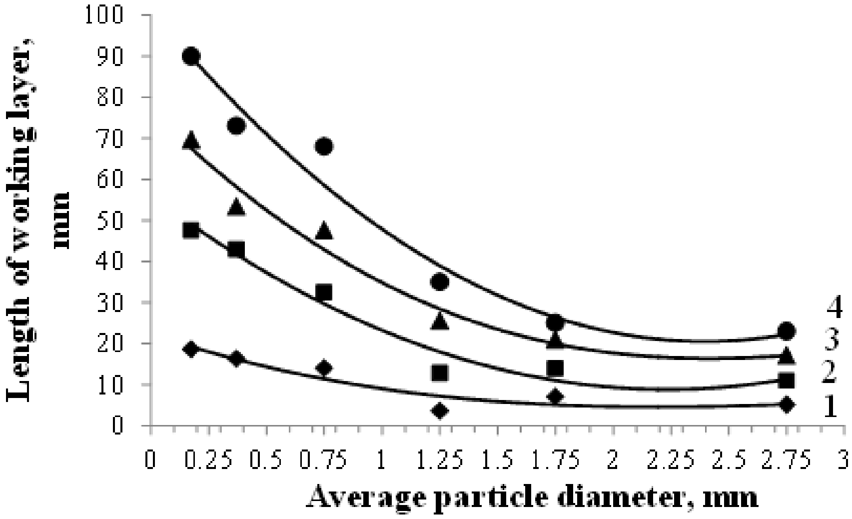

Figure 3 – Dependence of the length of the working layer of zeolite on the average diameter of the fractions, h: ***1** –1; **2** – 3; **3** – 5; **4** – 10*

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During the first hour, visually, sorption occurs almost the same for different fractions of clinoptilolite. But later, a significant increase in the length of the working layer of zeolite for more dispersed fractions was observed. Taking into account the data obtained, fraction 2.0…3.0 was not used in further studies. At the same time, a very important indicator that characterizes the effectiveness of each sorbent, in particular for oil absorption, is the sorption capacity. It primarily depends on the total mass of sorbed oil.

As expected, the largest amount of oil was sorbed by clinoptilolite with the largest dispersion – 0.1…0.25 mm. It is obvious that in this case there is both a movement of the sorption front along the length of the layer and the sorption of oil due to its diffusion into the internal pores of the particles. Since the process is heterogeneous, a decrease in the average diameter of the particles contributes to the speed of diffusion processes.

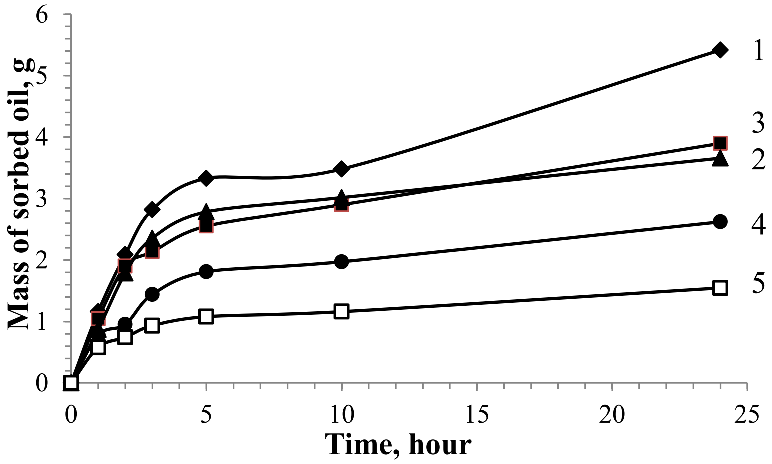

Figure 4 – Dependence of the mass of sorbed oil on time for fractions, mm:

1 *– 0.1…0.25;* ***2*** *– 0.25…0.5;* ***3*** *– 0.5…1.0;* ***4*** *– 1.0…1.5;* ***5*** *– 1.5…2.0*

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Based on the results obtained, the sorption capacity of different clinoptilolite fractions with respect to oil was calculated. However, it turned out that the sorption capacity, paradoxically at first glance, in all cases decreases over time (Table).

Table – Data from a study of the sorption capacity of natural clinoptilolite for oil

Time, hour	Sorption capacity value (g/g) for fraction (mm)				
	0.1…0.25	0.25…0.5	0.5…0.1	1.0…1.5	1.5…2.0
3	0.88	0.98	0.92	1.92	1.29
10	0.70	0.76	0.70	1.40	1.05
24	0.68	0.63	0.63	0.84	0.80

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Moreover, in the case of fractions with a larger average diameter, their sorption capacity becomes greater than for dispersed ones.

This result is explained by the fact that the sorption capacity was calculated relative to the length (volume) of the working layer. In the case of highly dispersed fractions, the length and, accordingly, the volume of the working layer are much larger. For example, for fraction 0.1…0.25, the length of the working layer is 6 times greater than for fractions and 1.5…2.0. At the same time, the mass of sorbed oil is ~5 times greater. At the same time, due to this, the integral sorption capacity of clinoptilolite with a dispersion of 1.0…1.5 and 1.5…2.0 mm is greater than that of highly dispersed ones: 0.80…0.84 versus 0.63…0.68, i.e. by 18…33%. Therefore, in the case of significant spills of oil or petroleum products, it is economically more expedient to use coarsely dispersed clinoptilolite, since its production requires less energy, it is easier to transport and scatter at the site of such spills.

Conclusions.

1. Data were obtained on the ability of natural clinoptilolite to effectively sorb oil, namely: the dependence of the mass of sorbed oil and the sorption capacity of clinoptilolite on the fractional composition was established. The sorption capacity is on average 0.63…0.84 (g of oil)/(g of zeolite).

2. Sorption of oil occurs almost immediately after its contact with clinoptilolite particles, and the greatest intensity of oil sorption occurs within 5…8 hours.

3. Clinoptilolite as a cheap natural sorbent of domestic mines can be used to eliminate spills of oil and petroleum products, since they are components of oil. Spent sorbent. First of all, highly dispersed, can be used as additives to the charge from which ceramic products are produced by high-temperature processes.

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Анотація. *У статті наведено результати досліджень сорбції нафти природним клиноптилолітом з метою створення основ технології ефективного і доцільного в економічному аспекті ліквідації розливів нафти і нафтопродуктів. Встановлено, що нафта починає швидко сорбуватись частинками клиноптилоліту різного ступеня дисперсності зразу після контакту з ними. При цьому формується фронт адсорбції, який рухається шаром сорбенту вгору (за умов досліду). Візуально можна спостерігати за його переміщенням за зміною забарвлення шару клиноптилоліту. У разі використання високо дисперсних фракцій цеоліту низькомолекулярні фракції нафти швидше переміщуються шаром клиноптилоліту. Завдяки цьому довжина працюючого шару приблизно у 6 разів більша, ніж для грубо дисперсного клиноптилоліту. При цьому маса поглинутої нафти дрібнодисперсних клиноптилолітом також більша – у ~5 разів. Водночас завдяки цьому інтегральна сорбційна ємність клиноптилоліту дисперсністю 1.0…1.5 і 1.5…2.0 мм більша, ніж високодисперсних: 0.80…0.84 проти 0.63…0.68, тобто на 18…33%.*

Ключові слова: *клиноптилоліт, сорбент, сорбція, сорбційна ємність, нафта, очищення ґрунтів, очищення твердих поверхонь.*