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Use of sorption minerals to remove petroleum substances from water

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ABSTRACT

Purification of water from petroleum compounds is a very complex process depending on many factors. De-oiling of water is a very complex process, which is affected by a number of factors: variety of oils, nature of the oil–water emulsion (mechanical or chemical), degree of dispersion, presence of other compounds such as surfactants or other emulsifiers and stabilizers in water. For this reason, there are no universal de-oiling systems that can be used in any case. One of the methods that deserves special attention is the use of porous materials, that is, sorbents, which are readily available, simple to use, cheap and, which is important, non-toxic to the environment. The most accessible materials are natural. The aim of the work was to demonstrate the effectiveness of sorption minerals during the process of removing petroleum from water and to assess the absorbance capacity of the minerals studied. The removal process in presented studies was carried out using two natural sorbents: pumice and clinoptylolite. The pumice used was obtained from crushed and sifted natural pumice, while clinoptylolite came from tuffs mined in Slovakia. The study was conducted on simulated water (distilled water with a mixture of diesel and gasoline). The research was carried out to determine the efficiency of removal of petroleum substances by static and dynamic methods applying sorbents: pumice, clinoptylolite, and a mixture of clinoptylolite with pumice. Absorptivity of a given sorbent was tested and the value of mineral oil index was determined using gas chromatography. The absorption capacity of minerals was investigated by weighing a given sorbent before and after the test. The most absorptive material turned out to be the pumice that absorbed most of the solution: 199.8% – which was almost twice as much sorbate than the weight of the sorbent. The weakest absorption characteristics were revealed by clinoptylolite with the highest value being 70.3%, whereas for the mixture of clinoptylolite with pumice, the value was moderate – 152.5%.

Keywords: Sorbents; Pumice; Clinoptylolite; Water; Petroleum substance

1. Introduction

The possibility of penetrating petroleum components into the groundwater as well as their presence in surface waters leads to the search for effective solutions to their disposal. It is important not only to remove them but also to the economics and safety of the solutions used. Due to the spillage of oil products into the water, it is important to react promptly and remove the substance immediately from a tank, especially if the water is taken to drinking by nearby residents or by water treatment stations [1].

Removal of petroleum contaminants from water is an extremely complex process, which is influenced by many factors: type of oils, properties of oil and water emulsion (chemical or mechanical), degree of dispersion, presence of other compounds in water (e.g., emulsifiers, stabilizers, surfactants) [8]. There are many different ways to remove toxic petroleum substances from water. One of such methods is sorption, or physical de-oiling, during which two processes occur in parallel: absorption of petroleum derivatives in the pores and voids of the sorbent and their adsorption on its surface [3,5]. The most commonly used sorbents for the removal

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of petroleum substances are porous materials. Sorbents are readily available, simple to use, cheap and environmentally friendly [5]. The most accessible materials are natural sorbents due to the lack of environmental toxicity and no costs associated with their production.

The aim of the study was to determine the effectiveness of two sorption minerals (pumice and clinoptylolite) for the removal of petroleum derivatives from water.

2. Materials and methods

Two sorption materials were used to remove crude oil from the model water: pumice and clinoptylolite. The study used clinoptylolite derived from tuffs extracted in Slovakia (around Košice) with granulation of 0.80–1.2 mm. It was characterized by the following parameters:

- specific surface area 21.0 m^2/g,
- total pore volume 0.073 cm^3/g,
- the average pore diameter is around 10.5 nm

The mineralogical composition of the clinoptylolite tuff used is given as follows: SiO_2 70%–72%, Al_2O_3 12%–13%, Fe_2O_3 1.5%–2.0%, MgO 0.3%–1.5%, K_2O 1.24%–4.5%, CaO 2%–11.7%, Na_2O 0.1%–3%.

The pumice powder used in the experiment is very light in weight, which makes it possible to float on the water. Because of the small size of the particle, the clinoptylolite is characterized by a large outer surface. Clinoptylolites are bi-porous substances. They are characterized by primary porosity, which is conditioned by the crystalline structure of their particles and the secondary porosity. Secondary pores are responsible for the absorption of relatively large particles and play a role in sorption and catalytic processes.

Another material used for the study was natural pumice. Manufactured from crushed and sifted natural pumice with the trade name Hydro-Filt, it had granulation of 1.5–2.5 mm and specific surface area of 4.12 m^2/g. The mineral contained SiO_2 – 73%, Na_2O – 15%, CaO – 7%, MgO – 4%, Al_2O_3 – 1%.

Water purification was performed on individual sorbents: clinoptylolite, pumice and a mixture of pumice with clinoptylolite. Pumice to tests was crushed into grains with a diameter of about 1 cm.

The study used model water called sorbate. Its base was distilled water enriched with a mixture of petroleum and diesel fuel in a ratio of 1:3. In order to uniformly disperse petroleum substances in water, they were subjected to sonication (ultrasonic treatment). The petroleum products tested were expressed as mineral oil index (IOM). In the research process, model water was used with three different IOM concentrations: 55, 68 and 73 mg/L.

Technological research was carried out by means of two methods: static and dynamic. The static method used 20 g sorbent sample for clinoptylolite and 3.98 g pumice. The assumed mass resulted from the specific surface area of sorbents. The sorbents were flooded with the test solution. Conducted adsorption kinetic studies provided information that the adsorptive equilibrium for both sorbents was set after about 50–70 min. In further studies, 60 min were taken as the optimal contact time. This is the limit, when only minimum reduction in IOM concentration occurred. After 60 min, the sample was filtered and weighed. The absorptivity of the sorbent was calculated from the formula [6]:

$$R = \frac{m_2 - m_1}{m_1} \cdot 100\% \qquad (1)$$

where R is the capability of oil sorption by mineral sorbent; m_1 is the sorbent sample weight; m_2 is the saturated sorbent weight.

In the dynamic method, three sorption columns with a diameter of 6.8 cm were used. One column was filled with pumice, the other with clinoptylolite, while in the third, pumice with clinoptylolite was mixed. In the last sorption column, pumice and clinoptylolite were scattered alternately at a volume ratio of clinoptylolite to pumice 1:5. The assumed ratio was due to the specific surface area of sorbents. Volumes of 500 mL of the model solution were filtered through a column filled with sorbent with a constant filter bed loading of 1.0551 $m^3/m^2 h$. The IOM value was determined in samples before and after filtration.

Determinations of individual samples were performed using a gas chromatograph coupled with mass spectrometer VARIAN 4000. The stationary phase of the column was a polydimethylsiloxane with 5% phenyl groups. The procedure for preparing the sample for analysis was divided into several stages: fixation, extraction, purification and concentration.

3. Results and discussion

Absorptivity of the investigated sorbents is shown in Fig. 1. The lowest absorption capacity of petroleum derivatives was observed for the clinoptylolite that absorbed 46.8%–70.3% of sorbate per gram of weight. On the other hand, the highest absorption was revealed by pumice, with the value of sorbate absorption capacity of almost 200%. Intermediate results characterized mixture of pumice and clinoptylolite, which ranged from 110% to 152.5%. When comparing the adsorption of pumice with the clinoptylolite, it absorbed 4.3 times more model water than the clinoptylolite and the worst case, it was 2.8 times more absorbed sorbate. It should be noted that the absorption capacity in this case concerned not only the petroleum substances themselves but also the water that has penetrated the pores. Chemical composition of the sorbents tested is similar and probably has no effect on the absorbance capacity. Their structure is completely different, which means that

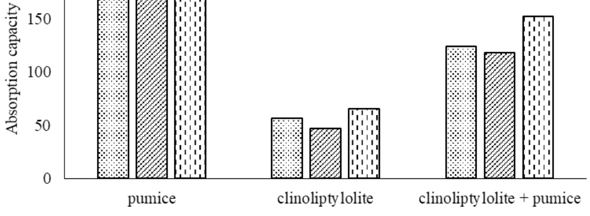

Fig. 1. Absorption capacity of sorbents (%).

their sorption abilities are significantly different. Pumice has open pores with relatively high capacity and absorbs water in macropores, while clinoptylolite is characterized by primary porosity, which is conditioned by the crystalline structure of particles and secondary porosity caused by the existence of different admixtures.

The results of the removal of petroleum substances on the pumice stone and the clinoptylolite from the model water in static method are shown in Fig. 2. The most effective sorbent for removing pollutant concentrations of 52 mg/L was pumice. For higher concentrations of 68 and 73 mg/L, the highest results were obtained for clinoptylolite and a mixture of clinoptylolite with pumice. In the static method, two sorbents (mixture of clinoptylolite and pumice) were distinguished: 84.6% and 82.1% (for 73 and 68 mg/L, respectively) and clinoptylolite: 84.4% and 84% (for 68 and 73 mg/L, respectively). Pumice was characterized by a balanced removal of IOM for all concentrations and did not exceed 80%.

Pumice was characterized by relatively small fluctuations in petroleum removal at all concentrations in dynamic method (Fig. 3) at 1.1 m/h rate, for which the percentage difference between the highest and the lowest removal rates was 8.9%, while for clinoptylolite 18.2% and for a mixture of clinoptylolite with pumice, up to 29%. It was noted that higher concentrations of petroleum derivatives were best removed on the mixture of clinoptylolite with pumice, while slightly worse on the clinoptylolite and the lowest on pumice. In the dynamic method, using clinoptylolite with pumice, the efficiency of contamination reduction exceeded 86% at a concentration of 68 mg/dm^3, while for the concentration of 73 mg/dm^3 the effects were lower and amounted to about 76%. Probably, in addition to the adsorption process, the coalescence process has also occurred on the filtration beds, which has influenced on the course of petroleum contaminants removal. This is sometimes indicated by one-time, much higher IOM values in the leakage. In addition, a thin layer of oil was observed at the top of the filter, which was removed after filtration. This layer was formed from emulsified molecules of petroleum substances that in contact with the surface of the adsorbent were subject to coalescence [3,4,7]. Theoretically, this phenomenon could be prevented by forcing the flow of water from the bottom up, but such a solution would cause crumbling of filtration media.

Based on the research, it was found that pumice is more effective in removing impurities in a static than dynamic method. Similar efficacy was observed for clinoptylolite, but only for concentrations of 68 and 73 mg/dm^3. In the remaining samples, the dynamic method proved to be more effective for clinoptylolite at a concentration of 52 mg/dm^3 and for a mixture of clinoptylolite and pumice at a concentration of 68 mg/dm^3.

Clinoptylolite has been found to be a better adsorption material, which has less absorptive capacity than pumice stone. Slightly better sorption of petroleum derivatives on clinoptylolite may have been caused by the occurrence, in addition to typical physical adsorption, by specific interactions (related to the crystalline internal structure of clinoptylolites), and secondary pores that are responsible for absorbing relatively large particles. The adsorption process took a place on the surface inside the mesopores and macropores for the clinoptylolite and pumice. The absorption process due to the nature of the adsorbents used (small number of micropores) was only slightly changed by clinoptylolite. Pumice has smaller specific surface and large open pores that affect the lower effect of removing the impurities. Emulgated oil substances, characterized by large molecules, may however, partially block and plug the access to the active sites of the sorbent, thereby reducing its sorption capacity. Despite the existence of the above restrictions, natural sorbents are a very effective weapon in the fight against pollution due to oil substances and are increasingly used. Work is continuing to optimize their use [2,3,8,9].

The positive aspect is that it is a natural product that does not need to be treated (possibly fragmented), as opposed to artificial materials [8–10]. It should also be noted that the pumice absorbed much more solution than the other sorbents and yet the difference between the petroleum removal was insignificant. The amount of adsorption probably depends on the degree of moisture content in the adsorbent, with the higher the degree of humidity, the smaller the adsorption. Only at a concentration of 52 mg/L, a slight advantage of pumice was observed over the remaining sorption materials, which may indicate a better ability to remove the lower concentrations of impurities. It was also found that sorption of the petroleum derivatives using pumice in the dynamic method was weaker than applying other sorbents. It was also noted

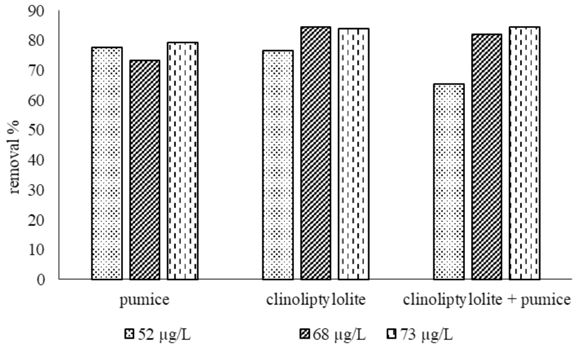

Fig. 2. Degree of removal (%) of different oil concentrations in static method for pumice, clinoptylolite and mixture of clinoptylolite with pumice.

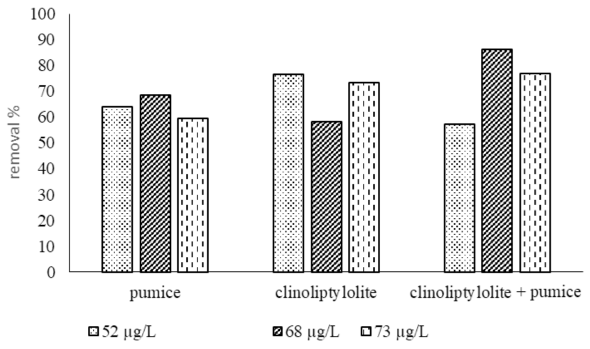

Fig. 3. Degree of removal (%) of different oil concentrations in dynamic method for pumice, clinoptylolite, and mixture of clinoptylolite with pumice.

that the clinoptylolite sorbent and the mixture of clinoptylolite with pumice had better physicochemical conditions to remove the oil compounds [10–13]. This can be a result of the size of the clinoptylolite molecules, thus the oil particles had a larger contact area with the sorbent grains, and therefore their sorption on the material has increased. Of course, the matter of determining the exact parameters, mixing ratio, location of the use of minerals in the purification process, as well as combination of sorption with other methods of pollution removal, remains an open question. Nevertheless, it should be noted that clinoptylolite and pumice, due to their sorption properties, remain one of the most prospective minerals when it comes to removing the oil contaminants.

4. Conclusions

The research has shown that the purification of water from petroleum contaminants is possible and the effectiveness of this method is high. Textural properties of the tested sorbents may be of key importance for the phenomenon of petroleum sorption, which will be determined in further studies.

The obtained results allowed to draw the following conclusions:

(1) Removal of petroleum substances by clinoptylolite is effective in the static and dynamic method at the level of 74.5% effect.
(2) Mixing of clinoptylolite with pumice improves the effectiveness of oil-based substances removal in relation to pumice only by 5% in the static method and 23% in the dynamic method.
(3) The weakest sorbent was pumice, despite its highest absorbance capacity. Pre-purification should be carried out prior to the use of higher concentrations in the static method.
(4) The most effective method to remove low crude oil concentrations in the case of pumice was the static method from 73% to 79%.

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