Application of Natural Zeolites of the Khonguruu Deposit (Yakutia) for Purification of Oil-Containing Waste Water

ELENA A. GLAZKOVA, EUGENIA B. STREL'NIKOVA and VICTOR G. IVANOV

*Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences,
Pr. Akademicheskiy 3, Tomsk 634055 (Russia)*

E-mail: eagle@ipc.tsc.ru

Abstract

The problems concerning the application of natural zeolite of the Khonguruu deposit (Yakutia) to the sorption purification of oil-containing waste water are considered. Physicochemical and sorption properties of the zeolite are described. It is shown that khongurin can be used for the extraction of both molecularly dissolved and emulsified oil products. The curves of filtration of oil-containing water and results of the experimental tests of the natural sorbent are reported. The application of khongurin in water preparation processes and in waste water purification from oil products seems to be reasonable because of its large resources and low cost.

INTRODUCTION

The growth of industrial production is known to cause an increase in the amount of toxic emissions into the environment. Waste water containing oil and oil products accounts for a substantial part of these emissions. Annual amount of oil and oil products entering the oceans of the Earth with waste water is about 6 mln t [1], which causes death of phytoplankton and has destructive action on vital functions of living creatures. Because of this, one should prevent contamination of environment when launching industrial development of the promising territories, especially such ones as East Siberia and Far East.

Oil and oil products can be present in the aqueous medium both as large-size inclusions (drops and surface films) and also in emulsified or dissolved state. The large-size inclusions can relatively easily be removed from water by mechanical methods, while the destruction of microemulsions and especially extraction of water-soluble oil products is still rather complicated technical problem. Purification of waste water from oil impurities is usually carried out in several stages. At the first stage, waste water is subjected to primary purification: settling, filtration through mechanical filters, coagulation, floatation, *etc*. Fine purification includes adsorption, membrane filtering, *etc*.

Adsorption purification is a universal method allowing almost complete extraction of impurities from an aqueous medium; it is efficient over the whole range of concentrations of oil impurities. However, the advantages of this method in comparison with other purification procedures are exhibited in the case of low concentrations of pollutants. Because of this, adsorption processes are often used in the technology of drinking water preparation and in the additional purification of waste water [2, 3].

The use of adsorption technologies is one of the basic means to improve the efficiency of waste disposal plants of various industrial enterprises, including the plants of oil production, transportation and petroleum refining. Various filtering materials are used to purify water from oil and oil products: quartz sand, polymeric and mineral fibrous materials, Circulite, schungite, clayish minerals, activated carbon, *etc*. [2, 4, 5]. Local natural adsorbents are often preferred due to their relatively low cost and availability.

For instance, it seems reasonable for intensively developing regions of East Siberia, and in particular for Yakutia, to develop local sources of natural raw material for the production of adsorbents. Zeolites mined in Yakutia are natural mineral sorbents able to extract hydrocarbons from aqueous media.

The goal of the present work is to investigate the possibility to apply natural zeolites from the Khonguruu deposit (khongurin) and to estimate their efficiency for purification of water from dissolved and emulsified hydrocarbons of oil coming from the Talakan deposit (Yakutia) which is under intense development at present.

EXPERIMENTAL

In order to make a sorbent, the samples of natural zeolite were crushed; a fraction of 0.5–2.5 mm was separated. The resulting zeolite fraction was washed with distilled water and dried at first at room temperature, then at 100 $^{\circ}$C for 2 h. Activation of the zeolite was carried out by calculation of the fractionated sample at the temperature of 350 $^{\circ}$C for 2 h.

Sorption properties of zeolites were investigated under static and dynamic conditions. The solutions of oil products of the petrol and diesel fractions of the Talakan oil and water-oil emulsion were used as model compositions.

The initial oil of the Talakan deposit was separated into the petrol and diesel fractions with an ARN-2 set-up. The model solutions in water were prepared by periodic mixing and settlement of a mixture of distilled water with the Talakan oil or oil fractions for 15 days at room temperature. The concentration of the dissolved oil products was determined by means of IR spectrophotometry using the Specord M80 instrument [6].

An oil-water emulsion was prepared by mechanical dispersion of oil in water with a high-frequency mixer (2500 rpm) for 10 min. The concentration of emulsified oil products was determined by means of photocolorimetry using Sudan III dye and FEK-60 photocolorimeter [7].

In order to achieve the required final concentration of oil products in water, purifica-
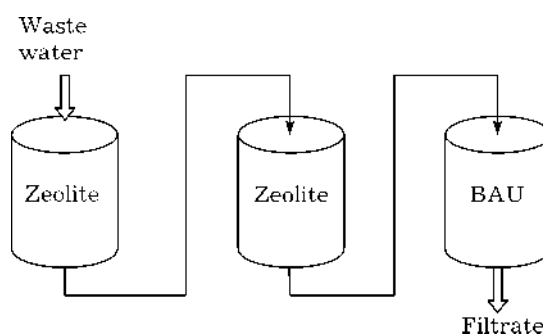

Fig. 1. Schematic technological flowchart of purification of the oil-containing waste water.

tion process was carried out in several stages. The natural and activated zeolite was used in a three-stage process of water purification from the dissolved hydrocarbons (Fig. 1). The set-up included three adsorbers. Water polluted with oil products was filtered by passing sequentially through the first and the second adsorber filled with the zeolite sorbent (20 g of zeolite per each of them). Additional purification of water was performed with activated carbon of BAU grade by passing oil-containing water through the third adsorber. In the first flowchart, natural zeolite was used as a sorbent; in the second, activated one was used. Experimental conditions and analysis procedures were identical in both cases.

RESULTS AND DISCUSSION

Khongurin belongs to heulandite-clinoptilolite zeolites which are natural microporous sorbents. The existence of two types of channels is characteristic of this kind of zeolites; the windows of these channels are built of 8-membered rings (with a diameter within 0.49–0.55 nm) and 10-membered ones (with a diameter within 0.44–0.72 nm). The limiting volume of micropores in khongurin with respect to water and methanol is equal to 0.09 and 0.10 cm^3/g, respectively. The density of zeolites from the Khonguruu deposit is within 2.41–2.43 for different layers, and porosity is 30–31 % [8].

The sorption properties of zeolites are determined by the unique lattice characterized by the developed inner surface and strictly definite size of the inlet windows. Zeolites are

a kind of molecular sieves able to sorb molecules of definite size from mixtures. Only the molecules with critical size below the inlet window can enter the adsorption cavity. Critical diameters of the molecules of some hydrocarbons are listed in Table 1 [8].

The results of sorption of the dissolved hydrocarbons on natural zeolites under static conditions are shown in Fig. 2. It is shown that the equilibrium is achieved within 7 days of contact between khongurin and water containing 5.9 mg/l of dissolved hydrocarbons at the ratio of 1 : 10. The maximal sorption of the hydrocarbons of the Talakan oil on natural zeolite is $12 \cdot 10^{-3}$ mg/g of the sorbent. Water purification degree reaches 25 %.

Extraction of the dissolved and emulsified hydrocarbons under dynamic conditions on the initial zeolite are shown in Figs. 3, 4. Water-oil emulsion was fed at the linear rate of 3 m/h. The concentration of oil products was 32 mg/l. According to the data shown in Fig. 3, a, maximal degree of water purification during filtering of the diluted emulsion reached 50 % with passing 150 column volumes (3 l).

With an increase in the concentration of oil emulsion to 115 mg/l, the maximal degree of water purification does not exceed 20 % after passing 250 column volumes (5 l) of the emulsion (see Fig. 3, b). However, independently of the initial concentration of emulsified oil products (see Fig. 3, a, b), the capacity of the initial
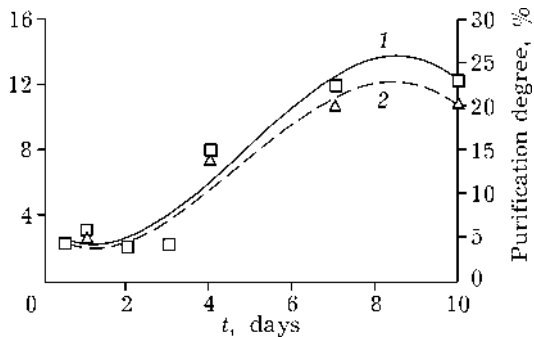

Fig. 2. Kinetic curves of sorption of dissolved hydrocarbons of the Talakan oil on natural zeolite under static conditions: 1 − adsorption, 2 − purification degree.

zeolite is 7−7.5 mg/g got emulsions with the initial concentration within 32−115 mg/l.

When extracting oil products from emulsions, a clearly exhibited initial period is observed, during which the «charging» of the filtering load occurs [4] due to the formation of a layer of dispersed phase on the surface of zeolite grains. An increased concentration of oil products is observed in the filtrate during this period (see Fig. 3, a, b). It is known [3, 4] that the separation of oil-water emulsions

TABLE 1

Critical diameter d_{cr} and length l_{mol} of the molecules of various compounds, nm

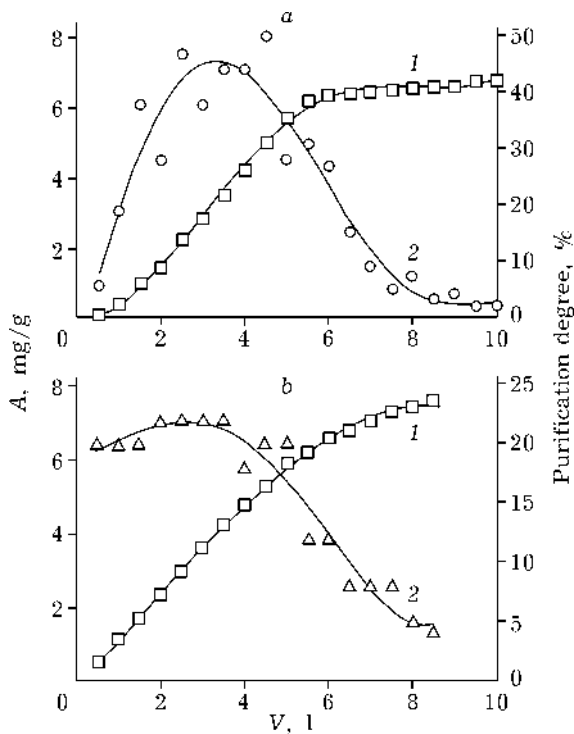| Compound	d_{cr}	l_{mol}
Propane	0.49	0.65
n-Butane	0.49	0.78
n-Pentane	0.49	0.90
n-Hexane	0.49	1.03
n-Heptane	0.49	1.15
Cyclopropane	0.49	−
Cyclohexane	0.61	−
Benzene	0.60	−
Toluene	0.67	−
Isobutane	0.56	−
Isopentane	0.56	−
Water	0.27	−

Fig. 3. Curves of filtration of the oil-water emulsion on natural zeolite from the Khonguruu deposit. C_{init}, mg/l: 32 (a), 115 (b); 1 − sorption, 2 − purification degree.
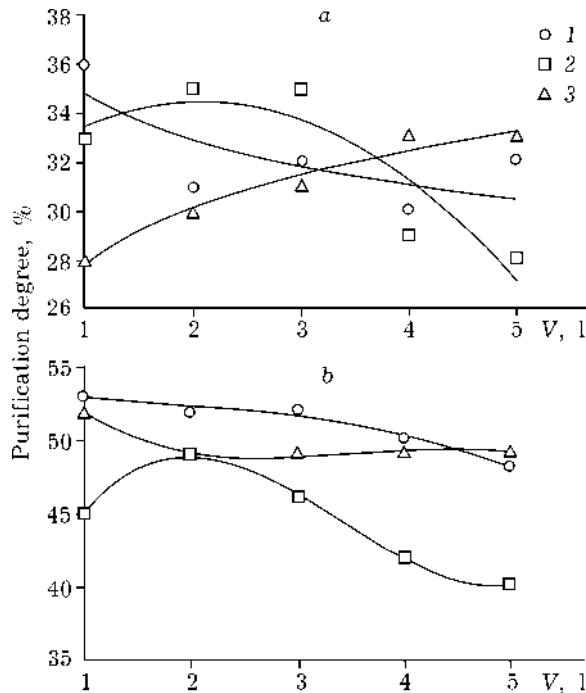
Fig. 4. Curves of filtration of the solutions of the Talakan oil and its fractions on the initial (*a*) and activated (*b*) khongurin: *1* − oil, *2*, *3* − petrol and diesel fractions, respectively.

is based on adhesion and wetting phenomena. Oil products belong to non-polar liquids with low surface tension and are able to wet almost any solid. When the oil emulsion passes through the filtering layer, at the initial period of time the drops of oil products get adhered to the grains or fibres of the load. With time, the adhered drops of oil products replace the hydrate shell gradually involving the entire grain surface into the process. A layer of the dispersed phase is formed on the surface of the filtering material. The surface becomes hydrophobic, which improves adhesion conditions for the emulsified oil products on the surface of the filtering load [4].

The samples of initial zeolites were investigated in dynamic processes of water purification from the dissolved hydrocarbons by passing water through the layer of adsorbent. The results of extraction of molecularly dissolved hydrocarbons are shown in Fig. 4, *a*. The concentration of the Talakan oil in water was 6.90 mg/l, petrol fraction 16.70, diesel fraction 4.47 mg/l. The degree of water purification from molecularly dissolved hydrocarbons was 30−35 %.

Improvement in the sorption characteristics of mineral sorbents is achieved by various sor-

bent activation procedures. The natural zeolites were modified in the present work by dehydration at 350 °C. Thermal activation causes an increase in specific surface of zeolite from 6.84 to 7.85 m^2/g. The results of investigation of the sorption of dissolved hydrocarbons of the Talakan oil and its fractions on thermally activated zeolite are shown in Fig. 4, *b*. The data obtained demonstrate that dehydration of zeolites helps increasing sorption capacity of khongurin.

The degree of water purification from the dissolved hydrocarbons of the Talakan oil and the diesel fraction using the activated sorbent is about 50 %. Hydrocarbons of the petrol fraction are sorbed no so well (purification degree is 45 %) due to higher solubility of light-weighed hydrocarbons in comparison with the hydrocarbons of higher boiling fractions (see Fig. 4, *b*). This is connected with the fact that the solubility of hydrocarbons decreases with an increase in their molecular mass. The compounds with lower solubility are more easily sorbed from water by porous sorbents [2].

The efficiency of extraction of dissolved hydrocarbons by activated zeolite is higher than that by the initial zeolite sample (Fig. 5). The degree of water purification increases from 30 to 50 % as a mean. This is characteristic both of the Talakan oil in general and of its separate fractions. The highest adsorption is observed for the extraction of hydrocarbons of petrol fraction (up to 2 mg/g) due to higher initial concentration of light-weighed hydrocarbons
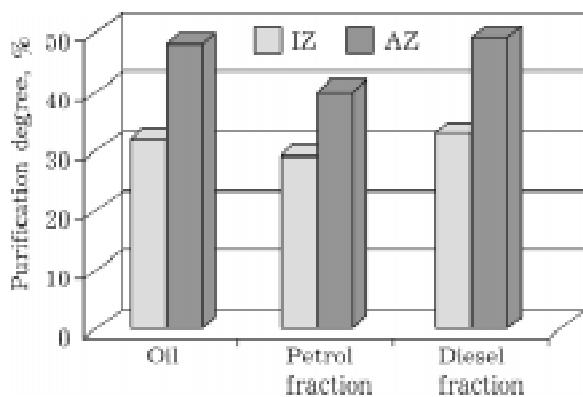

Fig. 5. Effect of dehydration of zeolite on the degree of water purification. Here and in Fig. 6, 7: IZ − initial zeolite, AZ − activated zeolite.
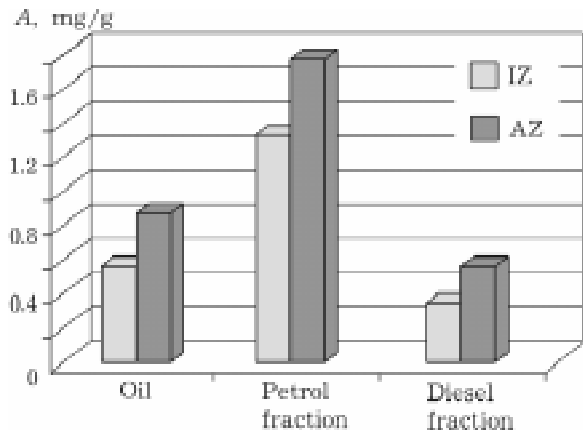
Fig. 6. Maximal adsorption of hydrocarbons on the initial and activated zeolite.

($C_0 = 16.70$ mg/l) in comparison with the diesel fraction and with the initial oil (Fig. 6). In addition, this can be connected with the fact that the formation of polymolecular adsorption layers is possible in the case of adsorption of small molecules, whereas preferably monomolecular layer should be formed in the case of larger size of molecule, other characteristics being kept constant [2]. However, the lower is the initial concentration of hydrocarbons in water, the lower is specific adsorption and therefore the lower is purification efficiency. The lowest sorption is observed for the diesel fraction: within 0.5−0.6 mg/g, with the initial concentration of hydrocarbons 4.47 mg/l (see Fig. 6).

When designing waste disposal works for use in industry to purify waste water before disposing them into water reservoirs or for preparation of drinking water, the concentration of contaminating substances in water is prescribed by specific initial data. The concentration of oil products in purified water is defined by the requirements to the quality of water used in the technological cycle, while for disposed water it is defined by the maximum permissible concentrations (MPC) for open natural water reservoirs or for sewage system. Because of this, for adsorption purification of oil-containing water, it is necessary to determine optimal consumption of the sorbent and reasonable number of the steps of adsorption purification in the system of sequentially connected absorbing filters [2].

The performed research allowed us to estimate the efficiency of multistage purification of water from oil using natural zeolites of the Khonguruu deposit. To carry out research, we used a model solution of the Talakan oil in water, the initial concentration of dissolved hydrocarbons being 6.27 mg/l. The required final concentration of oil products in water, that is, the MPC for oil products to be disposed into the city sewage system is about 2 mg/l, depending on the efficiency of the available waste disposal works in different regions [9].

One can see in the diagram shown in Fig. 7 that the concentration of oil product decreases at the first two stages to 4 mg/l, both for the initial and for activated zeolite. The third stage of purification with activated carbon of BAU grade allows one to decrease the concentration of oil products in the filtrate to the required value, which is 2 mg/l.

Thus, the use of khongurin at the first two stages of water purification allows one to reduce the consumption of expensive activated carbon and to decrease the concentration of oil products in the filtrate down to the MPC level.

CONCLUSION

The performed research showed that the capacity of natural zeolite in the processes of oil product recovery from aqueous media is not high under static conditions. Maximal adsorption is $12 \cdot 10^{-3}$ mg/g. The dynamic adsorption ability of khongurin is higher and can achieve 1.7 mg/g.
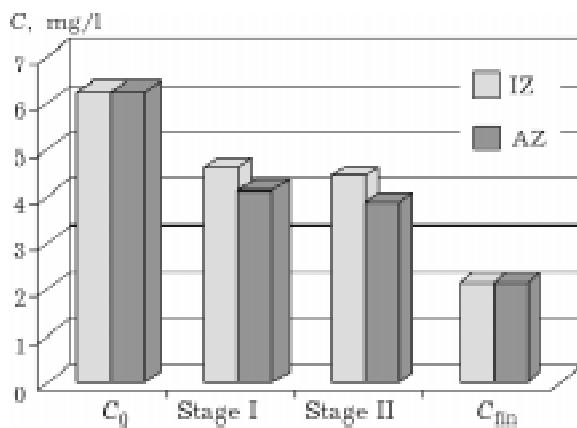

Fig. 7. Results of the recovery of dissolved oil products in a three-stage process of water purification with the initial and activated zeolite.

Modification of zeolite by thermal treatment and changes in the process parameters for water purification from oil products under dynamic conditions allow increasing sorption capacity of the sorbent to 8 mg/g, with the degree of water purification from oil emulsion reaching 50 %.

It should be noted that the sorption capacity of natural zeolites is lower than that of activated carbon; however, large resources and low prime cost allow using them in multistage processes of water preparation and purification of waste water from oil products and other pollutants at reduced cost of water treatment without any decrease in efficiency.

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