

EVALUATION OF USABILITY OF CLINOPTYLOLITE AND
DIATOMITE FOR SORPTION OF OIL CONTAMINANTS FROM
WATER SOLUTIONS

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COMMUNICATION

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OCENA PRZYDATNOŚCI KLINOPTYLOLITÓW I DIATOMITÓW DO
SORBOWANIA ZANIECZYSZCZEŃ OLEJOWYCH Z ROZTWORÓW WODNYCH

Streszczenie

Praca zawiera wyniki badań dotyczące zastosowania diatomitów i klinoptylolitów do usuwania zanieczyszczeń olejowych z roztworów wodnych w procesie sorpcji. Oceniono wpływ różnych czynników wpływających na ten proces oraz wyznaczono pojemności adsorpcyjne testowanych minerałów.

Summary

The objective of the research presented in the paper was to study the process of adsorption of oil impurities with the use of clinoptylolite and diatomite. The effect of various factors on process course was determined, the process was described with isotherms and the adsorptive capacities of tested minerals were determined on their basis.

INTRODUCTION

Incidents of contamination of both surface waters and deep, underground waters with oil products can be observed more and more often in recent years.

Oil and products of its distillation cause organoleptic (sensory) changes of water, make the natural aeration of water difficult and have toxic effect on fauna and flora, accumulate in tissues of living organisms, contaminate the fish as well as make problems in water conditioning [2].

The occurrence of oil substances in aqueous solutions take either dissolved, emulsified, or undissolved forms. Emulsions of all kinds are the most common form.

Because of complex composition of oil substances it is very difficult to find an indicator that would positively determine their concentrations. A universally applied index for summary contents of oil compounds is the value of ether extract of water.

Despite many years of studies, the problems of water purification, involving removal

of oil substances, still remain open. Well known and commonly used are the methods of mechanical separation, chemical methods, filtration and ultra-filtration. Sorption is one of a few processes that are both highly effective and simple in respect of the needed apparatus. Such materials as active carbon, polyurethane foams, mineral-carbon materials, carbonizing cokes, semicokes, diatomites and natural zeolites are used as sorbents [6, 8, 9].

OBJECTIVE AND SCOPE OF STUDY

The objective of the performed study was to describe the process of sorption of oil impurities on natural sorbents, as well as to determine the optimum process conditions.

On the basis of theoretic analysis it was assumed that the following factors shall affect the course and the effectiveness of the sorption process:

- type and doses of applied sorbents,
- the manner of process conductance (contact time),
- concentration and pH of adsorptive solutions.

In the course of tests the adopted assumptions were subject to experimental verification.

METHODS OF TESTS

Tests were performed on clinoptylolite from Nižny Hrabovec area near Koszyce in Slovakia. Diatomite was purchased from Jawornik Ruski (Poland) [1, 3–5, 7].

The initial treatment of minerals consisted in isolation (through sieving method) of fraction 0,75–1,2 mm (typical granulation applied in (waste)water treatment processes), and then its washing. Clinoptylolite was roasted at 500°C and diatomite was dried at 105°C. Two types of oil were used for tests: Mixol engine oil and Diesel fuel oil (ON), which to some degree represent oil impurities. These oils differ from each other by their density and viscosity. Model emulsions of O/W type, prepared from the above-mentioned oils, had oil particles in a dispersed phase in aqueous medium. Ether extract prepared in accordance with Polish standards was used as the reference control.

The kinetics of the adsorption was determined for clinoptylolite and diatomite. A suitable absorbent was added in a dose of 10 g/dm³ to a number of conical flasks containing each 300 cm³ of specific emulsion at concentrations of 110 and 350 mg/dm³ and shaken for 10, 20, 30, 40, 50, 60, 80, 100 and 120 minutes. The clarification time was 1 hour. The control determination (ether extract) was carried out in decanted solutions.

The effect of pH of adsorptive solutions on the adsorption process was studied with the use of sorbents and their doses such as those for the determination of adsorption kinetics. The pH value of model emulsions was varied within 2–10. The shaking time was 30 minutes and the decanting time – 1 hour. Test were carried out only for initial concentration of 110 mg/dm³.

In order to determine the adsorption isotherms, growing doses (1–35 g/dm³) of suitable sorbent (roasted clinoptylolite, raw diatomite) were added to 10 conical flasks containing each 300 cm³ of specific emulsion. Sample temperature was stabilized at the level of 15°C and samples were shaken for 30 minutes in insulation-material protection. Then they were left for one hour and ether extract was determined in the decanted solution. Emulsions prepared on the basis of Mixol oil and Diesel oil at the concentrations of 110 and 350 mg/dm³ were subjected to testing.

TEST RESULTS AND THEIR DISCUSSION

Kinetics of adsorption process

Test results presented in Fig. 1 show that adsorption process effects on both clinoptylolite and diatomite stabilized after a similar time that was within the range 20–30 minutes. No larger differences in sorption process rate were noticed at various initial concentrations of oil in emulsion. The time of 30 minutes was assumed as optimum. It is the limit, after which the decrease of oil impurities was only minimal. A relatively short time of sorption process may be a good indication for the application of clinoptylolite and diatomite in filtration columns.

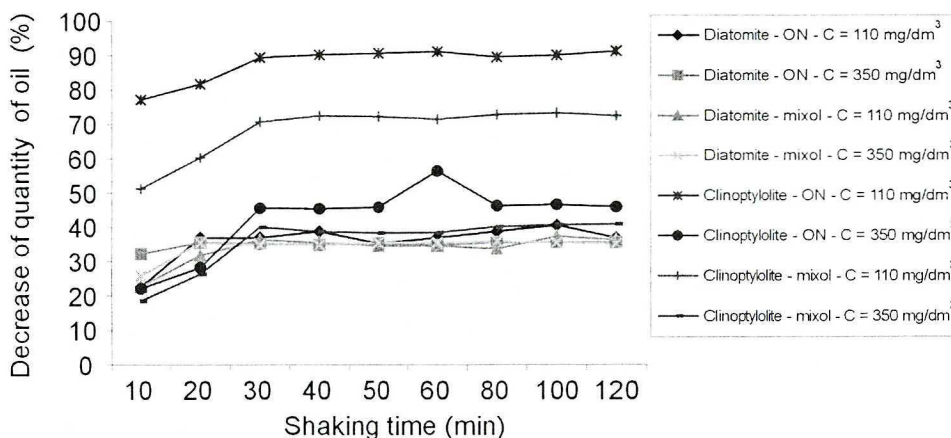


Fig. 1. Effect of shaking time on the result of adsorption process

Effect of pH of the adsorptive solution on adsorption process

When clinoptylolite was applied, the highest percentage of ether extract lowering (approx. 88%) was clearly noted for pH = 7. For pH within 3.0–7.0 the reported percentage of the removal was lower and, in some cases, e.g. for Diesel oil emulsion, the differences reached even up to 20%. In a strongly acidulous environment, pH = 2.0, slight improvement was observed in all cases. At alkaline pH (8.0–10.0) there was a step-by-step, nearly proportional worsening of process effectiveness – the percentage of removal reached only 55% (Fig. 2).

In the case of diatomites the sorption of oil impurities proceeded best at reaction lower than 8.0. The average percentage of oil reduction was approx. 28%. Much worse results were obtained at pH 9.0–10.0, where decrease of quantity of oil was 19.6% and 19.4% for Mixol-oil and Diesel oil emulsions, respectively. Besides alkaline pH, the samples were colored to brown which was caused by diatomite (Fig. 2).

Inferior results obtained in alkaline environment may be caused by increased wettability of sorbent with water, and thus the detachment of oil film from its surface.

Further testing was conducted with pH oscillating around neutral (pH = 7.0), for which good, or even mostly best, results were obtained.

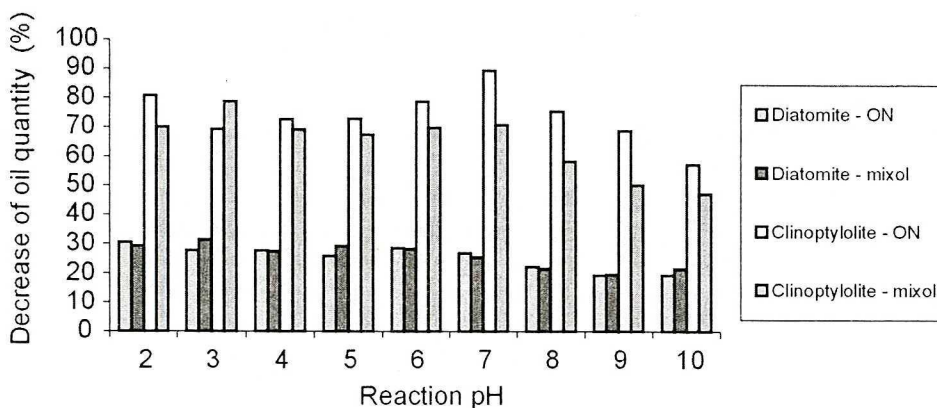


Fig. 2. Effect of reaction pH on the adsorption process

Description of adsorption process – isotherm

The results obtained in successive series of experiments performed in static conditions were described with basic equations of isotherms: i.e. those of Freundlich, Langmuir and BET. Langmuir's isotherm with clinoptylolite application clearly failed to describe the experimental data, whereas for diatomite the obtained fitting was low (at the level of 0.3–0.5). When describing the adsorption process with BET equations, the correlation coefficient appeared unsatisfactory for both clinoptylolite and diatomite. Freundlich's equations best described the process. Their choice was determined by high correlation coefficient, R , oscillating around the value of 0.9 (Tab. 1). Generally, the equation for Freundlich's isotherm is expressed with the general formula:

$$X : m = K \cdot C^{1/n}$$

where: $x = C_0 - C$, C_0 – initial concentration (mg/dm^3),

C – the equilibrium concentration (mg/dm^3),

m – adsorbent mass (g/dm^3), K, n – isotherm constants

after finding the logarithm it assumes the linear form:

$$\log(X : m) = \log K + (1 : n) \cdot \log C$$

Table 1. Constant of Freundlich adsorption isotherms and adsorption capacities of used materials

Material	Emulsion type, concentration (mg/dm^3)	Constant of isotherms		Correlation coefficient R	Adsorption capacity (mg/g) P_a
		K	n		
clinoptylolite	mixol 110	0.072	0.6967	0.85	22.18
clinoptylolite	mixol 350	0.172	1.2220	0.91	10.15
clinoptylolite	diesel oil 110	0.0479	0.6130	0.91	32.89
clinoptylolite	diesel oil 350	$3.0 \cdot 10^{-4}$	0.4852	0.85	10.75
diatomite	mixol 110	$7.4 \cdot 10^{-3}$	0.7095	0.81	2.50
diatomite	mixol 350	$9.1 \cdot 10^{-6}$	0.3932	0.91	3.39
diatomite	diesel oil 110	0.4003	2.2300	0.68	2.41
diatomite	diesel oil 350	$6.7 \cdot 10^{-5}$	0.4687	0.97	3.16

Freundlich's isotherms were determined in linear form, approximated with the least-squares method, described with mathematic equations and isotherm constants, n and K , were determined on their basis. The Freundlich's equation always describes the experimental data in a wide range of concentrations and therefore they were applied for each level of concentration separately, rather than integrated into one whole.

The analysis of the summary of Mixol oil adsorption isotherms on clinoptylolite and diatomite (Fig. 3) and a similar summary for Diesel oil (Fig. 4), indicates clearly that clinoptylolite, which is also characterized by higher mechanical resistance, exhibited better sorptive properties. During shaking diatomite underwent a slight wash-out and therefore the ether-extract determination was burdened with error that raised the value of the equilibrium concentration.

On the basis of determined isotherm constants, the adsorptive capacity P_a (Tab. 1) was calculated with the use of the following criteria of the equilibrium concentration, C , depending on the initial concentration, C_0 :

$$C_0 = 110 \text{ mg/dm}^3 - C = 55 \text{ mg/dm}^3$$

$$C_0 = 350 \text{ mg/dm}^3 - C = 155 \text{ mg/dm}^3$$

The adsorptive capacities of clinoptylolite were affected by the concentration of the adsorptive solution. Higher values of capacity were obtained at/for lower concentrations. Of the two tested emulsions the Diesel oil was sorbed slightly better.

The adsorptive capacities of diatomite stayed at significantly lower level. They did not vary significantly for various oil concentrations in emulsion, but reached higher values for Mixol oil.

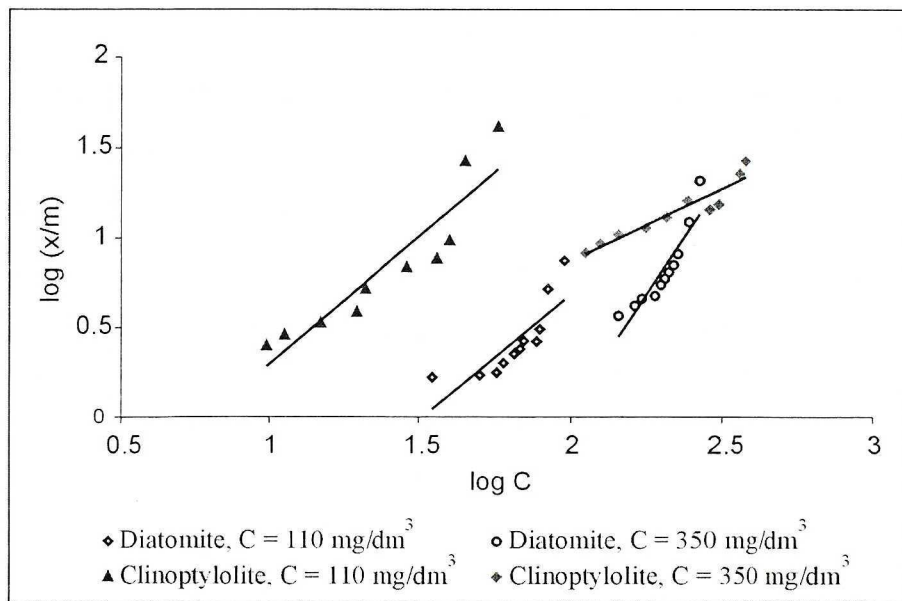


Fig. 3. Freundlich mixol oil adsorption isotherms

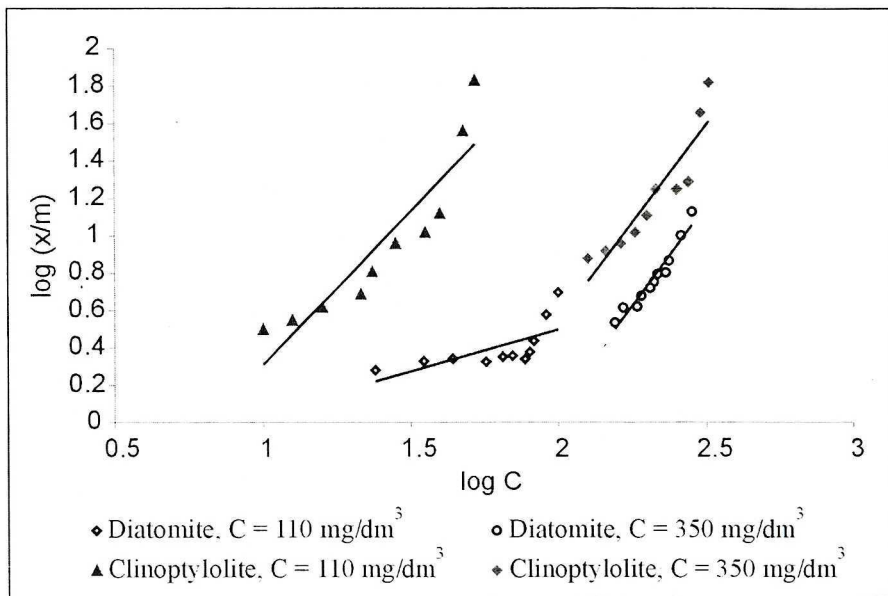


Fig. 4. Freundlich Diesel oil adsorption isotherms

CONCLUSIONS

1. Clinoptylolite and diatomite appeared to be good sorbents of two selected oil impurities (Mixel oil and Diesel oil) from water solutions.
2. The course of the impurity removal process was affected by pH of adsorptive solutions (neutral pH and pH within the range of 4–8 were found to be optimum for clinoptylolite and diatomite, respectively) and by the time of sorbent contact with oil (20–30 min.).
3. Approximation of experimental data to three most often used isotherm equations permitted selection of most suitable model of adsorption i.e. Freundlich's isotherm.
4. The adsorptive capacity values, determined for clinoptylolite for lower concentrations of oil in emulsion, ranged within 22.18–32.89 mg/g, whereas for higher concentrations they oscillated around the value of 10.6 mg/g. Diesel oil was sorbed slightly better. The adsorptive capacities of diatomite were considerably lower and stayed within 2.41–3.39 mg/g.

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