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## EXPERIENCE IN REMOVING PETROLEUM DERIVATIVES FROM AQUEOUS SOLUTIONS ONTO ADSORPTIVE DIATOMITE AND CLINOPTILOLITE BEDS

Application of diatomite and clinoptilolite deposits in purification of waters contaminated with oily substances is examined. Breakthrough curves, i.e. isoplanes, were plotted on the basis of the results obtained and adsorptive capacities of diatomites and clinoptilolites were calculated in dynamic conditions. The proportions of both adsorption and coalescence in filtration process were also determined. An attempt was made to regenerate the spent sorbents and to re-use them for removing the contaminants examined.

### 1. INTRODUCTION

In the process of removing petroleum derivatives, it is essential to remove not only separate, insolvable hydrocarbon phase, but also dissolved and emulsified hydrocarbons [8], [16]. To this end a number of mechanical, physical and chemical methods and costly and unique equipment are applied. That is why the purification of wastewater is usually confined to the level of 30–50 mg of pollutants per one dm<sup>3</sup>, while the rest is left to controlled processes of biodegradation [2], [3].

The methods for oil removal from wastewaters are frequently based on the interaction between the surface forces acting at the boundary of oil, water and solid interphase. Deoiling may take place in sorption, filtration, ultrafiltration and coalescence processes [12], [13], [15].

Sorption process may be very effective, but it is significantly affected by the sorbing agents applied. In the process, their specific absorptive properties in relation to the substances subjected to removal are utilized [14]. The effectiveness of the adsorption process may be raised mainly due to cheap and readily available adsorbent. The possibility of its regeneration is also of some importance.

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Up to now the literature indicates that these requirements may be fulfilled by the materials derived from natural minerals such as clinoptilolite and diatomite [3], [5]–[7], [15].

## 2. EXPERIMENTAL

The experiments were based on the applicability of diatomite and clinoptilolite deposits in purification of waters contaminated by petroleum derivatives. Break-through curves, the so-called isoplanes, were plotted and adsorptive capacities of diatomites and clinoptilolites calculated in dynamic conditions. The proportions of adsorption and coalescence in the filtration process were also determined. An attempt was made to regenerate the spent sorbents and to reuse them in removing the contaminants examined.

## 3. METHODS

The laboratory tests covered:

- preparation of model emulsions to be used as adsorptive solutions,
- preparation of diatomites and clinoptilolites,
- experiments on raw and regenerated beds in dynamic conditions.

A total content of petroleum derivatives was treated as a control/reference determination.

### 3.1. PREPARATION OF MODEL ADSORPTIVE SOLUTIONS AND THEIR CHARACTERISTICS

Two types of oils were tested: 'Mixel' engine oil and Diesel/fuel oil, as they represent, to a certain degree, petroleum derivatives. These oils are mainly the mixtures of aliphatic hydrocarbons of non-polar character. They differ from each other in density and viscosity (table 1).

Table 1

Characteristics of oil at the temperature of 15 °C

Type of oil	Unit	Mixel oil	Fuel oil
Oil body at 40 °C	mm <sup>2</sup> /s	min. 14.0	2.0–4.5
Density	kg/m <sup>3</sup>	893	803
Autoignition point	°C	min. 50	55

Model emulsions of O/W type were prepared from these oils, whose particles formed a phase being dispersed in water. These emulsions were not separated gravi-

tationally, and the microscopic examination showed that the diameters of oil drops were smaller than 3.0  $\mu\text{m}$ . Thus, they could be rated as fine-dispersed emulsions. The pH of the solutions ranged within 6.9–7.3. Medium concentration of oil in both emulsions was 110  $\text{mg}/\text{dm}^3$ .

### 3.2. CHARACTERISTICS OF CLINOPTILOLITES AND DIATOMITES USED IN THE STUDY

*Characteristics of diatomites.* Diatomite is a siliceous sediment made up of scums of single-cell microscopic algae called diatoms, illite-montmorillonite binder and small admixtures of metal oxides and quartz dust. It is exceedingly fine-grained, incoherent and highly absorbent. Polish diatomite deposits are related to tertiary formations of Carpathian Mountains, and occur in Podkarpackie province, mainly in the vicinity of Leszczawka and Błażowa (Poland). Diatomites that occur in Leszczawka deposit are generally uniform, highly porous and form silica-silty rocks [7]. Diatomites used in this study were sampled from Jawornik Ruski (Leszczawka region).

Diatomites were subjected to pre-treatment in order to obtain the material of a suitable granulation and better sorptive properties. It consisted in isolating raw diatomite fraction (by screening method) of 0.75–1.2 mm, and then liquid-classification or washing process to eliminate the dust fraction. Such a material rinsed and dried at 105 °C was further called *diatomite*.

*Characteristics of clinoptilolites.* Clinoptilolites are alumino-silicates of natural zeolite group displaying a skeletal structure. Due to their specific crystalline structure these minerals show monoexchangeable catalytic and sorptive properties [4].

Research was conducted on two types of clinoptilolites. The first clinoptilolite from Dylągówka village near Rzeszów, Poland, after chemical treatment (with concentrated hydrochloric acid) and thermal treatment (roasting at 500 °C) is further called *Polish clinoptilolite*. The second clinoptilolite was from Nižny Hrabovec area near Koszyce (Slovakia). It was subjected to thermal treatment (roasting at 500 °C) and further called *Slovakian clinoptilolite*.

The fraction of 0.75–1.2 mm was isolated from both clinoptilolites; then they were washed and dried at 105 °C.

### 3.3. METHOD OF TESTING

The experimental set-up consisted of a tank containing the emulsion tested, mechanical stirrer and pump supplying emulsion onto the bed. A pressurized filtration system with downward filtration was applied.

The laboratory filters, i.e. filtration columns made of organic glass, 35 mm in diameter, were filled with a suitable material up to the height  $h$  of 750 mm.

The optimum rates of filtration were determined in an initial phase of the experiment. They were 5 and 6 m/h for diatomite and clinoptilolite beds, respectively [6], [10].

Filtration lasted till the moment of bed exhaustion, i.e. a moment at which the oil concentration in the discharge reached that in the inlet solution. Upon completing each cycle, the beds were dried and weighed in order to determine the quantity of absorbed oil(s).

The bed breakthrough point was determined at  $C_p = 50 \text{ mg/dm}^3$  (these are such quantities of petroleum derivatives that may easily be subjected to biological treatment or to some other method of further water purification) [3].

Beds exhausted during filtration were thermally regenerated (at the temperature of  $500^\circ\text{C}$  to guarantee complete burning of oils) and filtrated again until the moment of bed exhaustion.

#### 4. METHOD OF CALCULATIONS

Calculations were done in order to determine a total adsorptive capacity (till the bed exhaustion point) and usable adsorptive capacity (till the bed breakthrough point) as well as the percentage share of coalescence in the filtration process.

Total quantity of oil impurities  $M_c$  (mg) removed due to the adsorption and coalescence was determined by using the filtration curves (isoplanes) represented by mathematical equations. The calculations were carried out according to the diagram in figure 1:

$$M_c = P_{ABCD} - P_{ABC}$$

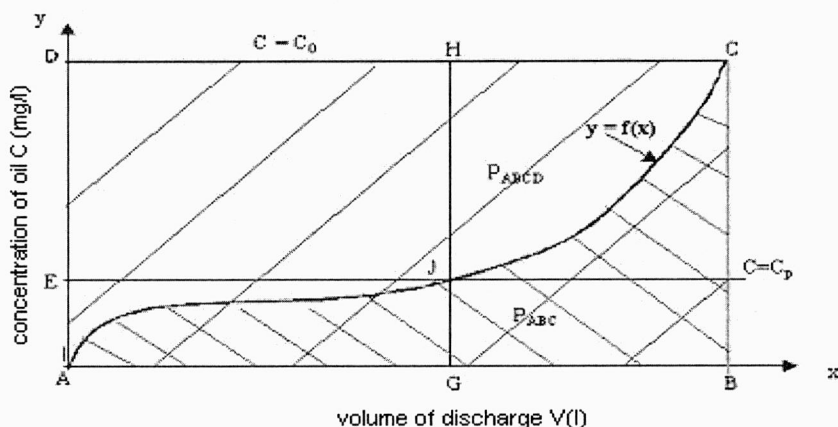


Fig. 1. Diagram allowing calculation of the total quantity of oil adsorbed by the filter  
 $G$  – breakthrough point,  $B$  – point of exhaustion,  $C_0$  – initial concentration of petroleum derivatives in emulsion ( $\text{mg/dm}^3$ ),  $C_p$  – concentration of petroleum derivatives at the breakthrough point ( $\text{mg/dm}^3$ ),  
 $C$  – concentration of petroleum derivatives in discharge ( $\text{mg/dm}^3$ )

The area under the isoplane (figure 1) may be calculated by integrating the equation within the limits from zero point  $A$  to bed exhaustion point  $B$ :

$$P_{ABC} = \int_A^B f(x) dx,$$

where:

$M_c$  – a total quantity of the oil impurities removed (mg),

$P_{ABCD}$  – the area representing the quantity of compounds introduced to filtration system,

$P_{ABC}$  – the area representing the quantity of compounds not absorbed on the bed.

Total adsorptive capacity  $P_c$  (mg/g) of specific material was calculated from the following formula:

$$P_c = \Delta M : M,$$

where:

$\Delta M$  – the difference between the weight of the bed after reaching the point of bed exhaustion and its weight prior to filtration,

$M$  – the weight of the bed prior to filtration.

Quantity of impurities removed in coalescence process  $M_k$  was calculated according to the formula:

$$M_k = M_c - \Delta M.$$

Per cent share of adsorption  $S$  (%) was calculated as follows:

$$S = \Delta M \cdot 100\% / M_c.$$

Per cent share of coalescence  $K$  (%) is calculated as follows:

$$K = M_k \cdot 100\% / M_c.$$

The usable quantity of impurities removed until the breakthrough point  $M_u$ , was reached:

$$M_u = P_{AGHD} - P_{AGJ},$$

where:

$$P_{AGJ} = \int_A^G f(x) dx.$$

The usable adsorptive capacity  $P_u$  (mg/g):

$$P_u = M_u \cdot S / 100\% \cdot M.$$

## 5. TEST RESULTS AND DISCUSSION

A number of emulsion of two types were passed through both clinoptilolite and diatomite beds. The first emulsion was based on Mixol oil, and the second on Diesel oil. The results are shown in figures 2, 3 and 4 in a cumulative form represented by isoplanes determined separately for each type of filtering media.

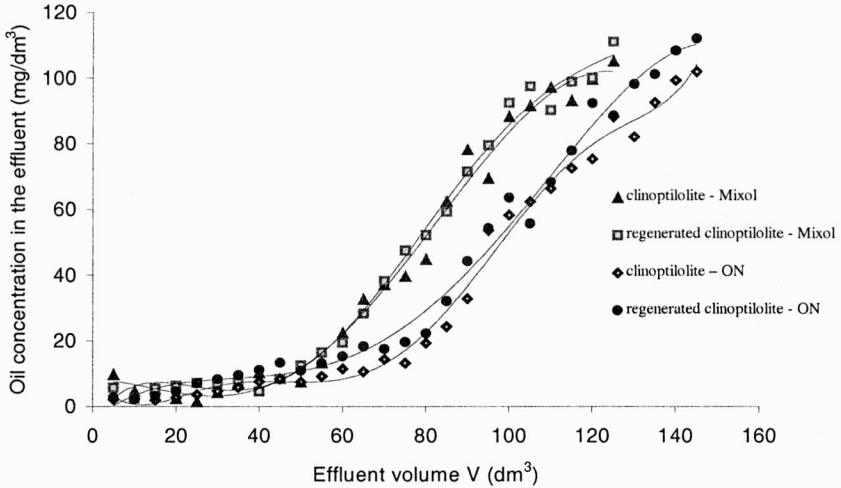


Fig. 2. Isoplanes – Slovakian clinoptilolites

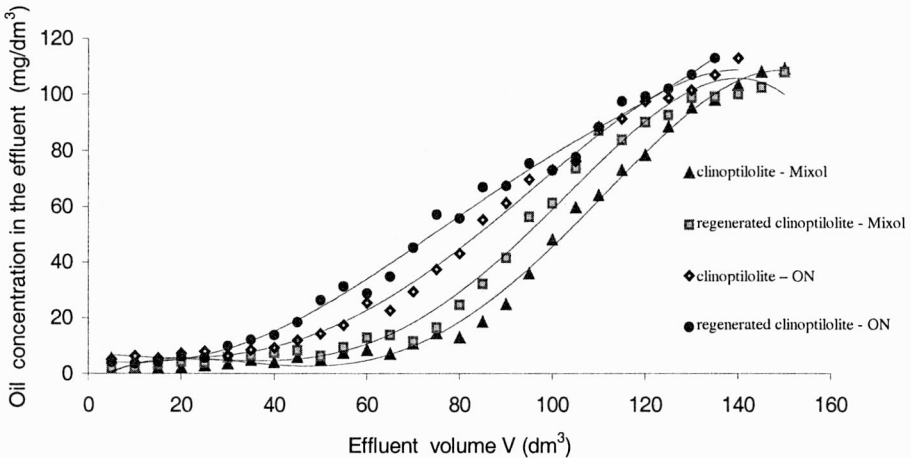


Fig. 3. Isoplanes – Polish clinoptilolites

While analyzing the performance of beds with Slovakian clinoptilolite (figure 2), it appeared that in each case filtration proceeded in a similar way. In an initial phase

of the process, the concentrations of oil in the filtrate were below  $10 \text{ mg/dm}^3$ . For the Mixol oil the concentration increased quickly after filtering approx.  $50 \text{ dm}^3$  of emulsion. The process appeared clearly more favourable for Diesel oil, because  $70 \text{ dm}^3$  of solution were filtered until the breakthrough point was reached, and the point of exhaustion was reached at twice as large volume of the filtrate. After bed regeneration, filtration of both emulsions was similar. Mixol oil was removed at practically the same rate, while Diesel oil removal was only slightly inferior.

Graphic representations of filtration through Polish clinoptilolite (figure 3), both in terms of the quantity of filtered emulsion and the concentrations reached, were very similar to isoplanes of the Slovakian clinoptilolite. Slightly better results were obtained for Mixol oil, as evidenced by larger volume of filtered emulsion and lower concentrations of oil compound in the discharge until the bed breakthrough point was reached. Analysis of isoplanes for regenerated Polish clinoptilolites showed that the efficiency of these beds proved to be as high as in the first filtration cycle. However, small differences in the filtration were beneficial in the case of the regenerated Polish clinoptilolite.

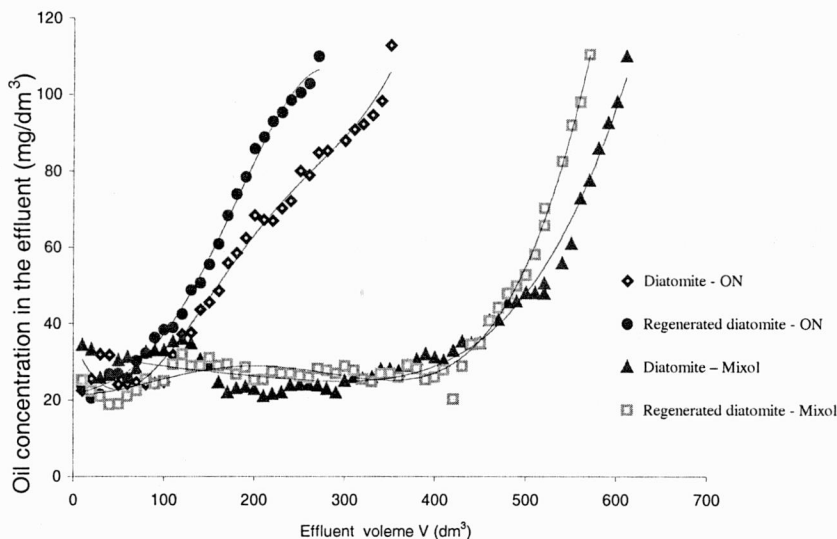


Fig. 4. Isoplanes – diatomites

As concerns the diatomites, the shapes of isoplanes (figure 4) were different for each filtration cycle and basically different from filtration curves for clinoptilolites.

Filtration of both emulsions lasted much longer, so that approx.  $600 \text{ dm}^3$  of Mixol oil and roughly half that volume of Diesel oil emulsions were filtered. The concentrations of petroleum derivatives in the discharge were within the range of  $20\text{--}30 \text{ mg/dm}^3$ . In the case of Diesel oil, the concentrations of petroleum derivatives in the discharge ranged from  $20$  to  $30 \text{ mg/dm}^3$  only in the first phase of the process (i.e. approx.  $100 \text{ dm}^3$ ), while in the case

of Mixol oil they were within this range through the most of the filtration process. Diatomite beds allowed a clearly better removal of Mixol. Regeneration of diatomites did not have a negative effect on the emulsion purification. Diesel oil was more efficiently removed by non-regenerated diatomite, whereas Mixol – by the regenerated diatomite (lower oil concentrations in the discharge were obtained at the beginning of filtration).

The usability of the above materials for the adsorption can be described as follows: diatomites removed the impurities much (even four times) longer than clinoptilolites, but the lowest (even three times lower) concentrations of both oils in discharge were found in clinoptilolite beds in the early phase of the process.

In filtration beds, the adsorption is accompanied by the coalescence which affects the removal of petroleum derivatives. This was evidenced by occasionally recorded single, high concentrations of oils in the discharge. Besides, a persistent thin layer of oil was observed in the upper part of the filter. It was removed after emulsion filtration. This layer is built up from the particles of emulsified oil, which undergo coalescence due to a contact with the adsorbent surface.

In order to determine the effect of coalescence on the entire process of removal of petroleum derivatives by filtration bed, an attempt was undertaken to calculate its percentage share.

The total and usable adsorptive capacities,  $P_c$  and  $P_u$ , were determined to compare the effectiveness of the beds in respect of the emulsions tested.

The isoplanes represented by mathematic equations were used for this purpose. The usable adsorptive capacity  $C_p$  equal to  $50 \text{ mg/dm}^3$  was calculated for determined bed breakthrough points. All calculations done according to point 4 were summarized in table 2.

Table 2

Effect of research and calculation for beds adsorption

Filtering medium	Mixol oil			Diesel oil		
	Total adsorptive capacity $P_c$ (mg/g)	Usable adsorptive capacity $P_u$ (mg/g)	Coalescence $K$ (%)	Total adsorptive capacity $P_c$ (mg/g)	Usable adsorptive capacity $P_u$ (mg/g)	Coalescence $K$ (%)
Diatomite	55.6	50.3	15.2	17.3	14.8	24.4
Polish clinoptilolite	15.9	13.2	29.7	12.7	9.6	29.5
Slovakian clinoptilolite	12.9	7.9	27.1	16.6	14.2	24.5

Adsorptive capacities obtained show clearly that filtering material affected the removal of oil. The highest adsorptive capacities of the beds in relation to Mixol oil were obtained for diatomite. They exceeded all other capacities several times and, moreover,



the usable capacity of diatomite constituted nearly 90% of the total capacity. All the remaining total adsorptive capacities were principally alike, or close to each other, and oscillated within 12.7–17.7 mg/g, whereas the usable capacities constituted, on an average, 80% of the total capacity. The Slovakian clinoptilolite appeared to be the best adsorption material, because, although it had slightly lower adsorptive capacity than diatomite, lower oil concentrations in the discharge were found during the bed operation. On the basis of small differences in adsorptive capacities of both clinoptilolites it may be said that their operation with respect to both oils was similar.

The coalescence process constituted, on an average, 25% in the whole cycle of testing and depended on the bed applied rather than on the type of oil. In respect of Mixol oil, the largest share of coalescence was recorded for Polish clinoptilolite, and the smallest, 15.2 %, for diatomite.

Mixol oil was better sorbed on diatomites, which might be connected with its physical properties (its higher density, viscosity and molecular weight compared to Diesel oil) and with diatomite structure. Diatomites may be ranked as nonspecific adsorbents characterized by some nonspecific effects, which are mainly caused by the occurrence of universal dispersion forces and by geometric arrangement of adsorbate particles in respect of adsorbent surface, produced during adsorption. When a small surface of adsorbent is occupied, the energy of interaction between adsorbent and adsorbate for homological series increases linearly with the growth in size of adsorbed particles. Substances of high molecular weights are considered to be better adsorbents than chemical compounds of low molecular weights. Multi-layer physical adsorption was a basic process [9], [11].

Mixol oil has been also adsorbed better by Polish clinoptilolite and it may be assumed that the main process consists in a multilayer physical adsorption on the surfaces of meso- and macropores as well as on the external surface of the packet structure of silty clinoptilolite-admixture materials.

Slightly better adsorption of Diesel oil by Slovakian clinoptilolite could be caused by typical physical adsorption and specific reactions (related to an internal crystalline structure of clinoptilolites). Larger share of pure clinoptilolite in Slovakian tuff determined its better adsorptive properties [4].

## 6. CONCLUSIONS

1. Clinoptilolite and diatomite beds proved to be efficient in removing two selected oil impurities (Mixol and Diesel oils).

2. Operation of diatomite beds was much longer compared to clinoptilolite, but the discharge quality (oil concentrations below 10 mg/dm<sup>3</sup>) in early phases of filtration was better in the case of the latter. The potential occurrence of coalescence in all filtration cycles should be taken into account, as it accounts for 25% of all oils removed.

3. Diatomite appeared to be the best adsorbent of Mixol. Its usable adsorptive capacity  $P_u$  reached 50.3 mg/g.

4. Slovakian clinoptilolite bed appeared to be most effective in removing Diesel oil ( $P_u = 14.2$  mg/g).

5. All filtration materials tested may be regenerated through roasting at 500 °C and reused. Regeneration of diatomites and clinoptilolites does not deteriorate their adsorption capacities.

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#### USUWANIE ZWIĄZKÓW ROPOPOCHODNYCH Z ROZTWORÓW WODNYCH NA DIATOMITOWYCH I KLINOPTYLOLITOWYCH ZŁOŻACH ADSORPCYJNYCH

Złoża klinoptylolitowe i diatomitowe usuwają dwa wybrane zanieczyszczenia ropopochodne (mixol i olej napędowy). Złoża diatomitowe pracowały znacznie dłużej, ale złoża klinoptylolitowe zapewniały

w początkowych fazach filtracji lepszą jakość wycieku. Mixol był najlepiej adsorbowany przez diatomit, o czym świadczy jego największa użytkowa pojemność adsorpcyjna. Olej napędowy był najefektywniej adsorbowany na złożu z klinoptylolitu słowackiego. Około 25% olejów usunięto w wyniku koalescencji. Wszystkie przebadane materiały filtracyjne mogą być regenerowane przez wyprażanie w temperaturze 500 °C i ponownie wykorzystane. Zregenerowane diatomity i klinoptylolity nie zmniejszyły swoich zdolności adsorpcyjnych.

