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L. Bandura, R. Panek, W. Franus
Department of Geotechnics, Lublin University of Technology
University of Management and Administration in Zamosc

THE USE OF CLINOPTILOLITE AND SYNTHETIC ZEOLITES FOR REMOVAL OF PETROLEUM SUBSTANCES

In the present paper the sorption of petroleum substances such as diesel fuels on zeolite beds was investigated. A natural occurring zeolite clinoptilolite, and mixtures of clinoptilolite and synthetic zeolites Na-P1 and Na-X type, in the ratio 3:1, were used in this study. Natural zeolite acquired from the mine tuffs in Sokyrnytsya (Ukraine). In order to obtain synthetic zeolites, F-class fly ash (Kozienice Power Plant, Poland) with sodium hydroxide was used and later it underwent the hydrothermal conversion. Two commonly used diesel fuels were chosen for this study; namely Verva On and Biodiesel. The zeolites were characterized with the use of X-ray fluorescence (XRF), scanning electron microscope (SEM), X-ray diffraction (XRD), and N_2 adsorption/desorption isotherm. The results indicated that clinoptilolite could constitute a good sorbent for petroleum substances removal. Moreover, the addition of synthetic zeolites improved the sorption capacity of the zeolite beds. In this study, when 25% of synthetic zeolite was added to the clinoptilolite bed, the sorption capacity increased approximately two times.

Key words: sorption, petroleum substances, clinoptilolite, synthetic zeolites

Досліджено сорбцію нафтопродуктів, таких як дизельне паливо, цеолітами. У дослідженнях використано природний цеоліт (клиноптилоліт), а також суміші природного і синтетичних цеолітів типів Na-P1 і Na-X у співвідношенні 3:1, зокрема природний цеоліт Сокирницького родовища (Україна). Синтетичні цеоліти одержано гідротермальним перетворенням суміші золи винесення F-класу (Козинецька електростанція, Польща) та натрію гідроксиду. Для досліджень вибрано два широко використовуваних дизельних палива, а саме VervaOn і біодизель. Цеоліт досліджено з використанням рентгенівської флуоресценсії (XRF), сканувального електронного мікроскопа (SEM), рентгенофазового аналізу (XRD) й ізотерми N_2 адсорбції/десорбції. Результати показали, що клиноптилоліт має добру сорбційну здатність і може використовуватися для очищення від нафтопродуктів. Крім того, додавання синтетичних цеолітів покращує сорбційні властивості цеоліту. Досліджено, що заміна 25 мас. % природного цеоліту синтетичним покращує сорбційну здатність приблизно в два рази.

Ключові слова: сорбція, нафтопродукти, клиноптилоліт, синтетичні цеоліти

Introduction

Petroleum products (gasoline, diesel fuels, motor oils, greases etc.) are one of the main sources of environmental pollution these days (Kingston 2002; Carmody et al., 2008). Progressive industrialization and development of automotive industry are undeniably related to an increasing demand for such hazardous substances. This, in turn, leads to an increase in of the potential risks associated with the aforementioned negative impacts of those petroleum substances on the environment and living organisms (Alonso-Alvarez et al., 2007; Aguilera et al., 2010).

Crude oil and petroleum substances can get into the environment during extracting, transporting, distributing, storing, and using (Wang et al., 2012). Particularly hazardous and tragic in consequences are leakages from oil-tankers during disasters, mechanical failures or road accidents. The risk of petroleum substances spreading occurs also around many objects such as places of crude oil extraction, petrol stations, oil refineries, industrial pipelines, storage facilities, industrial sites and brown fields, airports, railway tractions, as well as military bases. Thus, the sources of petroleum contamination can be divided into two groups: places with known location, which generate risk of long-term, constant contamination, and random incidents (Pastewski et al., 2009). In the era of growing industrialization and rising demand for petroleum products it is important to search for the effective methods for the removal of oil from contaminated sites.

The most popular methods used for the removal of oil leakages are adsorption techniques that use various kinds of adsorbents (Carmody, 2008; Wahi et al., 2013). According to Adebajo et al. (2003) sorbent materials used for the oil spills removal can be divided into three groups:

1) inorganic mineral materials;
2) natural organic materials;
3) synthetic organic polymers.

Among natural mineral adsorbents, zeolites play a significant role. They are porous aluminosilicates with a crystal structure, containing a system of channels and chambers. Their structure provides them with unique surface properties; such as ion exchange, adsorption, molecular-sieves and catalytic capabilities (Franus, 2012). Therefore, those mineral resources are widely used in many fields. So far, a variety of applications of natural and synthetic zeolites was described (Franus and Wdowin, 2010; Misaelides, 2011; Chaiupnik et al., 2013). However, zeolites have not been used as sorbents of petroleum substances yet. Their sorption properties and porous structure indicate the possibility of their application as adsorbents of this kind of substances.

In this study, we have explored diesel fuel sorption on zeolite beds, using natural clinoptilolite and clinoptilolite with a small addition of synthetic zeolites as adsorbents. XRD, XRF, SEM measurements were performed in order to characterize the zeolites. Textural parameters of adsorbents were studied with regard to adsorption of petroleum substances.

Materials and methods

Adsorbents

Natural zeolite clinoptilolite was acquired from the Sokyrnytsya deposit (the Transcarpathian region, Ukraine). The clinoptilolite samples were grounded in a metal mortar and divided into the fractions. Then, the material was washed with distilled water to remove turbidity and was dried at room temperature (air-drying). The fraction of 1-2 mm was chosen for further experiments.

Synthetic zeolites represent a type of gismondite (material Na-P1) and fauiasite (material Na-X). They were obtained in accordance with the chemical reaction:

Fly ash + x [mol/dm^3] NaOH **à** zeolite + residuum

This process has to be conducted at an appropriate temperature and for sufficiently long time. In order to obtain Na-P1 and Na-X zeolite type 10 g of homogenized raw fly ash, reaction time 24 h, and atmospheric pressure were used in all experiments. All reactions were carried out using polypropylene bakers. Details of zeolitie materials preparations were following:

• Material Na-X – fly ash + 200ml of 3M NaOH solution; temperature: 75 °C;

• Material Na-P1 – fly ash + 200ml of 1M NaOH solution + 100ml of 3M NaCl solution; boiling conditions (temperature: ca. 105 °C).

After reactions the products were washed three times with distilled water and dried. Prior sorption experiments zeolites were dried at a temperature of 110◦C for 12 h to get rid of part of the adsorbed water and stored in a desiccator.

The mineral composition of all zeolite materials was determined by the X-ray diffraction (XRD) using the Philips X'pert APD diffractometer with PW 3020 goniometer, Cu tube and graphite monochromator. The identification of phases was based on ICDD PDF-2 database and on the collection of patterns recommended by the International Zeolite Association (Treacy and Higgins, 2001).

The surface morphology and the chemical composition of the main mineral components were analyzed by scanning electron microscope (SEM) FEI Quanta 250 FEG equipped with a system of chemical composition analysis based on the energy dispersive X-ray-EDS of EDAX company.

The chemical composition of the tested zeolites was examined with the use of XRF method (Philips, PW 1404). An X-ray tube equipped with dual Cr-Au anode with a maximum power of 3 kW was the excitation source.

Textural characterization of the samples was performed by the low-temperature nitrogen adsorption–desorption method. Nitrogen adsorption–desorption measurements were made at 77 K using an ASAP 2020 volumetric adsorption analyzer (Micromeritics). The specific surface area, S_{BET}, of the investigated samples was evaluated using the standard Brunauer–Emmett–Teller (BET) method for nitrogen adsorption data in the range of relative pressure p/p_0 from 0.06 to 0.3. The total pore volumes were estimated from single-point adsorption at a relative pressure of 0.98. The pore size distributions were obtained from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) (Barret et al. 1951).

Adsorbates

As it was mentioned, two commonly used diesel fuels were chosen for this study; namely Verva On and Biodiesel B100. Both of them were purchased from PKN Orlen petrol station (Poland). The density of oils were measured by the pynometer method. The rotating rheometer Brookfield R / S + was used with Lauda Ecoline RE 206 thermostat, equipped with a digital temperature controller, was used to measure the viscosity of oils. The measurements were conducted with the use of a system of coaxial cylinders, according to standard DIN 53453. The determined parameters are listed in Table 1.

Table 1

Physical properties of examined oils

Oil type	Density ($g \cdot mL^{-1}$)	Viscosity ($Pa \cdot s$)
Verva ON	0,833	$0,0036 \cdot 10^{-5}$
Biodiesel	0,876	$0,0066 \cdot 10^{-5}$

Sorption experiment

The sorption of petroleum substances such as diesel fuels on zeolite beds was investigated. For this purpose, glass columns of 50 cm length and 1 cm internal diameter, were packed with clinoptilolite and mixtures of clinoptilolite/Na-X and clinoptilolite/Na-P1 in the weight ratio of 3:1. The weight of each bed was 20 g. The beds were poured with oil until the complete saturations of the pores were achieved. Then, the beds were left to drain from the excess of petroleum substance under the force of gravity. The experiment was conducted in a room temperature and repeated four times with the mean of the four runs used for calculations. The amount of sorbed oil was calculated from the mass balance of the bed before and after the oil sorption. The oil sorption capacities (Q, g-oil/g-sorbent) of zeolite beds were calculated according to the equation: $Q=(M_2–M_1)/M_1$, where M1 (g) is the initial weight of the sorbent, M_2 (g) is the weight of the sorbent after oil sorption.

Results and discussion

Characterization of adsorbents

The mineral composition of the zeolite materials are shown in Figure 1. In the products of the synthesis reaction, except for zeolite phases, the presence of unreacted mineral phases of fly ashes were determined; such as mullite, quartz and alluminosilicate glass.

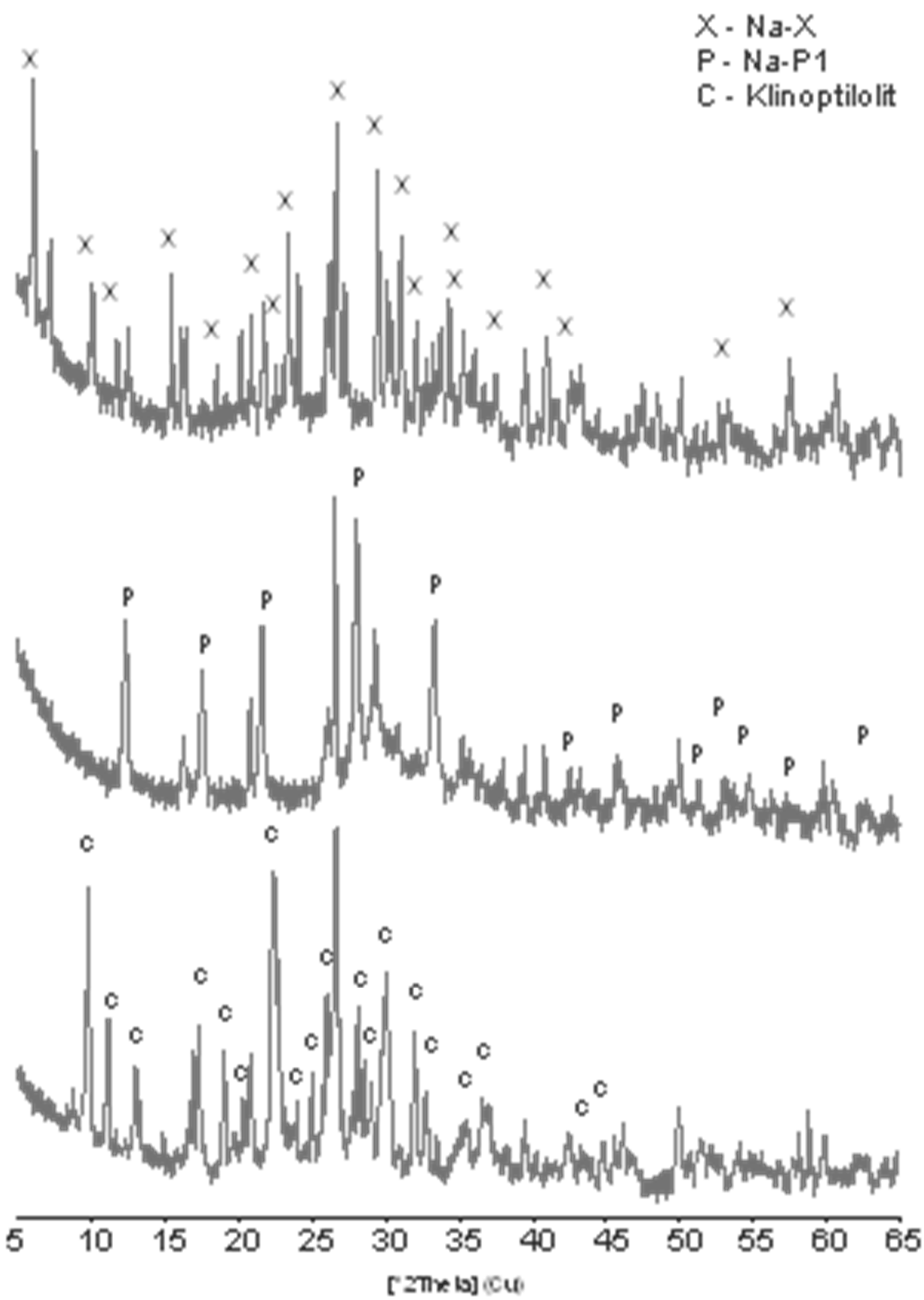


Fig. 1. XRD patterns of investigated zeolites

The obtained XRD patterns confirmed the presence of appropriate zeolite phases in the tested materials. Clinoptilolite represents a framework type of heulandite, Na-P1 a type of gismondite; and Na-X a type of fauiasite. The types of mineral frameworks are presented in Figure 2.

Scanning electron microscopy SEM was performed with the use of FEG Quanta 250 microscope. This method allows to obtain more pieces of information about the size and morphology of crystallites and their clusters. SEM images are presented in Figure 3.

Clinoptilolite occurs in the form of aggregates with a size of 20-30 µm with a lamellar and acicular form. Na-P1 zeolite type creates scaly clusters, whereas Na-X zeolite type forms isomeric crystals whose dimensions range from 5 to 7 µm.

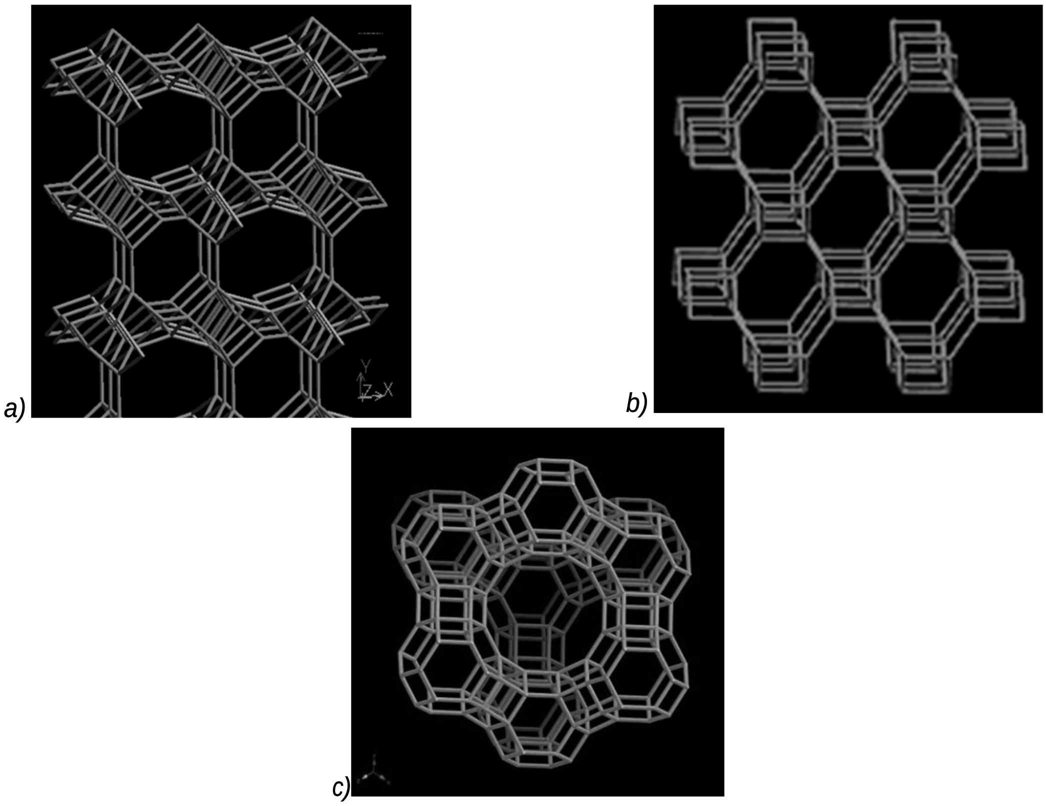


Fig. 2. Framework types of a) clinoptilolite (HEU), b) Na-P1 (GIS), c) Na-X (FAU) http://izasc.ethz.ch/fmi/xsl/IZA-SC/ft.xsl

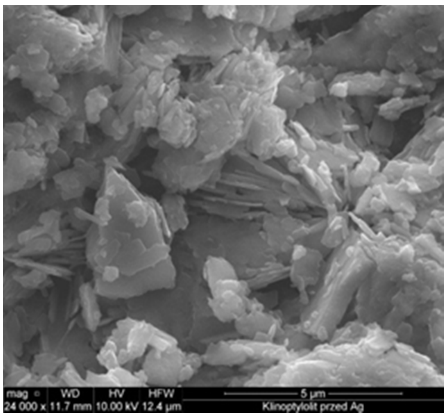
The chemical composition of the tested zeolites determined with the use of XRF is presented in Table 2. All tested zeolites contain a lot of oxides, but they are mainly composed of SiO_2 and Al_2O_3. Clionoptilolite contains 68,02 % of SiO_2 and 12,92 % of Al_2O_3, Na-P1 37,93 % and 18,83 % of SiO_2 and Al_2O_3 respectively, whereas Na-X contains 34,98 % of SiO_2 and 24,54 % of Al_2O_3.Those proportions are connected with the Si/Al ratio on the basis of which a surface charge and surface properties can be estimated. Si/Al ratio for clinoptilolite is 4,64, for Na-P – 1,78 and for Na-X – 1,26. Other oxides, such as Na_2O, MgO, K_2O, CaO and Fe_2O_3 are present in smaller quantities.

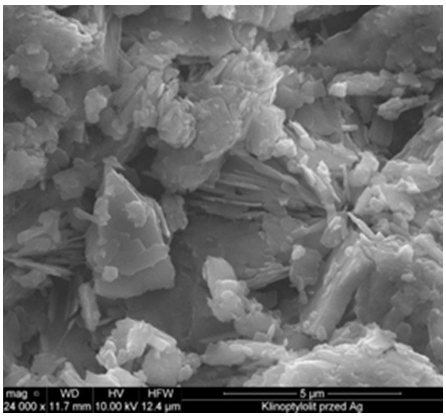
The low temperature N_2 adsorption/desorption isotherms of tested zeolites are shown in Figure 4. According to the IUPAC classification (IUPAC, 1976), the shapes of presented isotherms represents a mixed type I and IV (Shneider, 1995; Kubu et al., 2014), which indicates the microporous and mesoporous chracter of examined materials. The hysteresis loops are similar to the types H2/H3, distinctive for slit shaped pores or “ink-bottle” pores (Leofanti et al. 1998). The pore size distributions obtained from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) indicate that the materials are mesoporous, with the domination of the pores in the size of circa 4 nm.

Table 2

Chemical composition of tested zeolites

Component	Clinoptilolite, %	Na-P1, %	Na-X, %
Na_2O	0,69	6,57	5,41
MgO	0,75	1,15	2,59
Al_2O_3	**12,92**	**18,83**	**24,54**
SiO_2	**68,02**	**37,93**	**34,98**
P_2O_5	0,16	0,31	0,35
SO_3	0,09	0,25	0,16
K_2O	3,36	1,00	0,56
CaO	3,71	14,41	9,05
TiO_2	0,20	0,83	1,40
MnO	0,06	0,08	0,15
Fe_2O_3	2,11	5,09	7,23
LOI	8,57	13,89	15,61

a) 

b) 

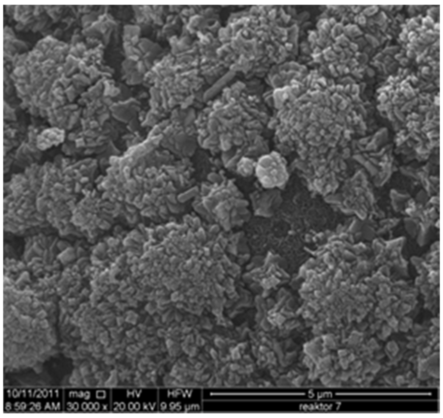
(c) 

Fig. 3. SEM images of tested zeolites a) clinoptilolite, b) Na-P1, c) Na-X

Table 3 presents textural parameters of tested zeolites. Material Na-X has the largest specific surface area - 236,4 m^2/g. This material contains a lot of micropores and narrow mesopores with average diameters of 3,6 nm. When it comes to material Na-P1, it also has mesoporous character with the specific surface area of 86,8 m^2/g, but contains less micropores than Na-X.

Table 3

Textural parameters of investigated zeolites

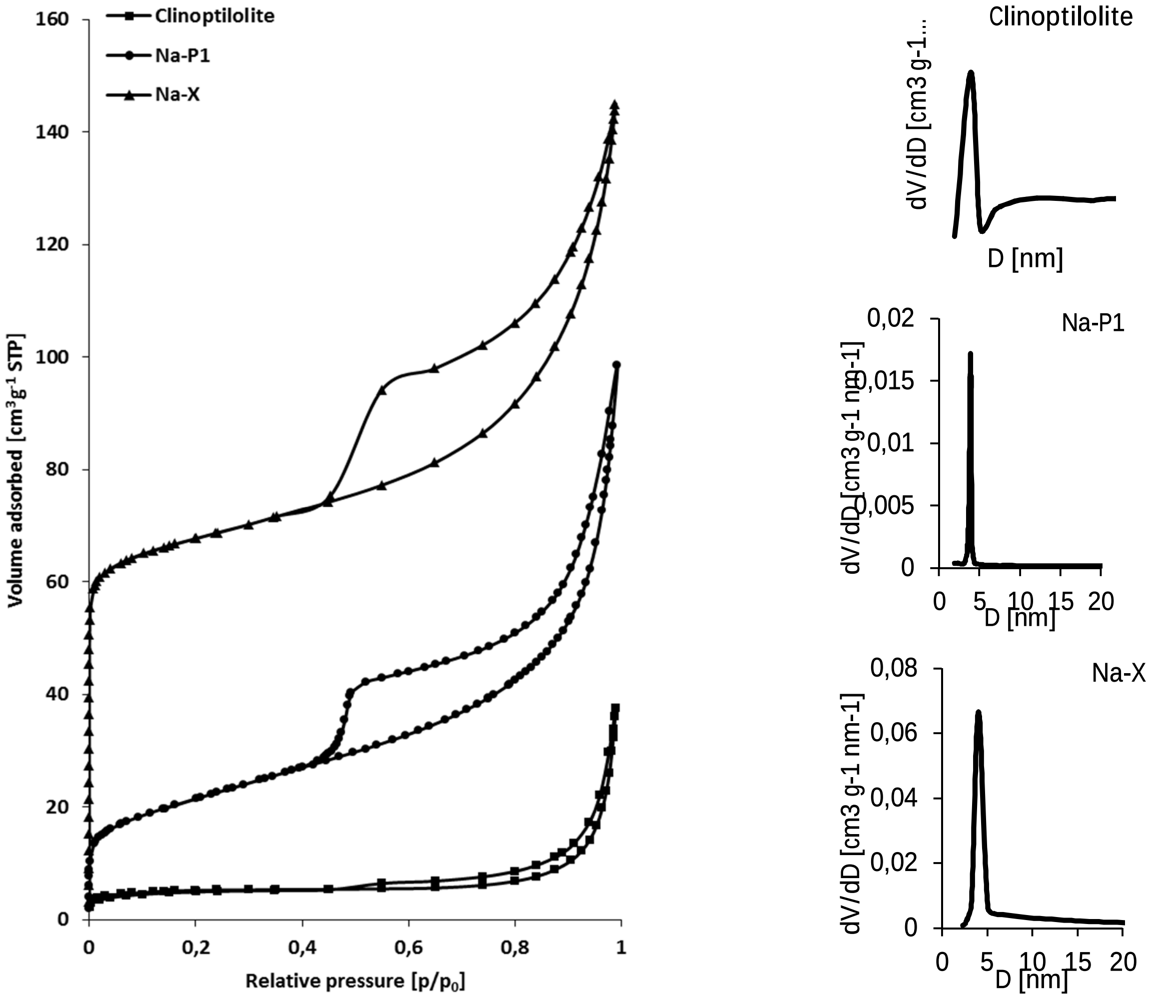
Material	S_{BET} m^2/g	V_{mic} cm^3/g	S_{mic} m^2/g	V_{mes} cm^3/g	S_{mes} m^2/g	D_p nm
clinoptilolite	18,3	0,05	7,68	0,0046	10,65	10,5
Na-P1	86,8	0,32	32,84	0,0143	54,01	11,6
Na-X	236,4	0,214	62,99	0,077	173,45	3,6

Where: S_{BET} – specific surface area, V_{mic}/V_{mes} – volume of micropores/volume of mesopores, S_{mic}/S_{mes} – surface of micropores/surfacde of mesopores, D_p – average diameter of pores

Mesopores of Na-P1 are wider, with the average diameter size of 11,6 nm. Clinoptilolite is characterized by smaller specific surface area – 18,3 m^2/g and the average diameter of pores is about 10,5 nm. Textural properties can be crucial for the oil sorption phenomena.

Oils adsorption experiment

Results of the oils sorption onto clinoptilolite and mixed zeolite beds are shoiwn in Table 4. Clinoptilolite beds (20 g) were able to sorb 4,97 g of Verva ON and 4,98 g of Biodiesel. It can be noticed that a small addition (25 %) of synthetic zeolite can significantly improve the sorption capacity of the mineral beds (about two times). Zeolite mixture with Na-P1 was able to sorb the largest amounts of oils. 9.91 g of Verva ON, and 10.72 g of Biodiesel was immobilized on this zeolite bed. A mixture with Na-X was able to sorb slightly less of petroleum substances than a fixed bed with Na-P1; about 8.29 g of Verva ON and 9.37 g of Biodiesel.



a) *b)*

Fig. 4. a) N_2 adsorption/desorption isotherms and b) pore size distribution of examined zeolites

Table 4

Average mass of oils (g) sorbed by 20 g of the bed

Bed	**Verva ON**	**Biodiesel**
Clinoptilolite	4,97	4,98
Clinoptilolite/Na-P1 mixture	9,91	10,72
Clinoptilolite/Na-X mixture	8,29	9,37

What is more, sorption capacity increased with the increase of oil density (Table 1). Thus, the sorption capacity was lower for Verva ON and higher for Biodiesel. The time that was needed for draining, depended on the type of material as well as the type of oil. For clinoptilolite it was about 6 hours, whereas zeolite mixtures drained about 24 hours. The form of clinoptilolite was a granulated fraction (1-2 mm), whereas synthetic zeolites were in a form of powder. Thus, the time needed for complet saturation of the fixed zeolite beds were much longer than for clinoptilolite bed. The differences in duration reflected the speed at which the oil penetration reached equilibrium state. Moreover, Verva ON runs down through the beds slightly faster than Biodiesel. These differences arise from the dynamic viscosity of the petroleum substances. More viscous oil (Biodiesel) penetrates the pores of the sorption bed with lower speed and thus, the complete saturation of pores and equilibrium is reached after longer period.

Textural parameters of tested materials, especially specific surface area and diameters of pores, are responsible for the sorption capacities of examined mineral beds. Specific surface area S_{BET} of Na-P1 was 86,8 m^2/g, Na-X was 236,4 m^2/g and of clinoptilolite – 18,2 m^2/g. Total S_{BET} is built by the surface of meso- and micropores, but the surface of micropores is not available for large particles of petroleum substances. The sorption of oils on mixed zeolite beds is higher than on clinoptilolite bed because of higher specific surface area of the synthetic zeolites. However, despite higher S_{BET} of Na-X, the sorption capacity for clinoptilolite/Na-X mixed bed is lower than for clinoptilolite/Na-P1. It is due to the fact that Na-X has a lot of micropores in the structure, which are not available for oils. Moreover, mesopores of Na-X are thinner than mesopores of Na-P1 (Na-X 3,6 nm of average pore diameters, and Na-P1 – 11,6 nm). What is more, the viscosity of oils is high. This parameter is a fluid resistance to flow. Thus, the sorption process into the depth of pore structure of the materials is hindered. Moreover, Na-P1 is characterized by a larger diameter of pores and the largest part of its surface area takes part in the process of oil sorption. Taking into account these dependencies, it could be assumed that oil sorption process has physical nature and occurs mainly on the external surface of examined materials.

Conclusions

The adsorption of diesel fuels on zeolite beds and the influence of the synthetic zeolites addition on the sorption capacities of the beds were investigated. It can be concluded that a small addition of synthetic zeolite (25%) significantly improves the sorption capacity of the beds (about two times). The most efficient was the mixed clinoptilolite/Na-P1 bed.

Therefore, it can be summed up that the clinoptilolite with added synthetic zeolites Na-P1 and Na-X possess high adsorption properties of oils and can constitute an effective sorbent for the removal of petroleum substances leakages that appear, for example, during road accidents.

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