Synthetic zeolites from fly ash as effective mineral sorbents for land-based petroleum spills cleanup

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GRAPHICAL ABSTRACT
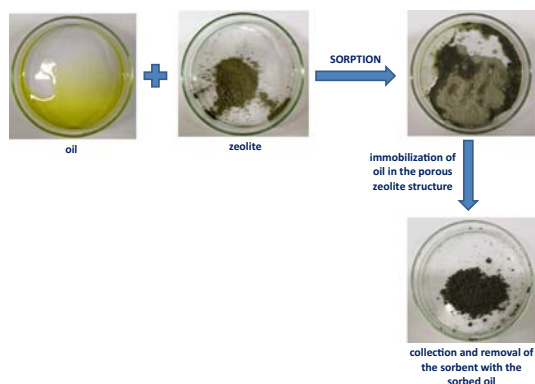
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ABSTRACT

Sorption of two diesel fuels and used engine oil by two synthetic zeolites Na-P1 and Na-X derived from fly ash was studied in comparison to natural clinoptilolite and commercial sorbent Absodan. The sorbents were characterized by X-ray diffraction, scanning electron microscope, nitrogen adsorption/desorption, bulk density and particle size distribution. Densities and viscosities of the oils were determined, as well. Synthetic zeolites exhibited around two times higher sorption capacity than Absodan, while for clinoptilolite the sorption capacity was the lowest. Na-P1 sorbed around $0.91\ g\ g^{-1}$, Na-X around $0.79\ g\ g^{-1}$, Absodan $0.52\ g\ g^{-1}$, and clinoptilolite $-0.36\ g\ g^{-1}$ of used engine oil. The sorption process had mainly physical character and mesopore filling seemed to play the dominant role, so particle size distribution and sorbents texture were decisive for petroleum products immobilization. Higher sorption capacities were noted for oils with higher densities.

1. Introduction

Sorption and removal of petroleum products currently attracts a wide interest of researchers due to increasing risks of environmental contamination during petroleum mining, processing, transport, distribution, storage and exploitation [1]. Numerous ecological disasters have been caused by undesirable petroleum products spills, for example [2]: in 1970 and 1971 – the Gulf of Mexico drilling rig incidents; 1978 – the breakdown of the Piper Alpha Platform in the North Sea; 1989 – the Exxon Valdez spill in Alaska; 1991 – operation Desert Storm that released a huge amount of oil into the Arabian Gulf; 1999 – the Erika spill in France; 2002 – the Prestige

spill in Spain; 2010 – the BP Deepwater Horizon spill in the Gulf of Mexico, and regular petroleum leakages in the Niger Delta since 1958. Apart from financial losses, such incidents cause huge and sustained devastation in Earth's ecosystems and harm living organisms [3–10]. These environmental disasters together with some local scale incidents seriously endanger the environment. It reveals the need for improving oil spill cleanup methods and the development of new materials which can be applied for this purpose.

Mechanical, biological and photochemical methods are used for the removal of petroleum products [11–14], among which the mechanical methods involving solid adsorbents have been identified as the most effective [15,16]. Adebajo et al. [17] distinguished three groups of adsorbents: synthetic mineral products, synthetic organic products and natural materials. These include active carbon [18], silica gels [19], fly ash [20], perlite [21], chrome shavings [22], clay minerals [23], exfoliated graphite [24,25], graphene [26], polyurethane [27], polystyrene [28], rice husk [29–31], kapok fiber [1,32,33] and many others.

The vast majority of the subject literature deals with the removal of petroleum products from aqueous media, however only a few papers concern land spills, mostly occurring during car accidents [34]. In the latter events mainly loose mineral sorbents are used to remove oil spills from pavements or roads because of their practical features. Mineral sorbents are non-flammable, cheap, easily available and re-utilizable. Moreover, they retain the adsorbed liquid inside a stable porous structure and do not release it under higher pressures. Among mineral sorbents, zeolites are extremely important and widely used due to their unique properties. Zeolites are porous, hydrated, crystalline aluminosilicates of mainly alkali or alkaline earth elements, possessing a three-dimensional lattice composed of tetrahedrons $[AlO_4]$ and $[SiO_4]$ connected by their corners [35]. Zeolites structure is characterized by regular system of channels and chambers which brings a number of unique properties, including large sorption capacity, ion-exchange, molecular-sieve and catalytic properties. Natural zeolites are represented by more than 100 minerals, but only a few of them (clinoptilolite, mordenite, philipsite, chabazite) occur in forms accessible for mining. Synthetic zeolites are commonly obtained from clay minerals [36], silicate group minerals [37], chemicals [38] or fly ash [39–47]. By varying synthesis conditions desired zeolite structures can be derived. So far, over 150 types of zeolites have been obtained artificially. Synthetic zeolites exhibit better sorption properties than the natural ones. Both natural and synthetic zeolites are widely applied in environmental protection [48–50] for sludge and water purification from heavy metals and ammonium ions [35,51–53], and radionuclides [54]. They are used for sorption of combustion gases, such as SO_x, CO_x and volatile Hg removal [55,56]. A few literature reports concern application of zeolites for the removal of organic compounds from aqueous systems or industrial gases [57–61]. However, zeolites have not been used as sorbents of petroleum products in land oil spills.

In this paper sorption of three oil products by synthetic and natural zeolites was studied. The effects of textural properties and particle size distribution of the sorbents, and oil physical parameters on the sorption process were elucidated. A commercial mineral sorbent, Absodan, most frequently used for the removal of petroleum spills from roads and pavements by rescue services was selected as a reference material.

2. Materials and methods

2.1. Materials

Natural clinoptilolite from Sokyrnytsya deposit (Transcarpathian region, Ukraine), two synthetic zeolites Na-P1 and Na-X produced in the hydrothermal conversion reaction as presented by Franus [44] and Wdowin et al. [47] from F class fly ash (Kozienice Power Plant, Poland), and a reference material Absodan (Damolin company, Denmark) were used as sorbents. Clinoptilolite and Absodan were gently ground in a ball mill and <2 mm fractions (dry sieving) were selected for further experiments. Prior to the experiments the sorbents were dried at 105 °C for 12 h to remove adsorbed water.

Likely to be involved in land-based spills, two commercial diesel fuels such as Verva On and Biodiesel B100 (Polish petrol stations network Orlen) and used engine oil purchased from the oils wholesaler "Oleum" Lublin were used as adsorbates.

2.2. Materials characteristics

Particle size distribution of the sorbents was analyzed by areometric method according to ISO 11277, 2009 [62]. Bulk density was determined using Hosokawa Powder Tester provided by Hosokawa Micron Ltd. The mineral composition of the sorbents was determined from powder XRD spectra (2θ from 5° to 65°) registered using Philips X'pert APD with PW 3020 goniometer, Cu lamp and graphite monochromator. The percentage content of pure zeolite phase in materials was estimated with the use of the Rietveld method. Scanning electron microscope images were taken using FEI Quanta 250 FEG microscope. Nitrogen adsorption/desorption isotherms were measured at −194.85 °C using Micromeritics ASAP 2020 device. The BET specific surface area, BJH (Barret–Joyner–Halenda) nanopore size distribution functions, the total pore volume at maximum p/p_o (desorption), and micropore volume, surface area, and external surface area by the t-plot method were estimated from the isotherms using ASAP 2020 software provided by the equipment manufacturer. The whole measured pore size range was divided into two subranges: micropores (less than 2 nm) and mesopores (from 2 to 50 nm).

The densities of the tested oils were measured pycnometrically. Their viscosities were determined using rotating rheometer Brookfield R/S Plus. Due to wide range of viscosity, diesel fuels were studied using coaxial cylinders system (DIN 53453 [63]), while for used oil the cone-plate C50-1 system was used (DIN 53018 [64]). The above measurements were performed at 20 °C controlled by Lauda Ecoline RE 206 thermostat.

2.3. Sorption experiments

Oil stains of different volumes/masses were placed in Petri dishes covered with 5 g portions of each (dried) sorbent. The weight ratio (w/w) of oil to the sorbent ranged from 0.25 to 2.0. After 24 h the samples were taken out and placed on a lignin layer to remove excess oil. Next, the amount of the sorbed oil was estimated from carbon content in the samples measured by dry combustion using Perkin Elmer 2000 CHN analyzer. Analyses for each sorbent and oil were performed as a background. All tests were carried out in triplicate at 20 °C.

3. Results and discussion

3.1. Physical properties of the materials

Diesel oils have similar densities (0.833 g cm^{-3} Verva On; 0.876 g cm^{-3} Biodiesel and 0.881 g cm^{-3} used oil) but various dynamic viscosities (0.36×10^{-7} Pa s Verva On; 0.66×10^{-7} Pa s Biodiesel and 0.1703 Pa s used oil).

Natural clinoptilolite has the highest bulk density, 0.841 g cm^{-3}. Bulk densities of both synthetic zeolites are similar (0.435 g cm^{-3} Na-X and 0.472 g cm^{-3} Na-P1) and this of Absodan equals 0.542 g cm^{-3}. Particle size distribution (PSD) of the studied

sorbents is presented in Fig. 1. The Na-P1 PSD distribution is homogenous with a single peak located around 20 μm. Similar particle size distribution was found for Absodan, however its 20 μm peak is broader. The peak of homogenous PSD function of Na-X 0.9 μm is shifted towards greater particle sizes, around 50 μm. Clinoptilolite particles are distributed bimodally (20 μm and 250 μm peaks). Comparing to the other sorbents the Na-P1 is composed from the smallest particles.

3.2. Mineralogical characteristics

Figs. 2 and 3 present XRD patterns and SEM images of the studied sorbents, respectively. Zeolite phase content in Na-P1, evidenced by the main *d*-spacing d_{hkl} = 7.10, 5.01, 4.10 and 3.18 Å, was about 80%. Microprobe chemical analyses showed that sodium is the main cation balancing the charge of the aluminosilicate lattice. Na-P1 has the form of pillars forming rosette blends of sizes usually exceeding 10 μm (Fig. 3a). Zeolite phase content in Na-X, evidenced by the main *d*-spacing d_{hkl} = 14.47, 3.81, 5.73, 8.85, 4.42, 7.54, 4.81, and 3.94 Å was about 60%. Sodium is also the main exchangeable cation. Na-X occurs as regular cubic forms of crystals about size of 3–6 μm (Fig. 3b). The content of clinoptilolite in natural zeolite is about 75%, and it is recognized from characteristic distances d_{hkl} = 8.95; 7.94; 3.96 and 3.90 Å. The other mineral com-

ponents which occurred are opal CT, quartz and feldspars. Calcium is the main exchangeable cation. Clinoptilolite occurs in forms of thin plates (around 10 μm), sometimes of distinct hexagonal shapes (Fig. 3c). Absodan is composed of opal/chalcedony, plagioclasic feldspars and traces of illite and hematite. In the SEM image some fragments of diatomites can be observed (Fig. 3d).

3.3. Nitrogen adsorption analysis

The nitrogen adsorption–desorption isotherms at −194.85 °C and nanopore size distribution curves are illustrated in Fig. 4. The adsorption branches of the isotherms belong to II type of IUPAC classification [65] that characterizes multilayer physical adsorption on porous solids with strong adsorbent–adsorbate interactions [66]. Generally the adsorption process in the range of low relative pressures (p/p_o below 0.35) is dominated by monomolecular adsorption. Next, polymolecular adsorption and capillary condensation processes dominate [67]. For the studied synthetic zeolites at very low relative pressures (below 0.01) extremely rapid increase of nitrogen adsorption is observed, that is most evident for Na-X. It suggests the existence of very strongly energetic adsorption centers on these adsorbents surfaces. Large amount of highly energetic centers may occur on roughnesses and/or defects present on large surface or between walls of very fine pores (more probably in the case
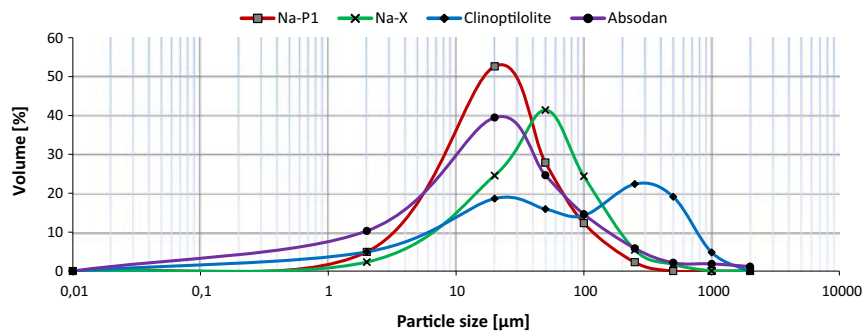

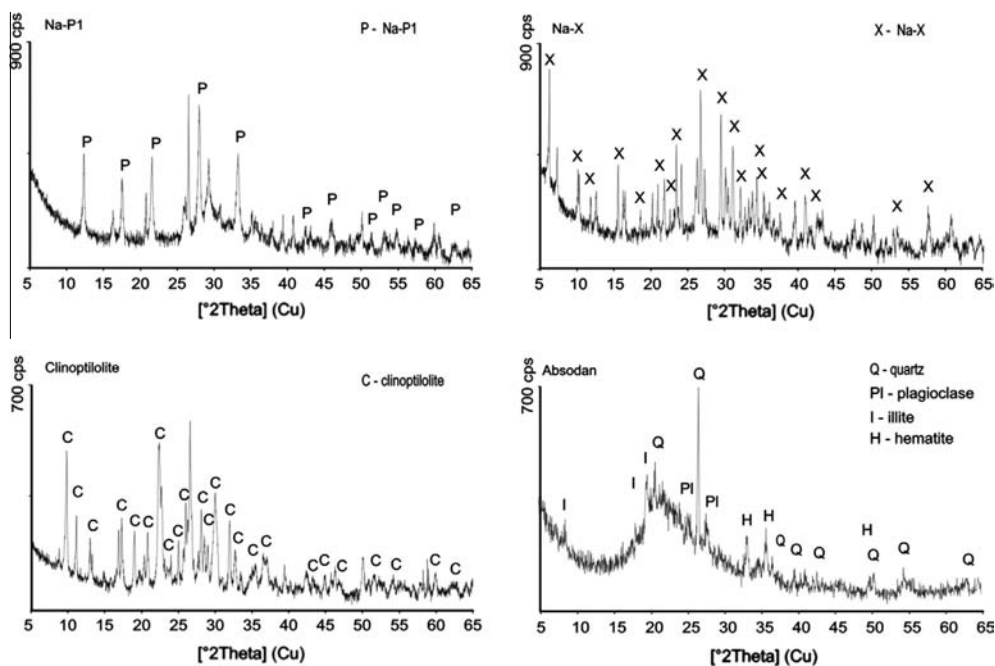**Fig. 1.** Particle size distribution of Na-P1, Na-X, clinoptilolite and Absodan.

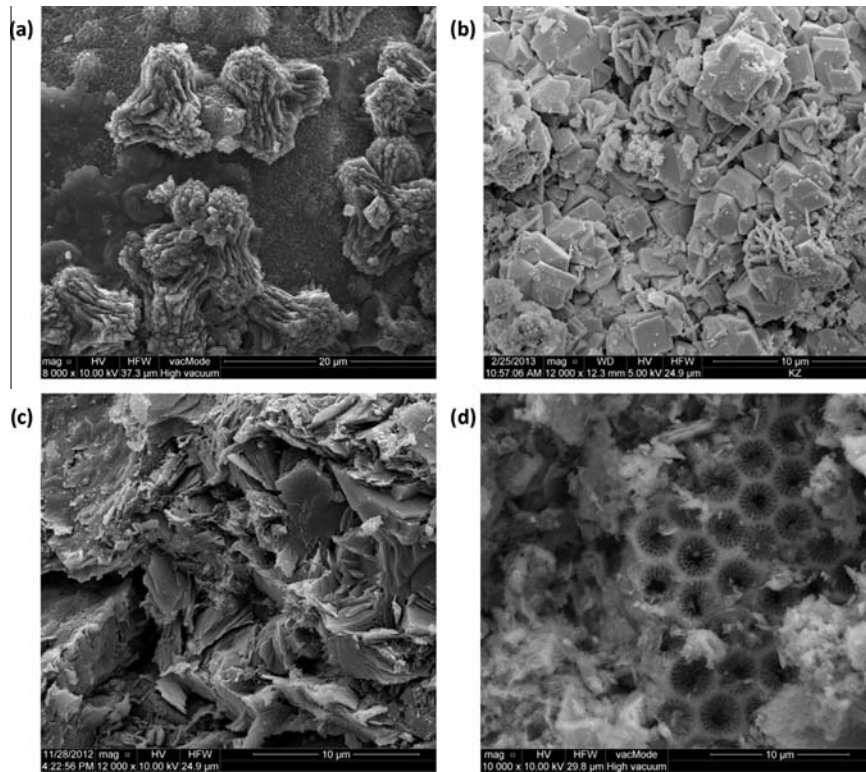**Fig. 2.** XRD patterns of Na-P1, Na-X, clinoptilolite and Absodan.

Fig. 3. SEM images of the investigated materials: (a) Na-P1, (b) Na-X, (c) clinoptilolite, (d) Absodan.

of zeolites) wherein the adsorbate molecules interact with the whole surface of the surrounding pore wall.

The adsorption–desorption hysteresis loops are observed at p/p_o range between 0.46 and 0.98 (maximum pressure) for all materials that indicates the existence of large amount of nano-size pores [68–70], particularly for the synthetic zeolites. Adsorption/desorption hysteresis loops are of H2/H3 type according to the IUPAC classification and they characterize solids with slit shaped pores (plates or faced/edges particles like cubes) of nonuniform sizes or shapes [67] or ink-bottle ones [58,71].

Nanopore size distributions determined from the isotherms for zeolites are homogenous. Pores of around 4 nm are determined in all above sorbents (3.9 nm Na-P1; 4.0 nm Na-X; 3.8 nm clinoptilolite). For Absodan the pore size distribution is bimodal in which 3.8 nm and 6.5 nm diameter pores are distinguished.

Textural parameters of the studied sorbents (BET micropore and external surface areas, micropore and total pore volumes, and average diameters of sorbents pores and grains) are presented in Table 1. The BET specific surface area of Na-X is the highest and for the natural clinoptilolite is the lowest. The surface area of Absodan is only slightly larger than for clinoptilolite. Na-X has the narrowest pores, whereas the widest pores are found for Absodan. Pores in clinoptilolite and Na-P1 are of intermediate and similar diameters. The total pore volume is the largest for Na-X and the lowest in clinoptilolite. Synthetic zeolites have significantly larger pore volumes than the other materials. The structure of all studied sorbents is characterized by significantly smaller volume of the nanopores than of the micropores, that is particularly evident for synthetic zeolites.

3.4. Oil sorption

The oil sorption equilibrium after 24 h is illustrated exemplary in Fig. 5 for Na-P1 and Biodiesel. At low ratios of oil to sorbent (0.25–0.5) practically whole oil was sorbed and only its thin layer remained on external surfaces of sorbent grains. With increasing oil mass, saturation of the sorbents increases up to their complete filling and further the saturated material formed greasy pulps for which the maximum sorption capacity has been certainly exceeded. Finally, a layer of excess oil was seen above the surface of the sorbent that occurred at different oil/sorbent ratios for various materials studied (1.5–2.0 for synthetic zeolites; 0.5–0.75 for clinoptilolite and around 0.75 for Absodan).

Fig. 6 presents amounts of oils sorbed by the studied sorbents at different oil/sorbent ratios. For oil/sorbent ratio exceeding 1, sorption of each oil reaches a constant level for every sorbent equal to its maximal sorption capacity. Na-P1 has the largest sorption capacities in respect to all oils studied (around 0.91 g g^{-1} for the used oil and around 0.86 g g^{-1} for Verva and Biodiesel). This indicates that synthetic zeolite Na-P1 is the most effective sorbent for petroleum products. Sorption capacities of Na-X are slightly smaller (around 0.79 g g^{-1} for the used oil and Biodiesel, and 0.75 g g^{-1} for Verva), and sorption capacities of clinoptilolite are the smallest (around 0.36 g g^{-1} for the used oil, 0.27 g g^{-1} for Biodiesel and 0.23 g g^{-1} for Verva). Absodan sorption capacities towards the examined oils are around two times higher than these of clinoptilolite, however they are still evidently lower than for synthetic zeolites (around 0.52 g g^{-1} for the used oil, 0.50 g g^{-1} for Biodiesel and around 0.41 g g^{-1} for Verva).

Sorption capacity increased with increasing oil density, being the lowest for Verva On, higher for Biodiesel and the highest for used oil that is presented in Fig. 7. Textural parameters of the sorbent materials seem to govern their sorption capacity for petroleum products, as this was postulated by Carmody et al. [66]. Sorption capacities of the studied sorbents (average sorption capacities of each sorbent for 3 studied oils, further abbreviated as SC) increase with specific surface area, however the dependence between both parameters is nonlinear (SC ~ 0.24ln(S_{BET}); R^2 = 0.90). Usually a linear dependence of surface area and sorption capacity characterizes pure adsorption processes therefore high
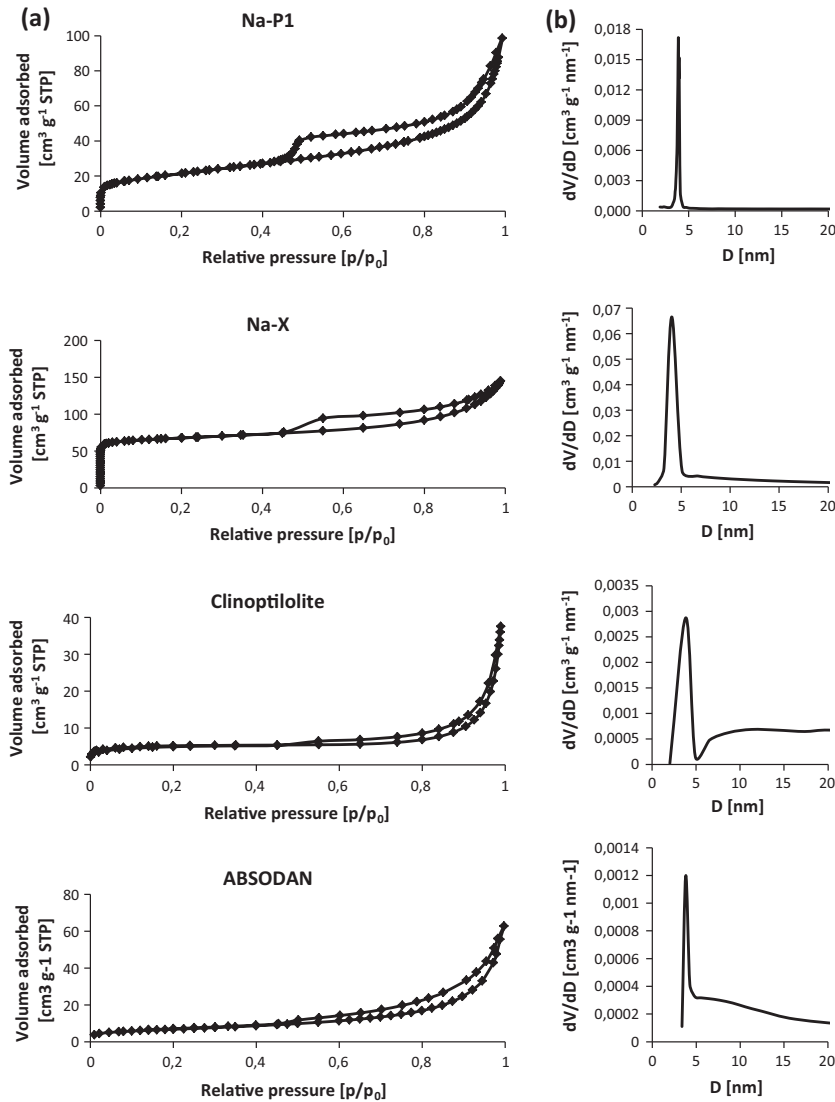
Fig. 4. (a) The N_2 adsorption–desorption isotherms at 77 K, and (b) BJH desorption pore size distribution of the examined materials.

Table 1
Textural parameters of Na-P1, Na-X, clinoptilolite and Absodan.

Sorbent	S_{BET} (m²/g)	S_{mic} t-plot (m²/g)	S_{ext} t-plot (m²/g)	V_{mic} t-plot (cm³/g)	V_{tot} single point desorption (cm³/g)	D_p (nm)	AGD (μm)
Na-P1	75.6	8.77	66.82	0.004	0.149	7.4	42.51
Na-X	236.4	173.45	62.99	0.077	0.214	3.6	75.50
Clinoptilolite	18.3	10.65	7.68	0.005	0.046	10.0	225.41
Absodan	24.1	2.39	21.72	0.001	0.089	16.1	101.84

S_{BET} – specific surface area; V_{mic}/V_{tot} – volume of micropores/all pores; S_{mic}/S_{mes} – surface of micropores/mesopores (external surface); D_p – average pore diameter, AGD – average grain diameter.

input of volumetric oil sorption should occur in all cases. Indeed the SC increases linearly with the volume of the sorbents mesopores, V_{me}, estimated as the total volume of pores minus volume of micropores (SC $\sim 5.8 V_{mes}$; $R^2 = 0.99$) and with the mesopore surface, as well (SC $\sim 0.01 S_{ext}$; $R^2 = 0.94$). The volumes of micropores does not correlate with SC that is probably connected with their very small quantities. However, the access of large hydrocarbon molecules to some narrow mesopores could be also hindered. Therefore, despite possessing higher volume of mesopores, Na-X exhibits lower SC than Na-P1 because of the smaller pore diameters. It is worth noting that the micropore surface area does not correlate with oil sorption capacities, as well.

Significant negative effect of the average size (diameter) of material grains, AGD, on sorption capacity was noted (SC ~ 0.0033 AGD; $R^2 = 0.88$). It can be possibly explained by that in larger grains more air is entrapped that suppresses penetration of oil into grains interior. In general physical mechanisms prevail in petroleum products sorption on the studied mineral sorbents.

We perform some other rough studies to estimate the penetration rate of the studied oils into the sorbents beds. The same masses of each sorbents were placed in polymer bags made from ordinary stocking, soaked in a given oil and weighed after the same time periods. The Verva ON penetrated all studied zeolites in 2–3 min and Biodisel in 20–30 min. It was visually assessed
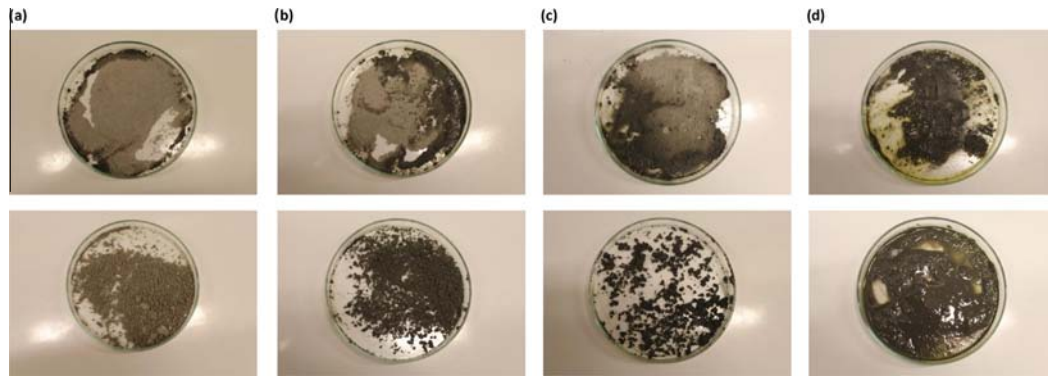
Fig. 5. Sorption of Biodiesel by zeolite Na-P1; above – oil spill covered by the sorbent, below – sorbent with immobilized oil, depending on different oil/sorbent ratio; (a) 50%, (b) 75%, (c) 100%, (d) 150%.
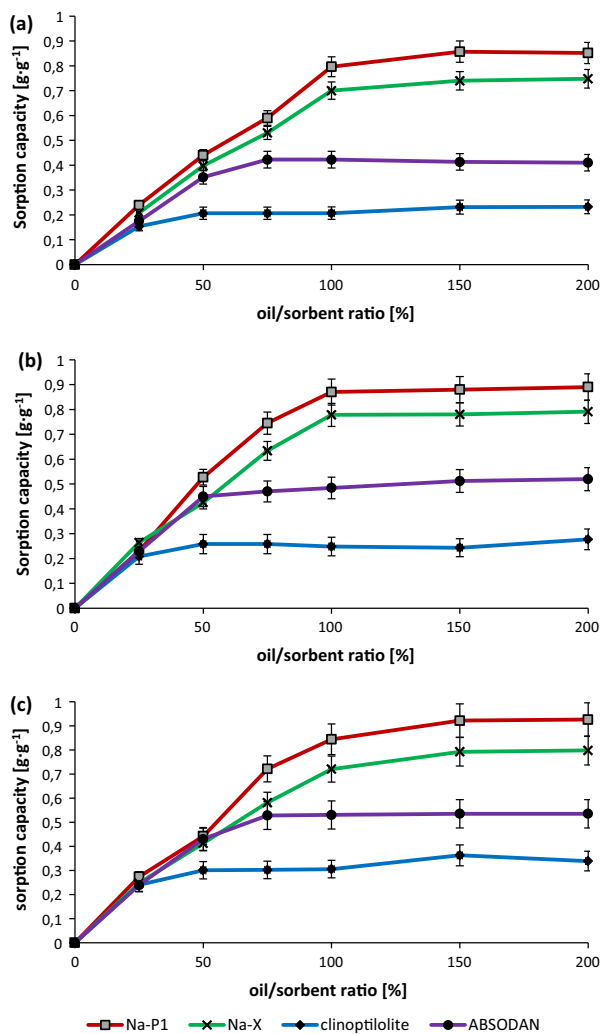

Fig. 6. Sorption capacities (g g^{-1}) of Na-P1, Na-X, clinoptilolite and Absodan depending on the oil to sorbent ratio (%) for the oils: (a) Verva ON, (b) Biodiesel, (c) used.

Fig. 7. Influence of oils density on the sorption capacity for Na-P1, Na-X, clinoptilolite and Absodan.

thicker layers than liquids of low viscosity. Therefore they "glue-up" parts of pores (or entrances to the next pores) having larger diameters thus entrapping more air inside the whole pore system.

For easy and effective oil removal, the used sorbent should be removed from a contaminated surface in a "dry" form. Thus, the maximum sorbent to oil ratio for synthetic zeolites should be around 0.75–1.0, for clinoptilolite around 0.5, and for Absodan 0.5–0.6.

4. Conclusions

Sorption of diesel fuels and used oil on natural clinoptilolite, synthetic zeolites Na-P1 and Na-X, and commercial sorbent Absodan is mainly of physical character and involves mesopore filling and external surface coverage. Therefore both particle size distribution and sorbents texture are decisive for sorption capacity towards petroleum products. Contrary to the surface of larger pores (mesopore surface area) that strongly correlates with oils sorption capacity, the BET specific surface area has seems not to affect the oils sorption.

Synthetic zeolites have two times higher oil sorption capacities than the other two sorbents. Higher sorption capacities were noted for oils with higher densities.

Synthetic zeolites obtained from fly ash are promising alternative for natural mineral sorbents for land-based petroleum spills cleanup. Moreover, application of zeolites obtained from waste fly ashes is an example of ecological and sustainable solution for environmental protection.

that both above oils penetrated the sorbents evenly. The used oil characterized by the highest viscosity was sorbed very slowly (12–15 h) and its penetration was uneven. It is possible that the used oil covers mostly the external surface of the sorbents grains while only small oil amount penetrates the pores. Moreover we think that oils of high viscosity may enter the pores as
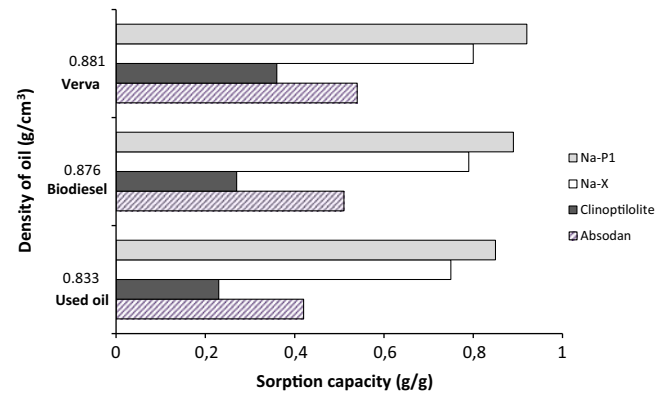
Acknowledgement

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