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

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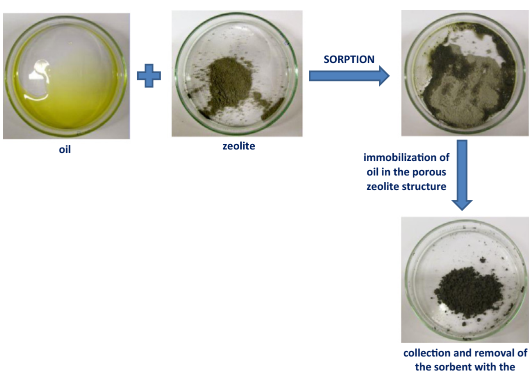
GRAPHICAL ABSTRACT



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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

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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