



Organically modified zeolites in petroleum compounds spill cleanup – Production, efficiency, utilization



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ARTICLE INFO

Article history:

Received 19 January 2016

Received in revised form 6 April 2016

Accepted 6 April 2016

Available online 23 April 2016

Keywords:

Sorption

Organo-zeolite

Gasoline

Diesel fuel

Motor oil

Ammonium salts

ABSTRACT

This study addressed the sorption of gasoline, diesel fuel, motor oil and used motor oil by various organo-zeolites. Clinoptilolite from the Sokyrnytsya deposit in Ukraine, zeolite Na-P1 synthesized from fly ash and their modifications with quaternary ammonium salts were used as adsorbents. The adsorption data shows that the materials prepared were effective in sorbing petroleum compounds, and that zeolite Na-P1 was the most efficient in the removal of petrochemicals. The absorbability of gasoline, diesel, engine oil and used engine oil occurs in the following order: Used engine oil > diesel > engine oil > gasoline. This was due to the physicochemical properties of the organic liquids – especially the viscosity and density. Gasoline with the smallest viscosity and density was the least-adsorbed petroleum compound. It has been found that the texture parameters, especially the ratio of mesopores in the zeolite's structure, determined the sorption properties of the material. Zeolites after the sorption of petroleum compounds can be re-used for the removal of organic liquids after the combustion process. The sorption capacity and texture parameters did not significantly decrease after each cycle of sorption-combustion-sorption. The results show that zeolite Na-P1 synthesized from fly ash is a suitable material to be used in the cleanup of petroleum compound spillages.

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1. Introduction

Petrochemicals are a crucial energy source in the world. Due to their widespread prospection, transport, storage and application, the probability for chemical spillages can be extremely high. The spillage of petrochemicals can result in substantial environmental damage and economic losses [1]. Many high profile cases of petrochemical spillages have been reported until now; such as: “Amoco Cadiz” [2]; “Erika” [3], “Exxon Valdez” [4]; “Atlantic Empress” with “Aegean Captain” collision [5] or the sinking of “Prestige” [6]. One of the most environmentally damaging ecological disasters in recent years was the British oil rig explosion of Deepwater Horizon in 2010 on the southern coast of the United States, in the Gulf of Mexico [7]. Due to recurring disasters in which petrochemicals are released into the environment, the concern for the pollution of water and soils by petroleum compounds is increasing and has led to research on the use of mineral sorbents [8–11].

For the removal of petrochemicals, various materials such as skimmers [12], solidifiers [13] and dispersants [14] are used. Studies on the use of sorbents which can be applied for both water treatment and contaminated soil treatment were carried out. The adsorbents used can be divided depending on the origin of inorganic mineral materials, organic

materials and natural and synthetic organic polymers [10]. Initially, attention was focused on natural organic materials such as asclepias [15], cotton fiber [1] and peat-moss [16]. However, such materials are buoyant, have a low sorption capacity in terms of oil and poor hydrophobic properties [17]. In practice, synthetic organic polymers such as polypropylene [18] and polyacrylate [19] are often used. Until now, studies on inorganic mineral materials include vermiculite [20], montmorillonites [1] and diatomites [21] were performed. Nowadays, studies on zeolites are becoming more frequent. Research on synthetic zeolites has confirmed their superior efficiency compared to the adsorbents currently used on a large scale to remove oil from hardened surfaces [10].

The primary components of crude oil and products from its processing are aliphatic (C_nH_{2n+2}), naphthenic (ie. cycloalkanes) and aromatic hydrocarbons [22]. It should be noted that in the aromatic hydrocarbon group, monocyclic, highly toxic compounds known as BTEX (benzene, toluene, ethylbenzene, xylene) are included [23,24]. Additionally, during the refining of crude oil, olefinic hydrocarbons (C_nH_{2n}) are produced. Previous studies on the sorption capacity of zeolites and organo-zeolites in the removal of BTEX, as well as studies on the removal of aromatic hydrocarbons from contaminated water have demonstrated very promising results [25–30]. Thus, conducting sorption experiments of petrochemicals on these materials is fully justifiable. Furthermore, these components tend to migrate – meaning that during the uncontrolled release of petrochemicals into soil, the contamination

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can also penetrate into other components of the environment, such as air or groundwater. So far, organically-modified zeolites have not been used in petroleum compounds' spill clean-up. However, all previous studies have suggested that they may be suitable sorbents.

Zeolites and organo-zeolites have attracted considerable attention for their use in contaminant treatment [31–38]. Due to the high demand for zeolites, methods to obtain their synthetic counterparts have been developed. Recently, the possibility of using fly ash for the synthesis of zeolites has been examined [39–41]. Natural and synthetic zeolites are characterized by a very good ion-exchange capacity and exhibit a high affinity with cationic forms. Their silicate packages are characterized by a negative overall charge. Therefore, all cations are willingly absorbed on their surface [42]. However, zeolites exhibit a weak affinity with the anionic form of metals and apolar organic compounds which limits their use [28,43]. Modification of these minerals by organic compounds such as quaternary ammonium salts brings a material with improved sorption properties [44,45]. To the best of our knowledge, the use of zeolite Na-P1 and clinoptilolite modified with various organic surfactants for the removal of gasoline, diesel fuel, motor oil and used motor oil has not been investigated to date. Zeolite Na-P1 is produced in the hydrothermal synthesis of F-class fly ash obtained from the Rybnik power plant in Poland. This synthetic zeolite is commercially available [29]. However, performing such experiments using organically-modified zeolites can help to identify a mechanism of adsorption of these compounds. Yet-to-be-documented information on the synthesis of the above organo-zeolites using unique surfactants, as well as their use for the sorption of petrochemicals would be found. Another challenge is to develop a method to utilize used sorbents. At the moment, sorbents with absorbed petrochemicals are not reused and are treated as hazardous waste.

The sizes of zeolite P1 and clinoptilolite chambers (4.5–7.0 Å) are smaller than the external particle size of surfactants (over 10 Å) [46]. Therefore, the modification process takes place only on the external surface of zeolites, where 10–30% of the active sites of the zeolite are located. Consequently, external cation exchange capacity (ECEC) is an important property in the synthesis of organo-zeolites. The previous study showed that apolar compounds' sorption takes place in the organic layer [28]. The surfactant layer of organo-zeolites is a solvent-like medium into which non-polar organic compounds tend to dissolve. It has been described that hydrocarbon chain length largely affects the hydrophobicity and subsequently influences adsorption properties [28,47]. HDTMA is the most widely used surfactant for the synthesis of organic derivatives of zeolitic minerals due to its availability, low cost and satisfactory results in improving the sorption properties of modified materials. The zeolites' surface modification process involves the introduction of a cationic organic form of HDTMA into the exchangeable positions (Ca, Mg, Na, K). The negative electrostatic charge of the structure is naturally compensated by organic cations adsorbed on the surface of crystallites [48]. As a result of the adsorption, organo-mineral complexes with unique sorption properties appear. Using surfactants such as HDTMA for zeolite modification has been extensively described in the literature referenced [27,28,38,49–51]. When it comes to the use of other surfactants with a shorter, longer or double carbon chain (eg DDTMA, DDDDMA, and DHDDMA), information is limited. All of described properties of zeolites generate an increasing need for thorough investigation into their application as petrochemical sorbents.

The objective of this study was to investigate a new method and set guidelines to select zeolites and surfactants for petroleum compounds' spill cleanup. The results would provide additional insight into evaluating the possibility of using zeolites and their organic modifications in enhancing petrochemicals spill cleanup. Additionally, the aim of the study was to find a regeneration method of mineral sorbents used in the removal of gasoline, diesel fuel, motor oil and used motor oil. The used sorbents were burned, and the properties of the solid matter were characterized. The subsequent material was then reused in the sorption.

2. Experimental

2.1. Materials

Clinoptilolite (Cp) from the Sokyrnytsya deposit (Trans Carpathian region, Ukraine) and synthetic zeolite Na-P1 were used in this study. Zeolite Na-P1 was produced from F class fly ash (Kozienice Power Plant, Poland) in the hydrothermal conversion reaction as presented by Wdowin et al. [52]. The synthesis of zeolite Na-P1 was performed under the following reaction conditions: 20 g of fly ash were mixed with 400 mL of 3 M NaOH at 75 °C for 24 h. The resulting product was of high purity, containing 81 wt.% Na-P1 zeolite, minor mullite and quartz. Both materials were described in the literature previously as materials used in the experiments of the BTX and heavy metals sorption [10,38,53,54].

2.2. Modification

Quaternary ammonium salts dissolve in the solutions dissociated into the anions (Br^-) and organic cations which possess a permanent positive charge. The mechanism of these cations' sorption onto zeolite surfaces includes the formation of a monolayer at the solid–aqueous interface via strong ionic bonds [31]. In the experiments of zeolite surface modifications, quaternary ammonium salts purchased from Sigma-Aldrich Co. were used. Eight surfactants were selected – with a differing number and length of carbon chain (Table 1). The selected salts contained tetra-substituted ammonium cations with a permanently-charged trivalent nitrogen and a single (C_{12} = DDTMA, C_{14} = TDTMA, C_{16} = HDTMA and C_{18} = ODTMA) or double ($2 \times \text{C}_{12}$ = DDDDMA, $2 \times \text{C}_{14}$ = DTDDMA, $2 \times \text{C}_{16}$ = DHDDMA and $2 \times \text{C}_{18}$ = DODDMA) long alkyl chain (Table 1). As the ammonium salt molecules are too large to enter the channels of the Cp and Na-P1, the modification of the zeolites takes place on the outer surface of the crystallites. Through ion exchange, naturally occurring inorganic cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} etc.) are replaced with organic cations. The external cation exchange capacities (ECEC) for Cp and Na-P1 were determined by the adsorption of HDTMA ions [38,55] and it was 11.45 meq/100 g for Cp and 24.40 meq/100 g for Na-P1. The surfactants used in the modification process are mainly composed of carbon, hydrogen and nitrogen [eg. HDTMA-Br: $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{Br})(\text{CH}_3)_3$]. By comparing the contents of C, H and N in the dried samples before and after the modification process, the calculation of the amount of surfactant adsorbed on the zeolite was possible. The difference in the percentage can be easily converted to the amount of adsorbed C, H, N [mg/100 g zeolite]. All calculations were made using the following formula: (eg. HDTMA):

$$\text{HDTMA}_{\text{ad}} = (\text{CHN}_{\text{difference}} / \text{mHDTMA})$$

where:

HDTMA_{ad} – the amount of HDTMA (mM) adsorbed on the 100 g of zeolite [mM/100 g zeolite];

$\text{CHN}_{\text{difference}}$ – the difference in the sum of: carbon + hydrogen + nitrogen before and after modification [mg/100 g zeolite]. The molar fraction of each element in the surfactant was taken into account during the calculation.

mHDTMA – molar mass of HDTMA.

After comparing the calculated amount with the value of the ECEC (meq/100 g of zeolite = mM/100 g of zeolite) the modification efficiency was found.

Due to advanced technology used to produce larger amounts of organo-zeolites which assume a maximum effective modification of 1.0 ECEC, the zeolites selected for the experiments were modified in an amount not exceeding of 1.0 ECEC [28] (Table 1). In order to obtain a surfactant coverage of 1.0 ECEC, it was necessary to use 11.45 and 24.4 mM of surfactant per 100 g of clinoptilolite and zeolite Na-P1 respectively. Each of the organo-zeolites were prepared by mixing 100 g

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