Abstract

The sorption process of organic substances on zeolites is limited by the negatively-charged surface of their crystallites. In order to increase the chemical affinity of the zeolite's surface organic cations in the form of quaternary ammonium salts were used. The modification of the synthetic zeolite Na-P1 and natural clinoptilolite was carried out using various surfactants as bromides: DDTMA (dodecyl trimethyl ammonium), TDTMA (tetradecyl trimethyl ammonium), HDTMA (hexadecyl trimethyl ammonium), ODTMA (octadecyl trimethyl ammonium), DDDDMA (didodecyl dimethyl ammonium), DTDDMA (ditetradecyl dimethyl ammonium), DHDDMA (dihexadecyl dimethyl ammonium), DODDMA (dioctadecyl dimethyl ammonium) in amounts of 1.0 of external cation exchange capacity (ECEC).

The aim of the study was to determine the sorption effectiveness of organically-modified zeolites: synthetic Na-P1 produced from waste fly ash and natural clinoptilolites in the form of benzene, toluene and p-xylene (BTX). Another objective was to investigate and compare the structural and textural features of synthetic zeolite Na-P1 and natural clinoptilolite modified by selected surfactants. Furthermore, the author investigated a novel method to select zeolites and surfactants for petroleum compounds' spill cleanup. The results provide additional insight into evaluating the possibility of using zeolites and their organic modifications in removal of volatile organic compounds from aqueous solutions and 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 synthetic zeolite Na-P1 and natural clinoptilolite used in this work show a significant ability to remove these compounds from an aqueous solution and it was observed that more than 80% of the initial concentration of BTX was removed from the solution. The adsorption data shows that the materials prepared were effective in petroleum compounds adsorption, and that zeolite Na-P1 was the most efficient in the removal of petrochemicals. The adsorption capacity of gasoline, diesel, engine oil and used engine oil was found to be in the following order: used engine oil > diesel > engine oil > gasoline. Moreover, it has been found that zeolites after the sorption of petroleum compounds may be re-used for the removal of organic liquids after the thermal regeneration process (combustion). The sorption capacity and textural parameters did not significantly decrease after consecutive cycles 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.

All experiments revealed that the surface modification of zeolites with organic surfactants is possible at room temperature (20°) with a very low water usage. The textural study of organo-zeolites indicated that the synthetic zeolite Na-P1 has better sorption properties than natural clinoptilolite. The modification process always reduces the specific surface area (S_{BET}) and porosity of the material. Moreover, with an increasing carbon chain length of surfactants all the texture parameters decrease. The novelty of this research was a comprehensive study of determining the effectiveness of modification using FTIR spectroscopy. This method can be adapted for various materials (synthetic and natural zeolites) modified with different surfactants. Thermal analysis revealed that the salt detachment begins through ammonium head-group decomposition which is followed by the hydrocarbon chain fragmentation and combustion.

The results of this research can be used in explaining the differences in sorption properties of various zeolites and their potential applications as sorbents of organic compounds and petrochemicals. All obtained results of this research can be used in environmental protection, the petrochemical industry and for further study regarding the properties of surfactant-modified zeolites.

Key words: Synthetic zeolites, organo-zeolites, BTX sorption, organic surfactants, petrochemical compounds removal, regeneration of used sorbents.