SYNTHESIS AND CHARACTERIZATION OF HYDROXYAPATITE/CLINOPTILOLITE ADSORBENT FOR REMOVAL OF ORGANIC POLLUTANTS

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ABSTRACT

Municipal wastewater, as well as agricultural drainage wastewater, is the main source of organic pollutants such as drugs and pesticides. Efficient, economically profitable and environmentally acceptable adsorbents for their removal are the subject of intensive research. In this work, a composite based on surfactant-modified zeolite and hydroxyapatite was synthesized. It was in detail characterized and examined as an adsorbent of two organic pollutants: one of the most commonly used antibiotics, ciprofloxacin, and an insecticide necessary in agricultural production, acetamiprid. The results showed that the obtained adsorbent removed 5.3 mg ciprofloxacin g^{-1} and 0.6 mg acetamiprid g^{-1} from the aqueous solution.

Keywords: zeolite, clinoptilolite, ciprofloxacin, acetamiprid, adsorption.

INTRODUCTION

The presence of organic pollutants in wastewater requires the development of new adsorbents that are economically profitable and environmentally acceptable. Before reuse or discharge into a water receiver, wastewater must be treated appropriately to meet strict quality standards. Natural zeolite-based composites available for the adsorption of organic pollutants can be prepared by simple synthesis methods and used as potential adsorbents in water purification systems. Pesticides can be found in drainage water due to their increasing use in agriculture. Acetamiprid (AC) is a new generation insecticide that is used instead of organophosphates and carbamates. Previous studies have shown that clinoptilolite from deposits in Ukraine removed 1.53 mg g^{-1} of lindane and 1.23 mg g^{-1} of aldrin from the aqueous solution with initial concentrations of 0.0405 μg ml^{-1} and 0.0250 μg ml^{-1}, respectively [1]. Ciprofloxacin (CIP) is one of the most commonly used antibiotics which has been detected in hospital wastewaters and the pharmaceutical industry. When adsorbing CIP from the aqueous solution with initial concentration of 15 mg dm^{-3}, clinoptilolite achieved maximum adsorption capacity of 4.39 mg g^{-1} [2]. In aqueous solutions at pH 7, CIP is found in the form of zwitter ions [3]. The aim of this work was the preparation of an adsorbent based on surfactant-modified zeolite clinoptilolite and calcium hydroxyapatite (HAp), its detailed characterization and an investigation of its potential application for the removal of AC and CIP from aqueous solutions.

EXPERIMENTAL

Natural zeolite (Z) modified with benzalkonium chloride (BC) was obtained according to the method described by Jevtic et al. [4]. Calcium hydroxyapatite (HAp) was synthesized on the surface of the modified zeolite by a hydrothermal process. Calcium chloride, ammonium hydrogen phosphate, urea and sodium ethylenediaminetetraacetate were added to the reaction suspension. In order to synthesize stoichiometric HAp, the Ca/P molar ratio was 1.67. The crystallization was carried out in hydrothermal conditions for 4 hours at 160 °C. The obtained adsorbent (ZHBC) was separated by filtration, washed and dried overnight at 105 °C. The adsorption properties of the prepared adsorbent were examined towards CIP and

AC from solutions with initial concentrations of 50 and 10 mg dm^{-3}, respectively. The adsorbent (0.1 g) was suspended in 40.0 cm^3 of CIP solution, i.e. in 20.0 cm^3 of AC solution under constant stirring at 105 rpm and 25 °C in a thermostated water bath. After predetermined time intervals, each sample was filtered through a membrane filter with a pore diameter of 0.45 μm. The residual concentrations of CIP and AC were determined using liquid chromatography-tandem mass spectrometry technique (Thermo Fisher Scientific).

X-ray powder diffraction analysis (XRPD) was used to check the crystallinity of the prepared adsorbent. XRPD patterns were recorded in the 2θ=5-55° at room temperature using an Ital Structure APD2000 diffractometer. Water and BC content were determined by thermogravimetric analysis (TG/DTG) using a SDT Q-600 simultaneous DSC/TGA instrument (TA Instruments). Interactions of BC with clinoptilolite lattice were studied by Fourier Transform Infrared (FTIR) Spectroscopy in the range 4000–450 cm^{-1} at room temperature using a Nicolet iS10 (Thermo Scientific) spectrometer. The morphology of the obtained sample was analyzed by a TESCAN MIRA 3 XMU electron microscope.

RESULTS AND DISCUSSION

The XRPD study (Fig. 1) of the ZHBC adsorbent showed that hydroxyapatite crystallized on the surface of the zeolite. The crystallinity of clinoptilolite was not significantly reduced after surfactant modification and HAp hydrothermal crystallization.

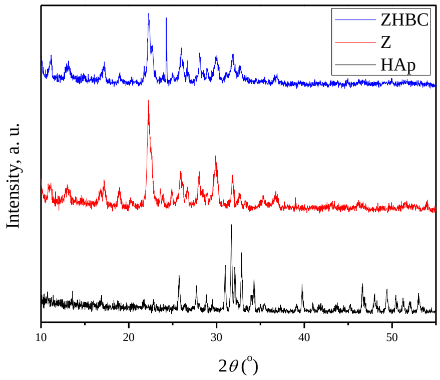

Figure 1. XRPD patterns of: ZHBC adsorbent, initial zeolite (Z) and calcium hydroxyapatite (HAp).

The results of the thermal analysis of the Z and ZHBC are shown in Fig. 2. By heating the samples to 800 °C, the total mass loss was 14.7 and 17.5 wt.%, respectively, which indicates the binding of surfactant molecules and the crystallization of HAp. It is observed that dehydration occurs in both samples at temperatures lower than 300 °C. DTG maxima in the ZHBC sample in the temperature interval 320-490 °C corresponds to the decomposition of the organic surfactant. Two step decomposition of BC is attributed to the presence of a bilayer on the clinoptilolite surface [5].

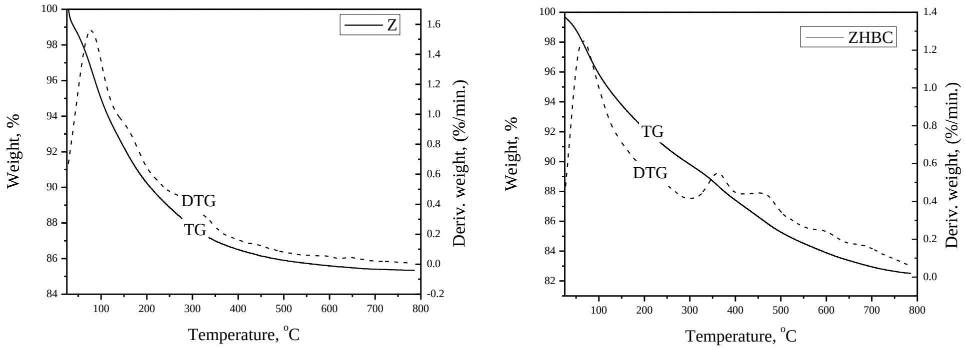

Figure 2. TG/DTG curves of Z and ZHBC samples.

FTIR spectra of Z and ZHBC are given in Fig. 3. The band at around 3600 cm^{-1}, present in both IR spectra, is characteristic for stretching vibrations of a free O-H bond. The band at 1640 cm^{-1} is associated with the absorbed vibrations of water, while the bands at around 1020 cm^{-1} are associated with the vibrations of the aluminosilicate lattice of zeolite. The characteristic stretching vibrations of the methyl groups from the BC (at 2920 and 2850 cm^{-1}) can be seen in the spectrum of ZHBC confirming the presence of BC in ZHBC.

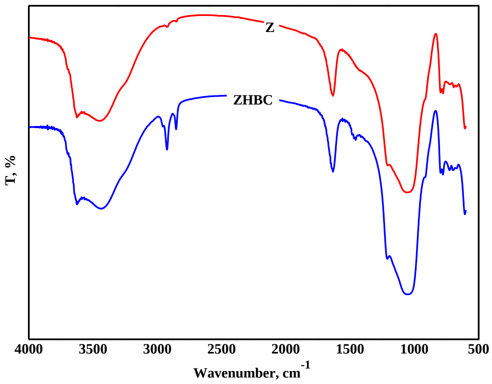

Figure 3. FTIR spectra of Z and ZHBC samples.

Fig. 4 shows the morphology of the ZHBC sample. It is observed that the formation of needle-like, unevenly distributed crystals of HAp occurred on the surface of the zeolite. In addition, spherical crystals with a diameter of 2-5 µm, characteristic of HAp were also detected in the sample.

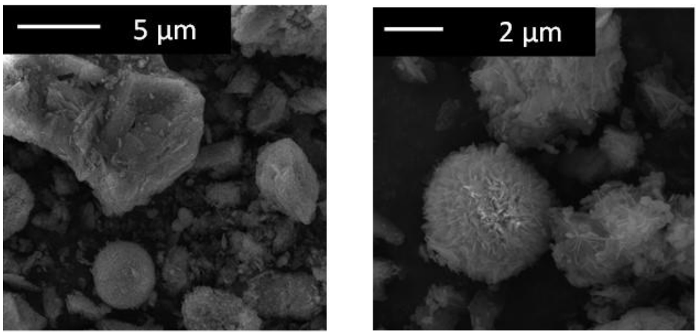

Figure 4. SEM images of ZHBC.

Fig. 5 shows the results of the adsorption capacity examination of the prepared composite towards CIP and AC. The ZHBC adsorbed 5.3 mg CIP g^{-1} and 0.6 mg AC g^{-1} from the aqueous solution.

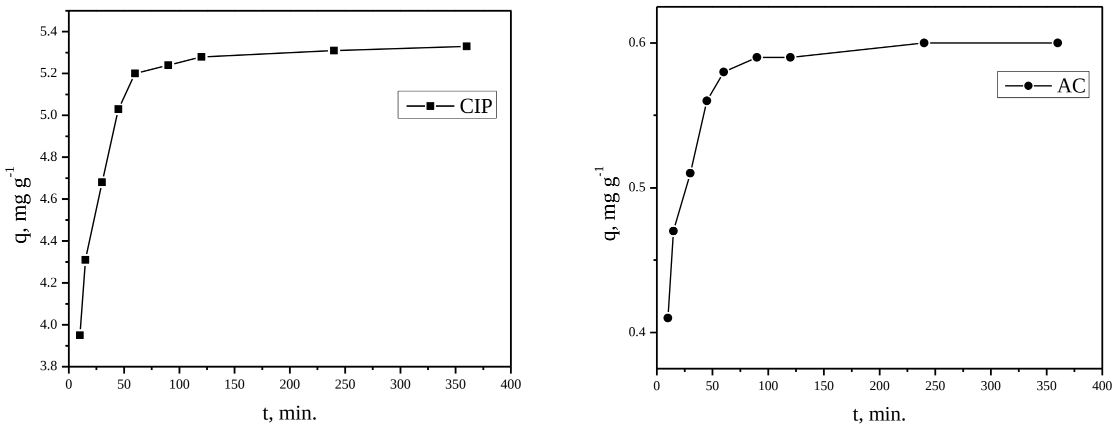

Fig. 5. Adsorption capacity of ZHBC towards ciprofloxacin and acetamiprid.

CONCLUSION

Adsorbent based on surfactant-modified natural zeolite and calcium hydroxyapatite was successfully prepared. TG/DTG and FTIR analyses confirmed the binding of the surfactant to the zeolite surface, while SEM microscopy confirmed the presence of needle-like crystals of HAp on the zeolite surface. During adsorption experiments, 5.3 mg CIP g^{-1} and 0.6 mg AC g^{-1} were removed. The prepared adsorbent showed the potential for further improvement and application in the purification processes of wastewater polluted with pesticides and antibiotics.

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