REMOVAL OF ARSENIC(III) OXYANIONS FROM WASTEWATER USING AMINOSILANE-MODIFIED NATURAL AND SYNTHETIC ZEOLITE

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ABSTRACT

Silanization of the natural and synthetic zeolites as well as their use as adsorbents for removing arsenic(III) oxyanions from wastewater are the topic of this paper. Two types of zeolite were used: natural zeolite-clinoptilolite from Zlatokop deposit, Vranjska Banja, Serbia, previously converted to H^+-form and synthetic zeolite, mordenite. The modification was performed with solution (3-aminopropyl) triethoxysilane (APTES). The presence of APTES on the surface of zeolite was confirmed using TG/DSC and FTIR analysis. The results showed that natural aminosilane-modified zeolite has a higher adsorption capacity for arsenic(III) oxyanions compared to mordenite prepared in the same way. The kinetic data follow the Lagergren pseudo-second-order model. This model implies a chemical interaction between AsO_3^{3-}- ions and functional groups on the silanized zeolite surface.

Key words: zeolite, aminosilane, modification, arsenic, wastewater.

INTRODUCTION

Into the environment arsenic comes from various sources, including industrial wastewater, the use of fertilizers and pesticides, the smelting of metal ores and the combustion of fossil fuels [1]. Due to its high toxicity even at low concentrations, it is considered one of the most undesirable metals, so its removal from wastewater is a major environmental challenge [1,2]. Zeolites are good adsorbents for the removal of different metals from aqueous solutions [3,4]. The adsorption mechanism is mainly based on an ion-exchange reaction between cations from zeolite lattice and metal ions from water solutions [5]. In order to improve the adsorption capacity of zeolites various organic compounds, such as amino-silanes are used. Amino-silanes are binding to the surface of the zeolite, whereby amino groups participate in the interaction with metal ions, thus improving the chemisorption's properties of the starting material. In this study, we performed a modification of clinoptilolite and mordenite with (3-aminopropyl) triethoxysilane (APTES) and examined their ability to remove As(III) from water solutions.

EXPERIMENTAL

Natural zeolite-clinoptilolite (Zlatokop, Serbia) and synthetic zeolite-mordenite (CZM20, SiO_2/Al_2O_3 molar ratio 20, Clariant) were chemically modified using (3-aminopropyl)triethoxysilane (APTES, 99%, Acros Organics). Before silanization, clinoptilolite was chemically treated and converted to H^+-form according to the procedure described by Garcia-Basabe *et al.* [6] while mordenite preliminarily was calcined for 30 minutes at 550 ºC in order to remove potentially present moisture. Silanization was performed in a balloon with a reflux condenser in an inert stream of nitrogen in the presence of toluene as a liquid medium. The silanization process was performed for 9 h with continuous stirring on a magnetic stirrer and on a constant temperature of 70 ºC. The APTES was added in drops to the reaction mixture

during the whole time of stirring. After the silanization, ethanol was added in drops at 10 min intervals several times. After completion of the silanization process, the modified zeolites were centrifuged and washed to remove toluene from the zeolite surface. The zeolite samples were dried for 24 h at 70 ºC. In the adsorption experiments, the liquid/solid phase ratio was 100:1. The initial concentration of As(III) solution was 10 mg As dm^{-3}. The suspensions were stirred at room temperature for 24 h. After the selected time (0.25, 0.5, 1, 2, 4, 6 and 24 h) aliquots were taken. The suspensions were separated by filtration and the concentration of As(III) before and after adsorption were determined by Perkin Elmer PinAAcle 900T Atomic Absorption Spectrometer (AAS)- Mercury Hydride System (MHS).

Characterization. Powder X-ray diffraction analysis (PXRD) was used to check crystallinity of the H$^+$-form of clinoptilolite after modification. PXRD patterns were recorded in the 2Θ=5-40° at room temperature using an Ital Structure APD2000 diffractometer. APTES content were determined by thermogravimetric analysis using a SDT Q-600 simultaneous TG/DSC instrument (TA Instruments). Interactions of APTES with zeolite surface were studied by Fourier Transform Infrared (FTIR) spectroscopy in the range 4000–450 cm^{-1} at room temperature using MB Bomem 100 Hartmann & Brown spectrometer. All samples were prepared by the KBr method.

RESULTS AND DISCUSSION

The PXRD analysis of the natural zeolite (Clin) and H$^+$-form of this zeolite showed that the clinoptilolite lattice after modification was not affected (Fig. 1).
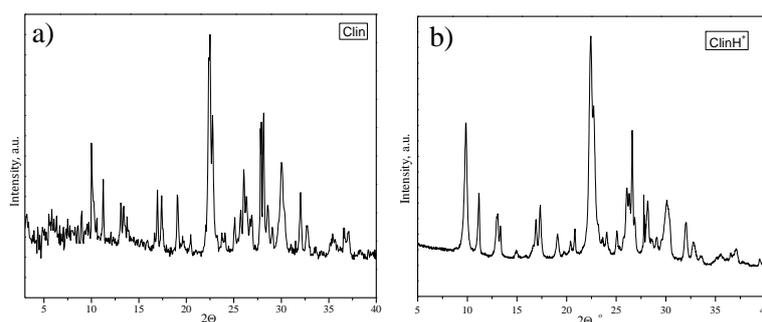

Figure 1. PXRD patterns of Clin (a) and ClinH$^+$ (b).

The results of thermal analysis (TG/DSC) are shown in Fig. 2 and 3. The total weight loss at 800 °C for samples ClinH$^+$ and ClinH$^+$-APTES is 12.4 and 15.3 wt.%, respectively. This confirms that the organic component has bound to the zeolite surface. DSC-curve of ClinH$^+$-APTES shows peak at 310 °C which is a consequence of the degradation of aminosilanes.
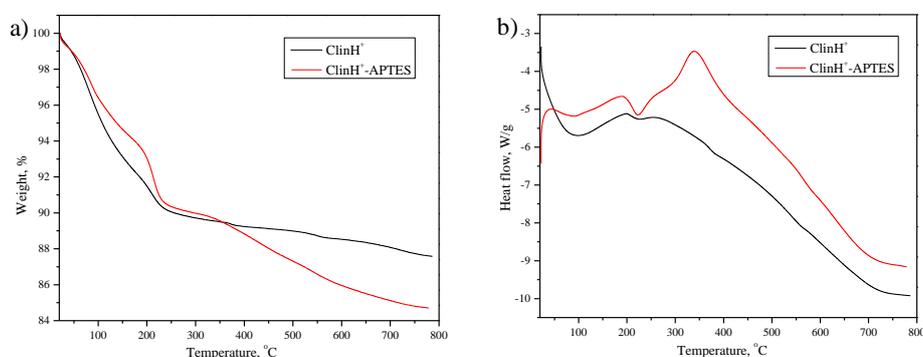

Figure 2. TG (a) and DSC (b) curves of ClinH$^+$ and ClinH$^+$-APTES.

As it can be seen from the Fig. 3, the TG curves of modernite shows that modified mordenite has a greater weight loss (15.4 wt.%) in comparison to the unmodified sample (12.5 wt.%) which confirms the presence of APTES. On the DSC curve of the modified sample a peak at about 320 °C can be observed which can be attributed to the organic component (Fig. 3b).
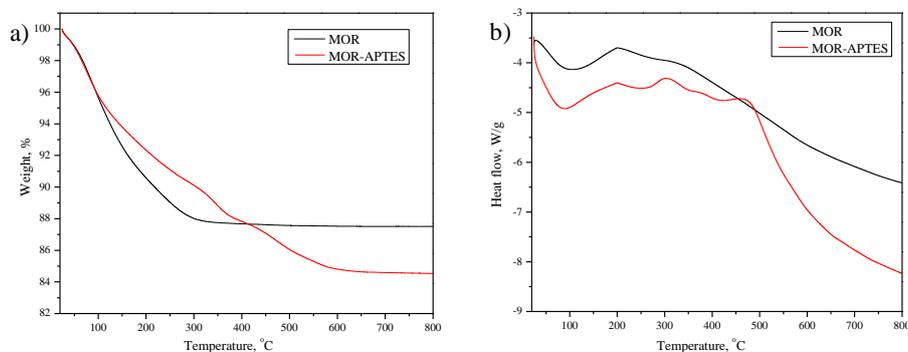

Figure 3. TG (a) and DSC (b) curves of MOR and MOR-APTES.

The FTIR spectra were used to analyse surface functionalities of ClinH+ and MOR, as well as the successfulness of their modification with APTES (ClinH+-APTES and MOR-APTES) (Fig. 4).
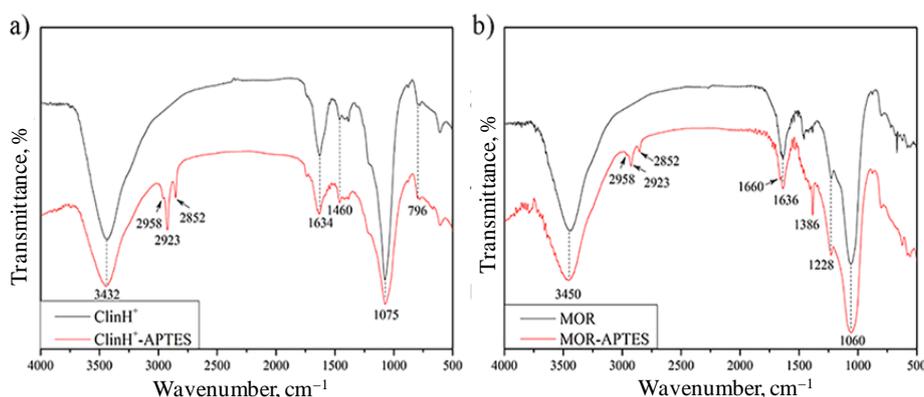

Figure 4. FTIR spectra of: (a) ClinH+ and ClinH+-APTES; (b) MOR and MOR-APTES.

FTIR spectra of all samples (Fig. 4) shows an intense band that occurs in the range between 3400-3500 cm^{-1} assigned with -OH stretching vibrations of surface functional groups, while the peak at 1634 cm^{-1} originates from -OH bending vibration, related with cations located in the structure of zeolite channels. The characteristic band at 1060-1075 cm^{-1} corresponds to the asymmetric stretching vibration of internal Si-O and Al-O bonds in SiO_4 and AlO_4 tetrahedral groups. The band at 796 cm^{-1} is assigned with the stretching vibration mode of O-Si-O and O-Al-O groups in the zeolite structure [7]. Besides the absorption bands of vibration frequencies of -OH, Si-O and Al-O groups, the appearance of new bands at spectra of silan-modified zeolites was observed and is associated with successful APTES modification. The peaks at 2958, 2923 and 2852 cm^{-1} are associated with stretching vibrations of C-H groups. The symmetrical and asymmetrical C-H in-plane bending vibrations of CH_3 groups can be expected in the region 1300-1500 cm^{-1}, as well as, the bands corresponding to N-H in-plane and C-N bond stretching vibration, which is overlapped with C-H vibration. The broad peak between 3300- 3600 cm^{-1} was due to the NH_2 stretch of the amine group overlapped with OH stretching vibration [7].

Adsorption was performed from the solution which contained 10 mg As dm^{-3}. It is evident that ClinH$^+$-APTES was more efficient adsorbent for As(III) ions than MOR-APTES (Fig. 5a). The modified natural zeolite ClinH$^+$-APTES adsorbed 2.5, while the synthetic zeolite prepared in the same way, bound 1.9 mg As/g zeolite.
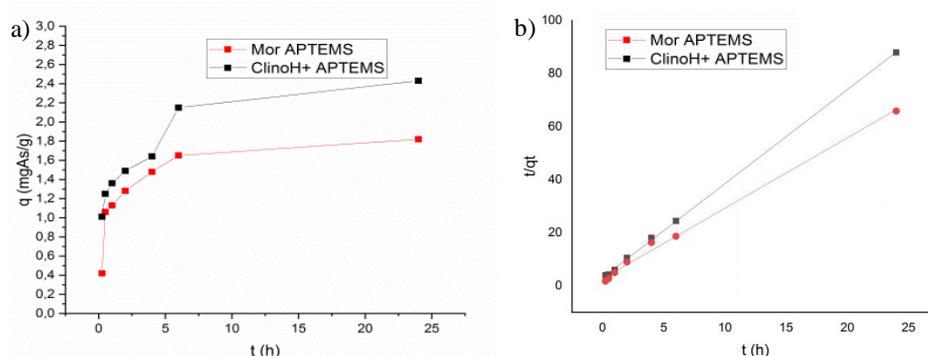

Figure 5. a) As concentration in mg/g on ClinH$^+$-APTES and MOR-APTES; b) Lagergren pseudo-second-order kinetic model applied to the adsorption data for ClinH$^+$-APTES and MOR-APTES.

Different kinetic models were used to describe the obtained experimental data. The correlation factors value (R^2) for both samples of 0.99 confirmed that adsorption kinetics follows the Lagergren pseudo-second order model (Fig. 5b).

CONCLUSION

The modification of natural and synthetic zeolite by (3-aminopropyl)triethoxysilane presents a new approach to the synthesis of efficient adsorbents for arsenic removal from aqueous solutions. This could contribute to resolving the real issues of wastewater treatment from different industries. The adsorbent containing low-cost natural zeolite-clinoptilolite showed a better affinity for As(III) adsorption than synthetic mordenite. The kinetic data follows the Lagergren pseudo-second-order model.

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