

SYNTHESIS AND CHARACTERIZATION OF THE ADSORBENTS OBTAINED BY MECHANOCHEMICAL MODIFICATION OF NATURAL CLINOPTILOLITE

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ABSTRACT

Preparation of the zeolite-based adsorbents for removal of toxic anions from waste water was studied in this work. The adsorbents were prepared mechanochemically using clinoptilolite-rich zeolitic tuff from Vranjska Banja deposit (Serbia). For the modification of clinoptilolite Fe(III)nitratnonahydrate and hexadecyltrimethylammonium bromide (HDTMA) were used. The milling process was performed in a ball mill and the modification was optimized regarding contact time, speed of milling and mass ratio of reactants (r) and balls (b). Milling speed of 250 rpm, contact time of 10 min and r/b= 1/15 were found to be optimal for the modification of zeolite. Element analysis of the obtained adsorbents showed that the adsorbents contain (wt. %): Fe - 8.4 and HDTMA - 8.9, respectively. Adsorption tests were performed using selenium ions as toxic model species. The Fe-containing adsorbent showed better adsorption affinity towards Se (30.1 mg Se g⁻¹) than HDTMA-containing one (16.5 mg Se g⁻¹).

Keywords: mechanochemical modification, zeolitic tuff, iron, HDTMA, selenite.

INTRODUCTION

Conventional methods for modification of natural zeolite are usually less environmentally friendly due to a large amount of liquid waste. Also, these methods are not energetically effective nor industrially sustainable. Accordingly, dry milling has been extensively studied as more suitable method for the modification of different types of zeolites. During milling, particle size of the reactants reduces, specific surface area increases and additional active sites form improving zeolite adsorptive properties [1,2].

Natural zeolites are effective adsorbents for various toxic ions present in water solutions. Thus, Fe-enriched zeolite efficiently remove selenium and arsenic oxyanions from water solutions [3,4]. Also, negatively charged zeolite surface can be modified to be accessible for capture of anions using a quaternary amines such as HDTMA [5].

The aim of this work was to prepare Fe(III)- and HDTMA-containing clinoptilolite using a mechanochemical dry process. The obtained adsorbents were tested in removal of selenium oxyanions from water solution.

EXPERIMENTAL

Natural clinoptilolite from the Vranjska Banja deposit (Z) was used for mechanochemical modification. Before milling, the sample was treated with NaCl solution, washed with distilled water and dried overnight. The milling was performed in a rotational mill Fritsch Pulverisette 7 using different milling parameters: speed (150-450 rpm), contact time (5-20 min) and mass ratio of reactants (r) and balls (b). Fe-containing clinoptilolite (FeZ)

was prepared by milling the reaction mixture with mass ratio of $\text{NaZ}/\text{Fe} = 10$. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich, p.a.) was used as a source of Fe(III). The HDTMA-containing clinoptilolite (HZ) was prepared using mass ratio $\text{NaZ}/\text{HDTMA} = 4.5$ (HDTMA-Br, Acros Organics, p.a.). The ratio was chosen to fit the external cation exchange capacity of Z [6]. The obtained FeZ and HZ were dried at 60 °C for 24 h. For the adsorption tests, liquid/solid ratio was 100 cm³/1 g. Suspensions were shaken in a thermostatic waterbath (Mettler, WNB 22) at 105 rpm during 24 h. The initial concentration of the selenium solution was $5.0 \cdot 10^{-3}$ mol dm⁻³. After chosen time (0.5, 1, 1.5, 2, 3, 4, 6 and 24 h), the suspensions were separated by filtration and Se concentration was measured in filtrate using atomic absorption spectroscopy (SpectrAA 55B, Varian).

Characterization. Powder X-ray diffraction analysis (PXRD) was used to check crystallinity of the prepared adsorbents. PXRD patterns were recorded in the $2\Theta = 5-40^\circ$ at room temperature using an Ital Structure APD2000 diffractometer. Water and HDTMA content were determined by thermogravimetric analysis (TGA/DTG) using a SDT Q-600 simultaneous DSC/TGA instrument (TA Instruments). Specific surface area was measured by N₂ adsorption-desorption experiments (Micromeritics ASAP 2020) and calculated according to the Brunauer, Emmett, Teller (BET) method. Interactions of HDTMA with clinoptilolite lattice were studied by Fourier Transform Infrared (FTIR) Spectroscopy in the range 4000–450 cm⁻¹ at room temperature using Nicolet iS10 (Thermo Scientific) spectrometer. Amounts of carbon, hydrogen and nitrogen in HZ sample were determined by Perkin Elmer CHN 2400 analyzer. An elemental analysis of the Z and FeZ was performed using energy dispersive X-ray spectroscopy (EDS) by a scanning electron microscope JEOL JSM-6610LV.

RESULTS AND DISCUSSION

According to the PXRD and element analysis the following optimal conditions of milling were determined: speed -250 rpm, contact time - 10 min and r/b = 1/15.

The PXRD analysis of the obtained adsorbents showed that the clinoptilolite lattice was not significantly affected by the modification process (Figure 1). EDS analysis of the clinoptilolite phase in the FeZ yielded 8.4 wt.% of Fe, whereas the content of HDTMA in HZ was calculated from CHN and TGA analysis to be 8.9 wt.%.

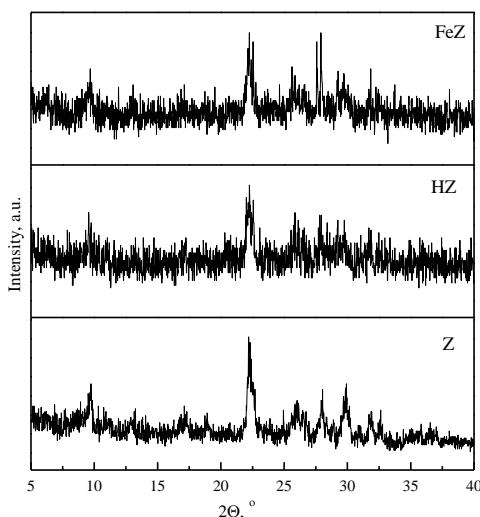


Figure 1. PXRD patterns of: Z, HDTMA-containing Z (HZ) and Fe(III)-containing Z (FeZ).

TG/DTG analysis of Z and FeZ (Figure 2a-b) indicated that a second layer was most probably formed during the transformation of Z into FeZ: the weight loss increased from 10 (Z) to 12 mas.% (FeZ). Moreover, thermogram of HZ (Figure 2c) displayed three weight

losses: the first one(4 mas.%) with DTG maximum centred at 98 °C is attributed to the water loss whereas the additional losses (9 mas.%)at 246 °C and 410 °C correspond to the decomposition of HDTMA. Two step decomposition of HDTMA is attributed to the presence of a bilayer on the clinoptilolite surface[7].

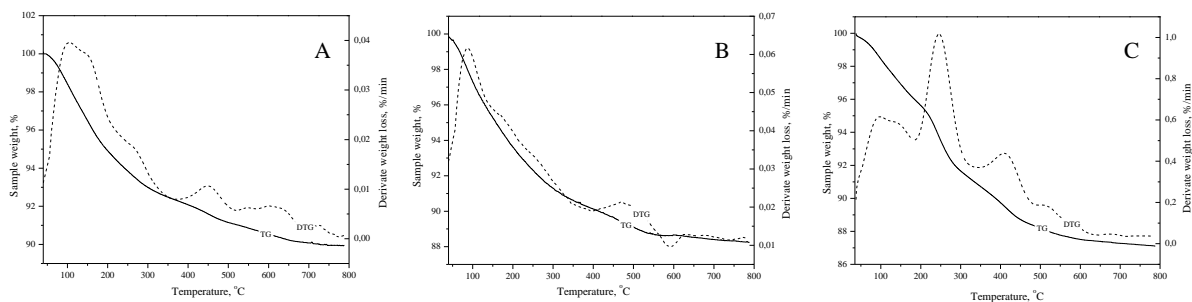


Figure 2. TG/DTG curves of: a) Z, b) FeZ and c) HZ.

FTIR spectra of Z, HZ and HDTMA are given in Figure 3. The characteristic stretching vibrations of the methyl groups from the HDTMA (at 2918 and 2849 cm^{-1}) can be seen in the spectrum of HZ confirming the presence of HDTMA in HZ. These bands are at slight higher wavenumbers (2920 i 2853 cm^{-1}) due to interactions of HDTMA with the aluminosilicate lattice [8].

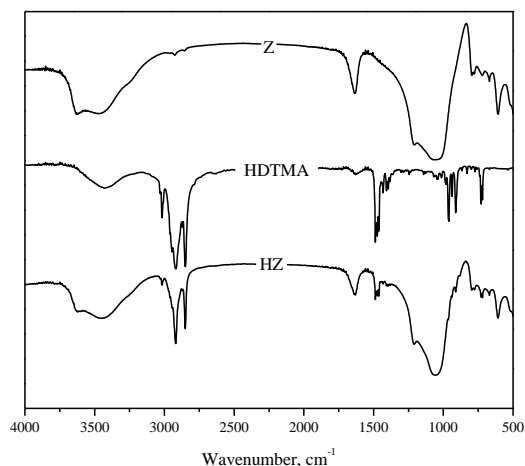


Figure 3. FTIR spectra of Z, HDTMA and HZ.

The results of the BET analysis showed that the modification with Fe(III) increased the specific surface area from 22 $\text{m}^2 \text{g}^{-1}$ (Z) to 56 $\text{m}^2 \text{g}^{-1}$ (FeZ) confirming the presence of the second porous layer on the clinoptilolite surface. The result is in agreement with the results obtained for modification of Z using Fe(III) solution [3]. For HZ the specific surface area decreased (7.5 $\text{m}^2 \text{g}^{-1}$) which can be explained by the coverage of the clinoptilolite surface with HDTMA layers.

The adsorption tests showed that the FeZ is more efficient adsorbent for Se ions than HZ. Fig. 4a showed the increase of Se concentration on the FeZ and HZ by time. For FeZ equilibrium was achieved faster (after about 5 h) than for HZ (approx. 25 h). The corresponding adsorbed amounts were 30.1 (FeZ) and 16.5 mg Se g^{-1} (HZ) suggesting better efficacy of the FeZ.

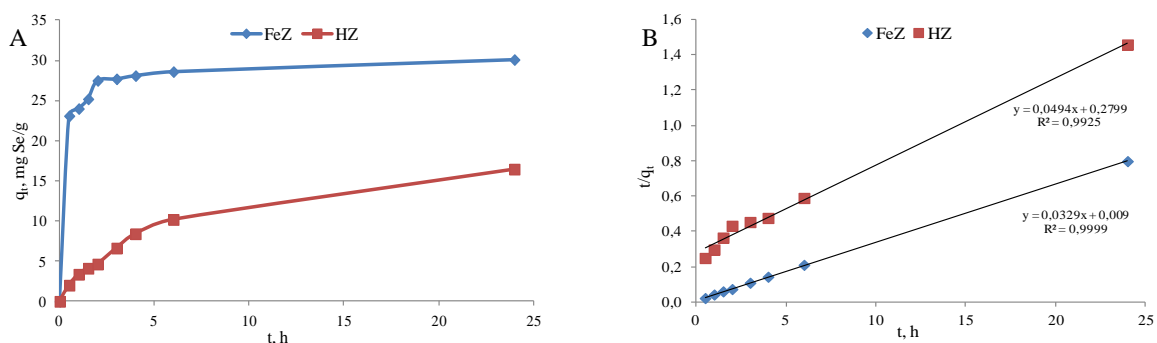


Figure 4. a) Se concentration in mg/g on FeZ and HZ; b) pseudo-second-order kinetic model applied to the adsorption data for FeZ and HZ.

The Lagergren kinetic models were used to describe the adsorption kinetics (Fig. 4b). The correlating factors (R^2) for both FeZ (≈ 1) and HZ (0.99) confirmed that the adsorption kinetics follow the Lagergren pseudo-second order model.

CONCLUSION

This work showed that dry milling can be used for the modification of clinoptilolite and preparation of adsorbents for removal of Se oxyanions from water solution. The adsorbent contained Fe(III) showed higher specific surface area and better affinity towards Se than that with HDTMA. Both adsorption kinetics are in excellent agreement with the Lagergren pseudo-second order equation.

REFERENCES

- [1] G. Majano, L. Borchardt, S. Mitchell, V. Valtchev and J. Perez-Ramirez, *Micropor. Mesopor. Mater.*, 2014, **194**, 106-114.
- [2] C. Xu, S. De, A.M. Balu, M. Ojedad and R. Luque, *Chem. Commun.*, 2015, **51**, 6698-6713.
- [3] S. Jevtić, I. Arčon, A. Rečnik, B. Babić, M. Mazaj, J. Pavlović, D. Matijašević, M. Nikšić and N. Rajić, *Micropor. Mesopor. Mat.*, 2014, **197**, 92-100.
- [4] M. Siljeg, S. Cerjan Stefanovic, M. Mazaj, N. Novak Tusar, I. Arcon, J. Kovac, K. Margeta, V. Kaucic and N. Zabukovec Logar, *Micropor. Mesopor. Mat.*, 2009, **118**, 408-415.
- [5] Z. Li, S.J. Roy, Y. Zou, and R.S. Bowman, *Environ. Sci. Technol.* 1998, **32**, 2628-2632
- [6] S. Jević, S. Grujić, J. Hrenović, and N. Rajić, *Micropor. Mesopor. Mater.*, 2012, **159**, 30-35.
- [7] H. Guan, E. Bestland, C. Zhu, H. Zhu, D. Albertsdottir, J. Hutson, C.T. Simmons, M. Ginic-Markovic, X. Tao, and A.V. Ellis, *J. Hazard. Mater.*, 2010, **183**, 616-621.
- [8] M. Rožić, D. Ivanec Šipušić, L. Sekovanić, S. Miljanić, L. Čurković, and J. Hrenović, *J. Colloid Interface Sci.*, 2009, **331**, 295-301.