

SYMULTANEOUS REMOVAL OF Fe³⁺, Mn²⁺ AND Cu²⁺ FROM AQUEOUS SOLUTIONS BY NATURAL AND SYNTHETIC ZEOLITES

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ABSTRACT

We have studied the performance of natural zeolite clinoptilolite from Serbia and synthetic zeolite A for the removal of Fe³⁺, Mn²⁺ and Cu²⁺ species from the aqueous solution. The efficiency of both zeolites for metal immobilisation was demonstrated for concentrations up to 5 mg of metal / 1 g of zeolite. The metal-loaded samples were analysed by using XRD, EDX and SEM analyses, which revealed homogeneous distribution of metals over the crystallites and confirmed the stability of zeolite frameworks after sorption treatment.

Keywords: clinoptilolite, zeolite A, metal removal, Fe³⁺ removal, Mn²⁺ removal, Cu²⁺ removal

INTRODUCTION

Natural and synthetic zeolites have a great potential as low-cost, non-toxic and highly selective sorbents in pollution control, especially in waste-water management. Comprehensive studies of metals sorption on natural clinoptilolite tuffs and synthetic zeolites have shown their great potential for the immobilization of cations and anions like chromium, zinc and arsenic in waste-waters and drinking water.¹⁻⁵ The results showed that metals like copper could be completely removed from aqueous solutions at low metal concentrations up to a few mg of metal / 1 g of zeolite. At higher concentrations the efficiency of zeolites slowly decreases, also in accordance with the theoretical sorption capacities.⁵ The studies confirmed that the pretreatment of natural zeolites with Na⁺ significantly enhanced the uptake of all metal cations. The reversibility of the metal uptake depend on the type of metal; for example, post-treatment of the samples with ammonium and sodium salts revealed irreversible sorption of chromium and arsenic and mostly reversible sorption of zinc and copper.

In this paper we report on the study of a simultaneous removal of three metal cations Fe³⁺, Mn²⁺ and Cu²⁺ from water solution by using natural zeolite tuff and synthetic zeolite A. The affinity of both zeolites to immobilize selected metals was evaluated by the elemental analysis of metal solutions after treatment and elemental and XRD analyses of metal-loaded zeolites.

EXPERIMENTAL

The sorption experiments were performed by using natural zeolite sample from Brus deposit in Serbia (Figure 1, left). The sample was first pretreated in NaCl solution to obtain the form, in which Na⁺ cations are predominantly present in the pores. The second sample used was zeolite 4A, which is produced commercially in Silkem d.o.o., Kidričevo, Slovenia (Figure 1, right).

The natural zeolite samples were first crushed in an agate mortar and washed with distilled water in order to remove the surface dust. Grain size fractions up to 0.1 mm were chosen for the experiment. 10.00 g of each zeolite sample was pretreated with 500 ml of 2 mol/l solutions of NaCl to obtain Na-form zeolite (NaZ). The mixture was stirred for 48 hours

by a magnetic stirrer at 25 °C. After the treatment, the samples were carefully washed with distilled water and dried in the oven at 60 °C. The Na-modified form of zeolite sample (NaZ) and commercially available zeolite 4A sample (4A) were placed in solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with different metal concentrations (from 0,5 to 50 mg/L of each, copper, manganese and iron). 1.00 g of each sample was mixed with the 100 ml of solution for 0.5 hour and 24 hours at 25 °C. The pH before and after metal treatment was in the range of 5.5 to 6.0 for all samples. Synthetic zeolite 4A (LTA-type zeolite) was treated similarly. 1.00 g of synthetic zeolite sample (4A) was mixed with the 100 ml of metal solutions for 0.5 hour and 24 hours at 25 °C. The exchange was again performed for different metal concentrations (from 0,5 to 50 mg/L). The pH before and after metal treatment was in the range of 7.5 to 9.0 for all samples (leaching of Na^+ from the structure might be associated with both the Cu^{2+} and H^+ sorption, the latter causing the slight pH rise in the solution). At the end of the treatments the samples were separated by decantation, filtration and thoroughly washed with distilled water and dried at 60 °C. The samples that were selected for detailed structure investigations and desorption experiments are listed in Table 1.

The concentration of copper in solutions was determined with Inductively-Coupled Plasma Atomic Emission Spectrometry (ICP-AES) on Thermo Jarrell Ash, model Atomscan 25. The size and the morphology of the crystals in the samples were studied by scanning electron microscope SUPRA 35 VP (Carl Zeiss). Elemental analyses of all samples were also carried out using Energy Dispersive X-ray Spectroscopy (EDXS) analysis within the Inca 400 (Oxford Instruments) system, attached to the scanning electron microscope SUPRA 35 VP (Carl Zeiss) in bulk, coated with carbon. An average elemental composition of the sample using EDXS was obtained by a data collection at five different mm^2 - sized windows on the sample surface.

The X-ray powder diffraction (XRPD) patterns were collected for six selected samples at room temperature on a Siemens D-5000 diffractometer using $\text{CuK}\alpha$ radiation at room temperature. The data were collected in the 2θ range from 5 to $80^\circ 2\theta$ in steps of $0.026^\circ 2\theta$ with a total measurement time of 20 minutes. The qualitative powder analyses of the collected XRPD patterns were performed using the Crystallographica Search-Match programs.

RESULTS AND DISCUSSION

The prepared samples were analyzed for their crystallinity, phase purity, elemental composition and porosity by using XRD, EDX, SEM and nitrogen physisorption.

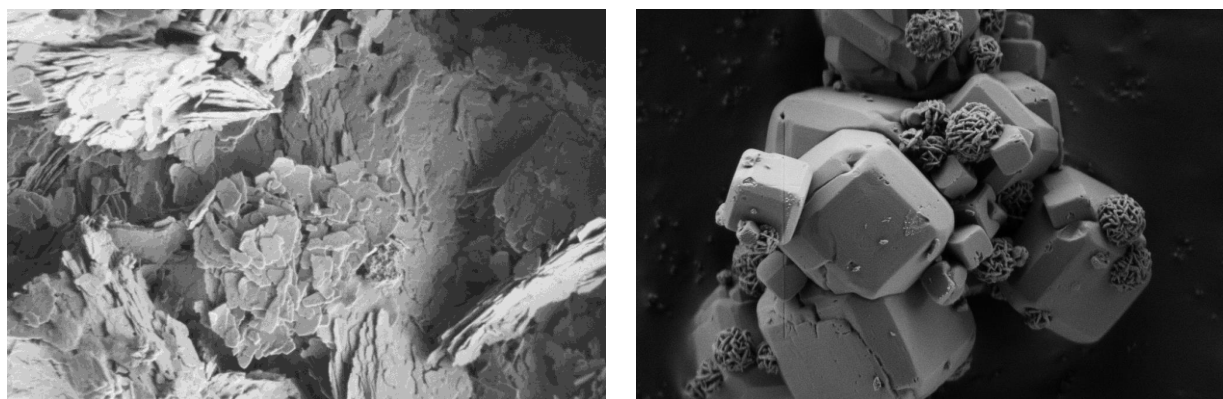


Figure 1. SEM photo of natural zeolite clinoptilolite from Serbia (left) and synthetic zeolite A (right) that were used in the study at the same magnification ($\times 40.000$).

Table 1. Concentrations of the three metals in the final solutions after sorption treatment (sample codes denote type of zeolite and initial concentration of all three metals), time of the experiment and concentrations of the three metals in the final solutions.

Sample	Time (h)	Fe (mg/L)	Cu (mg/L)	Mn (mg/L)
NaZ (50 mg/L)	0,5	15	20	17
NaZ (5 mg/L)	0,5	1,6	2,4	2,6
NaZ (0.5 mg/L)	0,5	< 0,1	< 0,1	< 0,1
NaZ (50 mg/L)	24	11	14	15
NaZ (5 mg/L)	24	0,3	0,5	0,9
NaZ (0.5 mg/L)	24	< 0,1	< 0,1	< 0,1
4A (50mg/L)	0,5	4	8	10
4A (5 mg/L)	0,5	< 0,1	< 0,1	0,6
4A (0.5 mg/L)	0,5	< 0,1	< 0,1	< 0,1
4A (50mg/L)	24	7	8	11
4A (5 mg/L)	24	0,6	0,4	0,5
4A (0.5 mg/L)	24	0,4	0,1	0,1

The concentrations of the metals in solutions before and after sorption on zeolites are presented in Table 1. The results proved high efficiency of both types of zeolites for metal immobilization, i.e. more than 99 % of all metals are sorbed onto both types of zeolites after 0,5 h of treatment at concentration 0,5 mg Me/L or 0,5 mg Me / 1g of zeolite (Me= Fe³⁺, Mn²⁺ and Cu²⁺). Furthermore, the concentrations of all three metals do drop below the threshold (0,4 mg Mn/L, 0,5 mg Cu/L, 3,0 mg Fe/L) for starting concentrations of metals of 5 mg/L. At higher concentration of metals (50 mg/L) the metals can only be partly removed from water solution. With natural zeolite we can remove up to 78% of Fe³⁺, up to 72% of Cu²⁺ and up to 70% of Mn²⁺ after 24 hours of treatment. With synthetic zeolite we can remove up to 92% of Fe³⁺, up to 84% of Cu²⁺ and up to 80% of Mn²⁺ after 0,5 hour of treatment. After 24 hours of treatment, small amount of metals is desorbed.

Table 2. An average elemental composition of samples obtained by the EDX analysis in at. % which reveals homogeneous distribution of metals over both zeolites.

Sample	O	Na	Mg	Al	Si	K	Ca	Mn	Fe	Cu
NaZ (50 mg/L) 0.5h	67.47	2.57	0.34	4.62	23.66	0.38	0.12	0.11	0.56	0.17
NaZ (50 mg/L) 24h	67.18	2.48	0.32	4.61	23.74	0.39	0.13	0.15	0.60	0.15
4A (50 mg/L) 0.5h	63.23	11.03	-	12.46	12.68	-	-	0.17	0.21	0.21
4A (50 mg/L) 24h	62.51	10.84	-	12.79	13.23	-	-	0.19	0.24	0.21

The results of the bulk EDX elemental analysis of metal-exchanged clinoptilolite tuff and zeolite A samples are presented in Table 2. The accuracy of the method is ±3 %. After sorption of metals on both zeolites, the increased amount of manganese, iron and copper was associated by the adequate reduced amount decrees of sodium and in the case of natural zeolite also decrees of remained potassium concentration (EDX of NaZ not shown).

The XRD analysis revealed that the crystallinity of both types of zeolites do not lower after the metal sorption. With present XRD data we could not confirm the formation of metal-oxo/hydroxo species on the surface of the zeolites, which was reported in the literature [5].

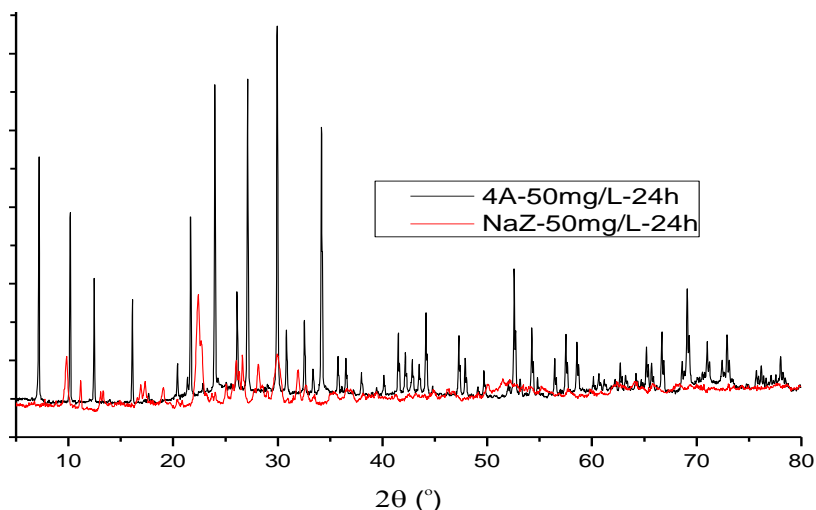


Figure 2. Powder X-ray diffraction pattern of NaZ (50mg/L)-24h sample and 4A (50mg/L)-24h sample.

CONCLUSION

The study confirmed the high potential of natural and synthetic zeolites for their use in waste-water treatment, i.e. a quick and efficient simultaneous removal of three metal cations was shown in the system with clinoptilolite and zeolite 4A used as adsorbents.

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