CROATICA CHEMICA ACTA CCACAA **69** (1) 281–290 (1996)

ISSN-0011-1643
CCA–2303
Original Scientific Paper

Metal Ion Exchange by Natural Zeolites

Štefica Cerjan-Stefanović,[a] *Lidija Ćurković,*[a] *and Tugomir Filipan*[b]

[a]*Laboratory of Analytical Chemistry, Faculty of Chemical Engineering and Technology, Marulićev trg 20, 10000 Zagreb, Croatia*

[b]*Institute for Development and International Relations, Lj. Vukotinovića 2, 10000 Zagreb, Croatia*

Recieved February 22, 1995; revised June 8, 1995; accepted June 9, 1995

The influence of pretreatment on the capacity and selectivity of natural zeolite for Zn^{2+} and Mn^{2+} ions has been studied. Natural tuff (sample 1), consisting mainly of zeolite clinoptilolite, was converted into the Na^+ form by conditioning with 2 M NaCl at 22 °C (sample 2) and 70 °C (sample 3), respectively. Simultaneously, 0.26, 0.31, 0.38 mmol Zn^{2+} and 0.20, 0.23, 0.30 mmol Mn^{2+} were taken up by 1.00 g of zeolite samples 1, 2 and 3, respectively. The results show that zeolites converted to the Na^+ form at 70 °C possess the highest capacity for metal ions. For all the zeolite samples tested, zinc was more selectively removed than manganese. The amount and composition of exchangeable cations as well as their impact on ion-exchange performances of zeolite in the process of Zn^{2+} and Mn^{2+} removal were determined.

INTRODUCTION

In recent years, zeolites have attracted growing interest in the field of ion-exchange separation processes. Their high sorption capacity and selectivity result from high porosity, ion-exchange and sieving properties. Zeolites have reversible hydration properties in addition to their cation exchange properties. These characteristics are related to the presence of exchangeable cations and to the dimension of channels. These features make zeolites very attractive from the aspect of water cleaning technology.[1–5] The structures of zeolites consist of a three dimensional framework of SiO_4 and AlO_4 tetrahedra. The aluminium ion is small enough to occupy the position in the centre of the tetrahedron of four oxygen atoms, and substitution of Al^{3+} for Si^{4+} in framework silicates is common. Since aluminium has one less positive charge than silicon, the framework has a net negative charge of one at the site of each aluminium atom and is balanced by the exchangeable cation (alkali and alkaline-earth metals, such as sodium, calcium and potassium).[6,7]

One of the most significant commercial applications of natural zeolites is the removal of heavy metals from waste water. Many toxic substances from waste water, such as heavy metals, are reduced by some form of chemical-physical treatment, such as chemical coagulation, flocculation, sedimentation and filtration. Small concentrations of specific contaminants may be removed by an ion exchange process. The ion-exchange properties of natural zeolite-clinoptilolite for inorganic cations have been investigated by many authors.[8–11] Barrer[7] has illustrated the high affinity of zeolites towards sorption and complexation of trace elements, particularly heavy metals and radionuclides.

In examination of the ion exchange behaviour of natural zeolites, it is desirable that the cationic form of the ion exchanger should be homoionic.[4] Several studies[4,9,12] have demonstrated that it is very difficult to convert zeolite to a single ionic form. Different conditioning procedures might have some influence on the ion-exchange behaviour of natural zeolite.

The goal of the present study was to determine and evaluate the influence of the pretreatment procedure on the exchange capacity and selectivity of a clinoptilolite for Zn^{2+} and Mn^{2+} ions. Experiments were performed on three zeolite types: natural zeolites (sample 1), natural zeolites treated with 2 M NaCl at 22 °C (sample 2) and natural zeolites treated with 2 M NaCl at 70 °C (sample 3).[13] The amount of Zn^{2+} and Mn^{2+} ions taken up by zeolites and the amount of Na^+, Ca^{2+} and K^+ ions released during the ion-exchange process are reported.

EXPERIMENTAL

Reagents

All chemicals used in this study were analytical grade reagents of the highest quality available, including p.a. reagents and high purity ion-free water. 10 mmol/L stock solutions of Zn^{2+} and Mn^{2+} were prepared by dissolving $ZnSO_4 \cdot 7H_2O$ and $Mn(NO_3)_2$, respectively, in redistilled water. The exact concentrations of metal ions were verified by AAS. Atomic absorption standard cation analyses were obtained from Merck. For chromatographic determination of anions, stock solutions (1.0 mg/L) of individual anions were prepared by dissolving their sodium salts in high purity water. More dilute solutions were prepared immediately before use.

Characterization of natural zeolite

The clinoptilolite obtained from a large sedimentary deposit in Donje Jesenje-Croatia was stated to be of 40% – 50% purity. The impurities included illite, quartz, feldspar, montmorillonite, halite and calcite. The tuff phase composition was determined, using a PHILIPS PW 1010 diffractometric system, by means of the counting technique and Cu$K\alpha$ radiation in the angle area from 3 to 60° 2θ at the observation speed of 1/2 °/min. Chemical composition of the tuff, determined by the usual analytical methods for silicate materials[14,15] is shown in Table I (sample 1).

The particle size of the sample used was in the range 0.1–1.0 mm. Some characteristic parameters of zeolite, such as the BET surface area, micropore area and volume, average pore diameter and adsorption surface area of pores and pore volume were determined by the Accelerated Surface Area and Porosimetry System (ASAP 2000). The BET surface area was 12.055 m^2/g, micropore area 1.919 m^2/g, micropore volume 0.813 mm^3/g, average pore diameter by BET method was 118.525 Å. The adsorption surface area of pores between 17.0 and 3000.0 Å was 0.036 cm^3/g.

The extent of dissolution and the presence of soluble anions in the zeolite sample, after treatment with high purity water, were determined by IC.[16,17] The ion chromatographic measurements were made on a Metrohm 960 Ion Chromatograph equipped with Super Sep anion column and 697 IC pump. The single column technique employs eluents of phtalic acid, in a low concentration, on ion exchange of very low capacitivity, which can be suppressed directly by electronic means. The conductivity detector followed the predcolumn and anion column. Whether or not this predcolumn can be used depends on the sample matrix and has to be tested in any case. The conductivity detector followed the two columns. The chromatogram was processed on a C-R5A Chromatopac calibration with external standard (Figure 1).

Conditioning

The sample of the clinoptilolite from Donje Jesenje-Croatia was conditioned to different extents. One untreated and two treated samples were prepared:

Sample 1 – No treatment, »as received« material.

Sample 2 – Natural zeolite was treated with 2 M NaCl at 20 °C for 24 hrs.

Sample 3 – The third sample of zeolite was prepared by treating zeolite with 2 M NaCl at 70 °C for 24 hrs.

The chemical composition of the natural and treatment zeolite, determined by the usual analytical methods for silicate materials, is shown in Table I.

Ion-exchange process

The ion-exchange process was carried out using a batch method. An accurate weight (1.00 g) of zeolite samples was mixed and stirred with 100.00 mL of solution containing metal ions of known concentration. Initial concentrations were from 1.0 to 10.0 mmol/L. All experiments were performed at initial pH = 4.0. The time of contact between metal ions and zeolites was 24 hrs. All the operations were conducted at 20 °C. After shaking, the solid phase was separated by filtration through a 0.45 m microporous membrane filter. The Na^+ and K^+ concentrations were determined by flame photometry, concentration of Ca^{2+} ions was determined by complexometric titration with EDTA, while the concentrations of Zn^{2+} and Mn^{2+} ions were determined by atomic adsorption spectroscopy (Varian AA 375, Varian GRA-90). The ion-exchange process followed pH-measurements (pH-meter ISKRA 5705) and soluble anions (960 Ion Chromatograph).

RESULTS AND DISCUSSION

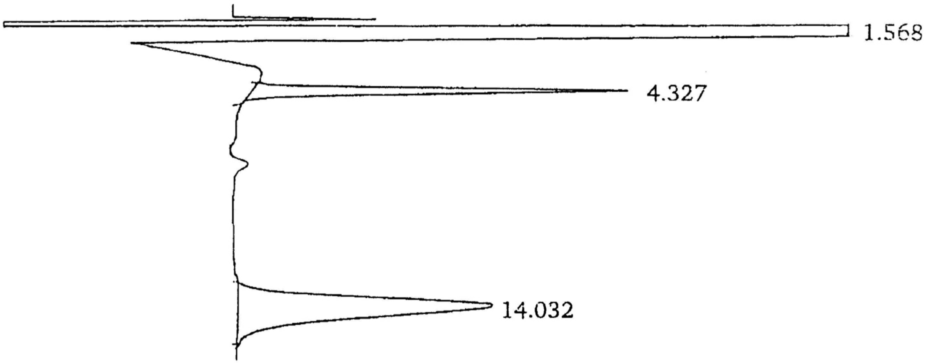
The natural zeolite clinoptilolite can play an important part in the fate of Zn and Mn compounds which may enter the environment through the disposal of industrial waste and chemical degradation.[18–20] The exchange sorption is an important process in the transport of pollutants[23,24] but mechanisms of their interaction have not been well classified yet. Experimentally determined selectivity sequences of natural zeolites for a range of metals differ among researchers, but they all agree that clinoptilolite shows a strong affinity to zinc and manganese.[2,3,6,8,21] Most of them suggest that pretreatment of natural zeolites enhances their ion-exchange ability. The present study demonstrates the ability of natural tuff to sorb zinc and manganese ions and also the selectivity of sorption.

TABLE I

Chemical composition of zeolite samples tested (%)

Components	Sample 1	Sample 2	Sample 3
SiO_2	55.80	55.80	55.80
Al_2O_3	13.32	13.35	13.36
CaO	5.57	5.42	5.01
K_2O	2.35	1.48	0.92
Na_2O	3.90	4.82	5.92
Fe_2O_3	1.30	1.28	1.29
MgO	0.70	0.66	0.67
loss of ignition	17.00	16.60	16.80

Chemical analysis of the treated zeolites yielded the data presented in Table I. The clinoptilolite sample from Donje Jesenje deposit contained exchangeable sodium, potassium and calcium ions. The selectivity series by Ames[2,3] demonstrated a great selectivity of clinoptilolite for potassium, as compared to other ions, such as barium, calcium and sodium. The selectivity series K > Ba > Ca > Na was investigated by Ames and Semmens.[2–4] Potassium, barium and calcium ions were strongly held by clinoptilolite in preference to sodium and extensive exposure to a high sodium concentration was required to displace these ions from the zeolitic matrix. The conditioning process led to the production of sodium rich samples. It is clear that, as the temperature of conditioning was increased, the sodium content of the zeolite also increased and this increase was mainly attributed to the exchange of potassium and calcium. The chemical composition of zeolite sample indicates that some of the cations are not exchangeable because some of them were associated with impurities in zeolite matrix.



C-R5A CHROMATOPAC

CHANNEL NO	1	FILE	0
SAMPLE NO	0	METHOD	2024
REPORT NO	14	SAMPLE WT	100

PKNO	Time	Area	MK	IDNO	C, mg/L	Name
1	1.149	20120 5193hi	E			
2	1.564	681 355hi				
3	1.768	10545 1973hi				
4	4.327	69071 3933hi		2	2.4675	Cl^-
5	14.032	162118 2654hi		6	9.2498	SO_4^{2-}
TOTAL		262535			11.7173	

Figure 1. Ion chromatographic determination of soluble anions (mg/L) in natural zeolite after the treatment with high purity water: m (zeolites) = 1.00 g; V (water) = 100.00 mL.

The IC analysis indicates that the presence of soluble anions in zeolite samples was Cl^- (2.4675 mg/L) and SO_4^{2-} (9.2498 mg/L) (Figure 1).

Addition of sample 1, sample 2, or sample 3 zeolites to stirred, high purity ion-free water of pH = 6.0 results in an immediate increase of the pH value due to the hydrolysis:[7,21,22]

$$NaZ_{(s)} + H_2O_{(l)} \rightleftharpoons HZ_{(s)} + Na^+ + OH^-$$

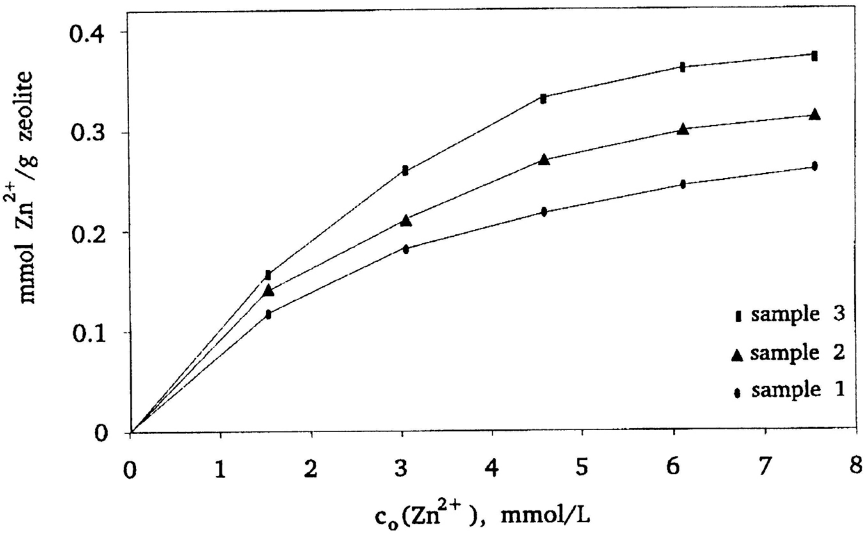


Figure 2. Adsorption of Zn^{2+} ions as a function of initial concentration by zeolite samples, *m* (zeolite) = 1.00 g; *V* (solution) = 100.00 mL.

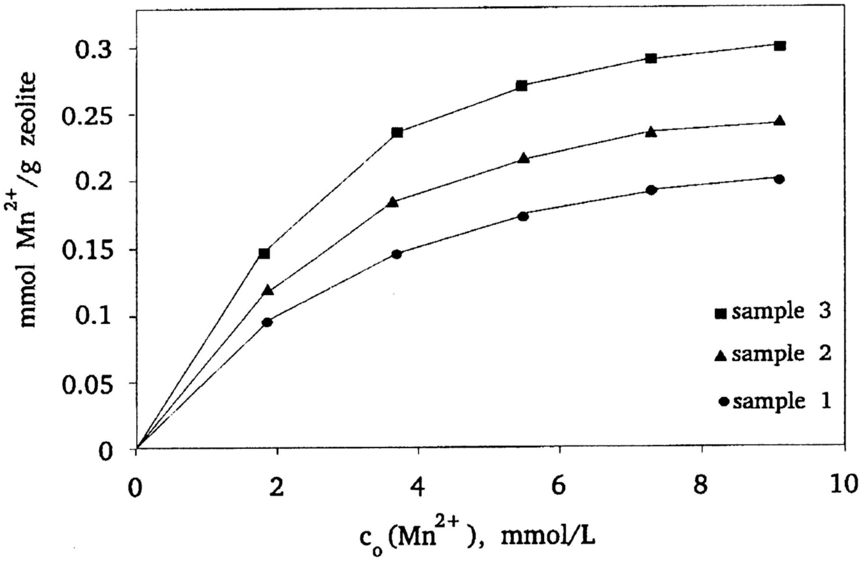
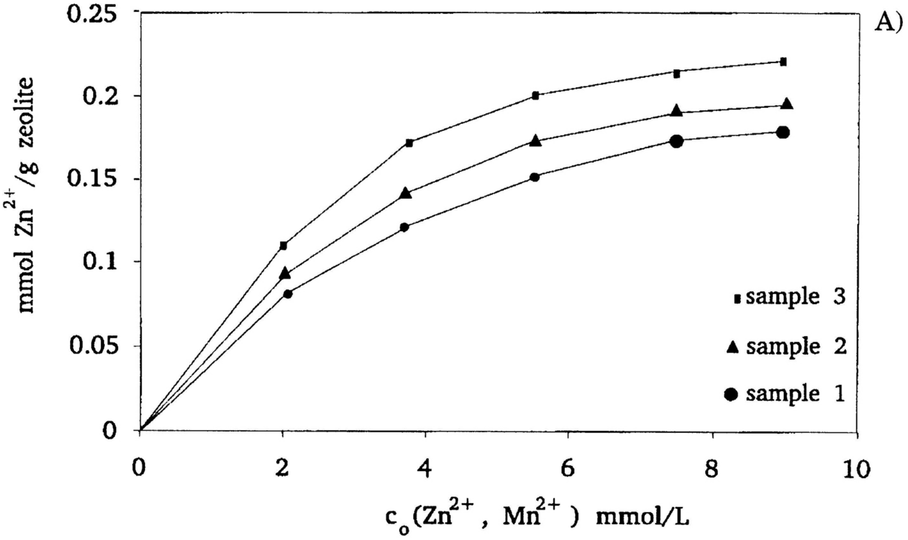


Figure 3. Adsorption of Mn^{2+} ions as a function of initial concentration by zeolite samples, *m* (zeolite) = 1.00 g; *V* (solution) = 100.00 mL.



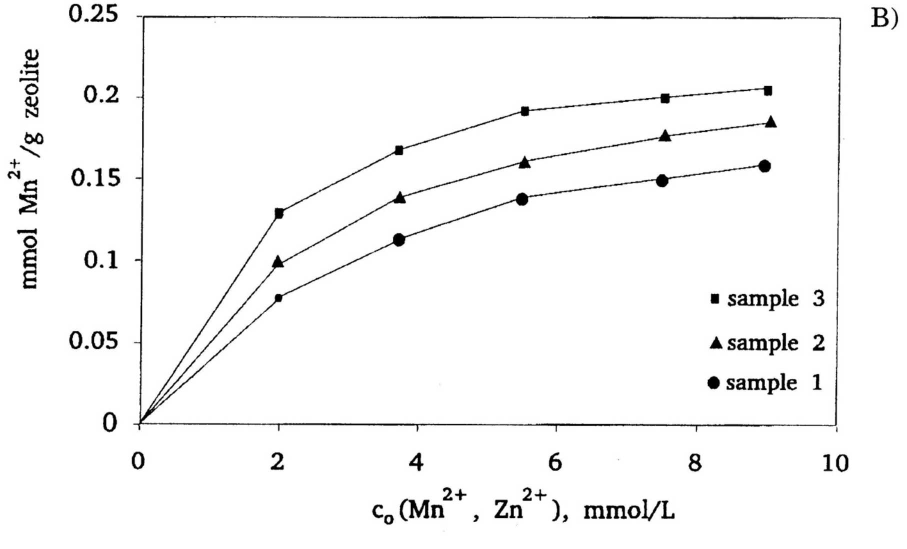


Figure 4. Competitive adsorption of Zn^{2+} and Mn^{2+} ions:
A) Adsorption of Zn^{2+} ions as a function of initial concentration Zn^{2+} and Mn^{2+} ions. *m* (zeolite) = 1.00 g; *V* (solution) = 100.00 mL.
B) Adsorption of Mn^{2+} ions as a function of initial concentration Zn^{2+} and Mn^{2+} ions. *m* (zeolite) = 1.00 g; *V* (solution) = 100.00 mL.

The pH value increased from pH = 6.0, which is the pH value of high purity ion-free water, to 9.0 in Na-zeolite solutions. Sodium cations are partially exchanged by hydronium ions, and the formed free hydroxide ions are responsible for the alkaline pH of the mixture.

Ion-exchange isotherms for zinc and manganese uptake by the zeolite sample are presented in Figures 2 and 3. Simultaneously, 0.26, 0.31, 0.38 mmol Zn^{2+} and 0.20, 0.23, 0.30 mmol Mn^{2+} were taken up by 1.00 g of zeolite samples 1, 2 and 3, respectively. These results indicate that the capacity of zeolite samples for both zinc and manganese was increased with the increased temperature of conditioning. The order of efficiency is as follows:

$$\text{sample 3} > \text{sample 2} > \text{sample 1}$$

However, it was also clear that, for all the zeolite samples tested, zinck was more selectively removed than manganese. A similar pattern was observed by studding the exchange process with a competitive adsorption mixture of Zn^{2+} and Mn^{2+} ions. These results are shown in Figures 4A i 4B. The results presented above clearly document the dependence of the measured zeolite capacity and selectivity data in the manner in which the zeolite was treated prior to testing.

The amounts of Na^+, Ca^{2+} and K^+ ions released during the ion-exchange process with 5.0 mmol Zn^{2+}/L are shown in Figure 5 and Table II. Calcula-

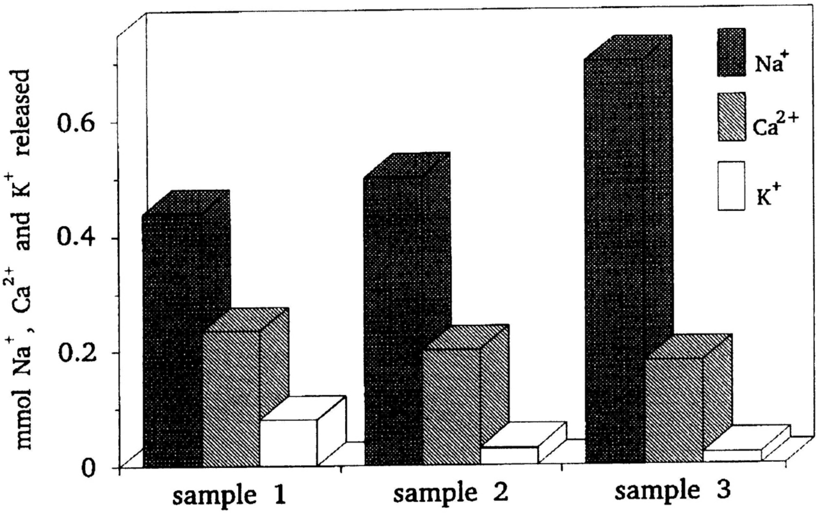


Figure 5. The amount of Na^+, Ca^{2+} and K^+ released during the ion-exchange process with 5.00 mmol Zn^{2+}/L. *m* (zeolite) = 1.00 g; *V* (solution) = 100.00 mL.

TABLE II

The exchange of Na$^+$, K$^+$ and Ca^{2+} ions from the zeolite samples with metal ions from solution

metal ions	zeolite sample	c (Na$^+$) mmol/100 mL	c (K$^+$) mmol/100 mL	c (Ca^{2+}) mmol/100 mL
c (Zn^{2+}) 5.0 mmol/L	sample 1	0.42	0.8	0.22
	sample 2	0.48	0.03	0.20
	sample 3	0.68	0.02	0.18
c (Mn^{2+}) 5.0 mmol/L	sample 1	0.38	0.07	0.23
	sample 2	0.40	0.03	0.19
	sample 3	0.63	0.02	0.15
c (Zn^{2+}+Mn^{2+}) (5.0+5.0)mmol/L	sample 1	0.48	0.08	0.23
	sample 2	0.53	0.03	0.21
	sample 3	0.76	0.02	0.18

tion of equivalent amounts of ions taken up and released in the process shows that the increased amount of Ca^{2+} ions is a result of partial dissolution of calcium-rich minerals present in the natural tuff. Furthermore, the increased equilibrium pH-value of solution (from initial value of 4.5 to 7.0 after ion-exchange process) was a result of competitive sorption of H$^+$ ions and their exchange for Na$^+$, Ca^{2+} and K$^+$ ions. A similar pattern was observed by studding the exchange process with 5.0 mmol Mn^{2+}/L and with a mixture of 5.0 mmol Zn^{2+}/L and 5.0 mmol Mn^{2+}/L. These results are shown in Table II. These results indicate that the concentrations of exchangeable Na$^+$, Ca^{2+} and K$^+$-ions depend on the types of zeolites and metal ions.

REFERENCES

1. R. M. Barrer, R. Rapadopulos and L. V. C. Ress, *J. Inor. Nucl. Chem.* **29** (1967) 10470.
2. L. L. Ames, *Am. Miner.* **45** (1960) 689.
3. L. L. Ames, *Am. Miner.* **47** (1962) 1310.
4. M. J. Simmens and W. P. Martin, *Wat. Res.* **22** (1988) 537.
5. Š. Cerjan-Stedanović, M. Kaštelan-Macan and T. Filipan, *Wat. Sci. Tech.* **26** (1992) 1185.
6. D. W. Breck, *Journal of Chemical Education*, **41** (1964) 678.
7. R. M. Barrer, *Zeolites and Clay Minerals as Sorbent and Molecular Sieves*, New York, Academic Press, 1987.
8. M. J. Zamzow, B. R. Eichbaum, K. R. Sandgren and D. E. Shanks, *Separation Science and Technology* **25** (1990) 1555.
9. H. S. Sherry, *Clays Clay Miner.* **27** (1979) 231.
10. I. A. Voinovitch, J. Debras-Guedon and J. Louvtier, *L' analyse des silicates*, Herman, Paris, 1966.

11. H. E. Allen and T. D. Brishen, *Environ. Sci. Tech.* **14** (1981) 441.
12. S. E. Jorgensen, *Wat. Res.* **10** (1976) 213.
13. Š. Cerjan-Stefanović and L. Ćurković, Proceeding of Symposium »*Metali u hrani i okolišu*«, Stubičke Toplice, 1994, p. 263.
14. D. R. Corbin, B. F. Burgess, Jr., J. A. Vega, and D. R. Farlee, *Anal. Chem.* **59** (1987) 2722.
15. S. Šćavničar and D. Tibljaš, *Geol. Vj.* **41** (1988) 99.
16. K. Ito, Y. Ariyoshi, F. Tanabtiki and H. Sunahra, *Anal. Chem.* **63** (1991) 273.
17. Š. Cerjan Stefanović and A. Rastovčan, *Croat. Chim. Acta* **66** (1993) 452.
18. R. Sersale in *Zeolites*, D. Držaj, S. Hočevar and S. Pejovnik (Ed.), Elsevir Science Publishers B. V. Amsterdam, 1985, p. 503.
19. D. Kalló and Kh. M. Minachev, *Catalysis on Zeolites*, Akadémiai Kiadó, Budapest, 1988.
20. M. Grace and R. S. Bowmen, *Environ. Sci. Technol.* **28** (1994) 245.
21. M. Wark, W. Lutz, G. Schulz-Ekloff and A. Dyer, *Zeolites* **13** (1993) 658.
22. R. Hajrula, A. Dyer, S. D. Pearson and R. P. Townsend, *J. Chem. Soc. Faraday Trans.* **88** (1992) 1591.
23. G. Tchobanoglous and F. L. Burton, *Wastewater Engineering Treatment, Disposal and Reuse*, New York, 1991.
24. A. Kabata-Pendias and H. Pendias, *Trace Elements in Soils and Plants*, CRC Press, Inc. Boca Raton, Florida, 1984.

SAŽETAK

Zamjena kovinskih iona prirodnim zeolitom

Štefica Cerjan-Stefanović, Lidija Ćurković i Tugomir Filipan

Proučavan je utjecaj obradbe prirodnog zeolita na kapacitet i selektivnost uklanjanja iona Zn^{2+} i Mn^{2+}. Prirodni zeolit, klinoptilolit (uzorak 1), bio je obradbom s 2 M NaCl pri 22 °C (uzorak 2) i 70 °C (uzorak 3) djelomično preveden u Na^+ oblik. Tako je 0.26, 0.31, 0.38 mmol Zn^{2+} i 0.20, 0.23, 0.30 mmol Mn^{2+} vezano na po 1.00 g uzoraka 1, 2 i 3. Rezultati pokazuju da zeolit preveden u Na^+ oblik pri 70 °C ima najveći kapacitet za uklanjanje kovinskih iona. Svi uzorci zeolita pokazuju veću selektivnost prema ionima cinka nego prema ionima mangana. Određena je količina izmjenjivih kationa iz zeolita, kao i njihov utjecaj na proces uklanjanja iona Zn^{2+} i Mn^{2+}.