



## METAL ION EXCHANGE BY NATURAL AND MODIFIED ZEOLITES

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**Abstract**—The lead and cadmium removal from wastewaters by natural and pretreatment zeolites was examined by using a batch-type method. The results demonstrated that the natural zeolites contained a complement of exchangeable Na, K and Ca ions but exposing them to 2 M NaCl solution at 22 and 70°C, respectively, converted them to a near homoionic state in Na-form. Lead and cadmium removal results using natural zeolites and treated zeolites showed that treatment improved both the exchange capacity and the removal efficiency. The influence of the temperature on the ion-exchange process was examined. It was found that the metal uptake was increased with increasing temperature during the ion-exchange process. Natural and modified zeolites remove toxic metals from waste waters. © 1997 Elsevier Science Ltd.

**Key words**—natural zeolites, modified zeolites, ion exchange, lead removal, cadmium removal

### INTRODUCTION

Clinoptilolite is a mineral zeolite of the Heulandite group. The structures of zeolites consist of a three-dimensional framework of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra. The aluminium ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Al<sup>3+</sup> for Si<sup>4+</sup> raises a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium and calcium). These cations are exchangeable with certain cations in solutions such as lead, cadmium, zinc and manganese (Barrer, 1987; Breck, 1964). The fact that zeolite exchangeable ions are relatively innocuous (sodium, calcium and potassium ions) makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters. One of the earliest applications of a natural zeolite was in removal and purification of cesium and strontium radio-isotopes (Hafez *et al.*, 1978). The removal of ammonium from municipal and industrial wastewater was one of the most significant commercial applications (Jorgensen *et al.*, 1976; Kesraoui-Ouki *et al.*, 1994). The ion-exchange capacity of natural zeolite Clinoptilolite for inorganic cation has been investigated by many authors (Blanchard *et al.*, 1984; Cerjan-Stefanović *et al.*, 1992; Joshi and Mohan, 1983). Among the most frequently studied natural zeolites, Clinoptilolite was shown to have high

selectivity for certain heavy metal ions such as Pb<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Cu<sup>2+</sup>. A significant number of researchers have done experiments which have determined different selectivity sequences of natural zeolites for a range of various metals, but they have all agreed that Clinoptilolite shows a strong affinity for lead and cadmium. Most of them have suggested that pretreatment of natural zeolites enhances their ion-exchange ability (Malliou *et al.*, 1994; Semmens and Martin, 1988; Wark *et al.*, 1994; Zamzow *et al.*, 1990). This study concentrates on the ion-exchange behavior of Croatian Clinoptilolite for lead and cadmium ions in wastewaters. The uptake of other toxic metals, such as Zn<sup>2+</sup> and Mn<sup>2+</sup>, by this mineral has already been indicated (Cerjan-Stefanović *et al.*, 1996). The chemical composition of a zeolite, the temperature at which the ion exchange takes place and its conversion to a single ionic form are three of the most important parameters that can influence the ion-exchange behavior of a natural zeolite. The goal of this study was to investigate these three effects on the uptake of lead and cadmium from wastewater.

### 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. We prepared 10 mmol l<sup>-1</sup> stock solutions of lead and cadmium using their nitrate salts, Pb(NO<sub>3</sub>)<sub>2</sub> and Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, respectively, in redistilled water. The exact concentrations of metal ions were verified by AAS. Atomic absorption standard cation analyses were obtained from Merck.

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### Characterization of zeolite samples

X-ray diffraction (XRD) analysis was performed on Clinoptilolite to confirm the crystal structure and the mineral identity of the zeolites. The analysis was performed on three zeolite samples: natural zeolites (sample 1) and treated zeolites (samples 2 and 3), in an attempt to determine their effect on the zeolite crystal structure. The Clinoptilolite obtained from a large sedimentary deposit in Donje Jesenje, Croatia, was stated to be 40–50% pure. The impurities include illite, montmorillonite, feldspar, calcite, quartz and halite. The tuff phase composition was determined by using a Philips PW 1010 diffractometric system by means of the counting technique and CuK $\alpha$  radiation in an angle area from 3 to 60° 2 $\theta$  with an observation speed of 0.5° min $^{-1}$ .

Chemical composition of the zeolite samples was determined by the usual analytical methods for silicate materials (Corbin *et al.*, 1987) (Table 1).

The particle size of the sample used was in the range of 0.1–2.0 mm. Some characteristic parameters of zeolites, such as BET surface area, micropore area and volume, average pore diameter and adsorption surface area of pores and pore volume were determined by accelerated surface area and porosimetry system (ASAP 2000). BET surface area was 12.055 m $^2$  g $^{-1}$ , micropore area 1.919 m $^2$  g $^{-1}$ , micropore volume 0.813 mm $^3$  g $^{-1}$ , and 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 $^{-1}$ .

### Lead and cadmium removal studies

Metal removal studies were carried out using Clinoptilolite from Donje Jesenje, Croatia, in three different forms: one untreated and two treated samples:

Sample 1: no treatment; natural zeolite.

Sample 2: natural zeolite was treated with 2 M NaCl solution at 20°C over a period of 24 h. After washing, Na-modified zeolites were dried at 105°C for 1 h.

Sample 3: the third sample of zeolite was prepared by treating zeolite with 2 M NaCl solution at 70°C over a period of 24 h, in thermostat.

The chemical composition of the natural and treated zeolites determined by the usual analytical methods for silicate materials is shown in Table 1.

The ion-exchange process was carried out by using the batch method. A constant amount of zeolite samples (1.00 g) was mixed with 100 ml lead and cadmium solutions of concentrate ranging from 1.0 to 10.0 mmol l $^{-1}$ . The initial pH value of all solutions was adjusted to a 4.5 prior to exchange with zeolite. The suspension was shaken for a period of 24 h. In preliminary experiments (Cerjan-Stefanović *et al.*, 1996) 24 h shaking of suspensions was found to be sufficient for equilibrium and for stabilization of pH. These first experiments were conducted at 20°C. In the second set of experiments is investigated the influence change of the temperature on the uptake of lead and cadmium ions. An accurate weight (1.00 g) zeolite sample 3

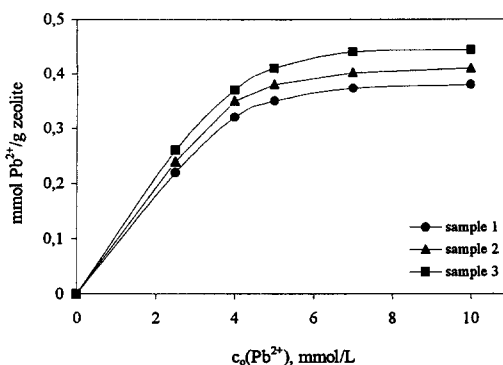


Fig. 1. Sorption of Pb $^{2+}$  ions by zeolite samples as a function of initial concentration;  $m$  (zeolite) = 1.00 g;  $V$  (solution) = 100 ml.

was mixed and stirred with 100 ml of 7.0 mmol l $^{-1}$  solutions of lead and cadmium, respectively. The investigated temperatures were 4, 22, 50, 60 and 70°C. After shaking in a thermostatic system, the solid phase was separated by filtration through a 0.45  $\mu$ m microporous membrane filter. The final pH of solutions was recorded by pH meter (pH-meter ISKRA 5705) and concentrations of lead and cadmium ions at equilibrium were determined by the atomic adsorption spectroscopy (Varian AA375, Varian Gra-90).

### RESULTS AND DISCUSSION

Chemical analysis of the treated zeolites is presented in Table 1. This study showed that natural zeolite (sample 1) contained a complement of exchangeable sodium, potassium and calcium ions. The selectivity series K > Ca > Na was investigated (Cerjan-Stefanović *et al.*, 1996). This selectivity series is in concordance with the investigation done by Semmens and Martin (1988). Potassium and calcium ions were strongly held by Clinoptilolite in preference to sodium and extensive exposure to high sodium concentration was required to displace these ions from the zeolitic matrix. The exposure of natural zeolite to 2 M NaCl solution at 22°C (sample 2) and 70°C (sample 3) led to the production of the sodium-rich sample. It is clear that, as the temperature of the conditioning was being increased, the sodium content of the zeolite was increasing in parallel and this increase was mainly attributed to the exchange of potassium and calcium. The chemical composition of the zeolite sample indicated that part of the calcium and potassium were not exchangeable because some was associated with impurities in the zeolite matrix.

The ion-exchange isotherms for lead and cadmium uptake by the zeolite samples are presented in Figs 1 and 2. Respectively, 0.38, 0.41, 0.44 mmol Pb $^{2+}$  and 0.12, 0.16, 0.21 mmol Cd $^{2+}$  were taken up by 1.00 g of zeolite sample 1, 2 and 3. It was clear that, for all the zeolite samples, lead was more selectively removed than cadmium.

These results indicate that the capacity of zeolite samples for lead and cadmium was increased with the

Table 1. Chemical composition of zeolite samples tested (%)

Components	Sample 1	Sample 2	Sample 3
SiO $_2$	55.80	55.80	55.80
Al $_2$ O $_3$	13.32	13.35	13.36
CaO	5.75	5.42	5.01
Na $_2$ O	3.90	4.82	5.92
K $_2$	2.35	1.48	0.92
Fe $_2$ O $_3$	1.30	1.28	1.29
MgO	0.70	0.66	0.67
Loss of ignition	17.00	16.60	16.80

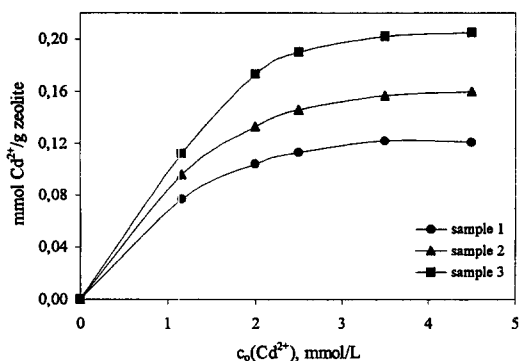


Fig. 2. Sorption of  $\text{Cd}^{2+}$  ions by zeolite samples as a function of initial concentration;  $m$  (zeolite) = 1.00 g;  $V$  (solution) = 100 ml.

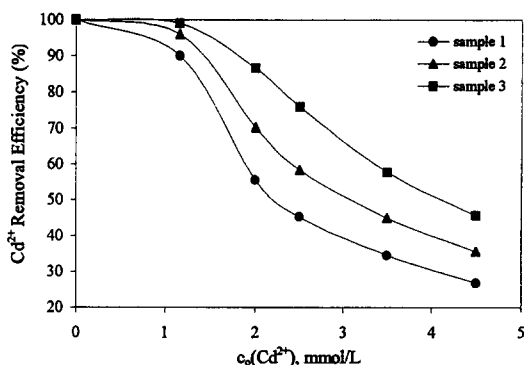


Fig. 4.  $\text{Cd}^{2+}$  ion removal efficiency by zeolite samples as a function of initial concentration;  $m$  (zeolite) = 1.00 g;  $V$  (solution) = 100 ml.

increased temperature of conditioning. The order of efficiency is as follows: sample 3 > sample 2 > sample 1. The pH value of lead and cadmium solutions was increased from 4.5, which is the initial pH value, to between 7 and 8 (equilibrium pH value). This significantly increased pH value during the experiments was due to the simultaneous uptake of hydrogen ions by zeolite samples and hydrolysis of zeolites (Wark *et al.*, 1994; Zamzow *et al.*, 1990).

The lead removal efficiencies for tested zeolite samples are shown in Fig. 3. At lead concentrations less than  $2.5 \text{ mmol l}^{-1}$ , removal efficiencies of about 90–99% were achieved by all zeolite samples. At higher lead concentrations, the removal efficiency decreased to a value of 38, 41 and 45% for zeolite sample 1, 2 and 3, respectively, at  $10 \text{ mmol l}^{-1}$  of  $\text{Pb}^{2+}$  (Fig. 3). Similarly, cadmium removal efficiencies for zeolite samples are shown in Fig. 4. The removal efficiency decreased drastically from 90, 96 and 99% at  $1 \text{ mmol l}^{-1}$  of  $\text{Cd}^{2+}$  to 27, 36 and 46% at  $4.5 \text{ mmol l}^{-1}$  for zeolite sample 1, 2 and 3, respectively (Fig. 4). A comparison between Figs 3 and 4 shows clearly that the sample 3 removal efficiency for both lead

and cadmium at concentration levels ranging from 1 to  $10 \text{ mmol l}^{-1}$ , is far superior to the removal efficiency of zeolite sample 2 and 1, respectively. However, it was also clear that for all the zeolite samples tested, lead was more selectively removed than cadmium.

Figures 5 and 6 illustrate the effect of temperature on the removal of lead and cadmium by zeolite samples, and it is furthermore clear that the lead and cadmium uptake is increased with increasing temperature.

## CONCLUSIONS

The heavy-metal uptake is attributed to different mechanisms of ion-exchange processes as well as to the adsorption process. During the ion-exchange process, lead and cadmium ions had to move through the pores of the zeolite mass, but also through channels of the lattice, and they had to replace exchangeable cation (mainly sodium, calcium and smaller potassium). Diffusion was faster through the pores and was retarded when the ions moved through the smaller diameter channels. In this case the lead

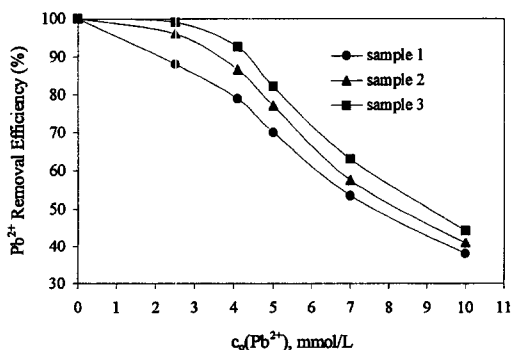


Fig. 3.  $\text{Pb}^{2+}$  ion removal efficiency by zeolite samples as a function of initial concentration;  $m$  (zeolite) = 1.00 g;  $V$  (solution) = 100 ml.

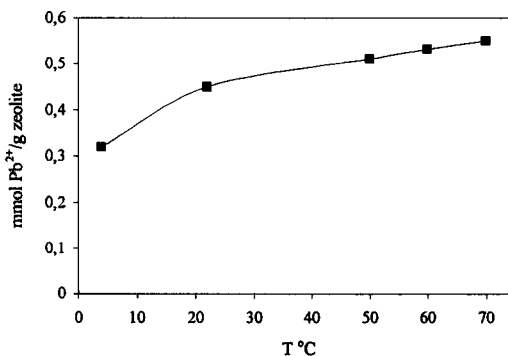


Fig. 5. Sorption of  $\text{Pb}^{2+}$  ion by zeolite samples as a function of temperature of ion-exchange process  $m$  (zeolite) = 1.00 g;  $V$  (solution) = 100 ml.

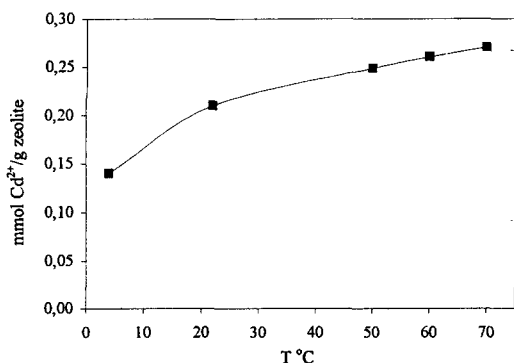


Fig. 6. Sorption of Cd<sup>2+</sup> ions by zeolite samples as a function of temperature of ion-exchange process;  $m$  (zeolite) = 1.00 g;  $V$  (solution) = 100 ml.

and cadmium uptake could mainly be attributed to the ion-exchange reactions in the microporous minerals of the zeolite samples. Therefore, the adsorption on the surface of the minerals (ilite, montmorillonite, feldspar, calcite, quartz and halite) also plays a significant role.

The pH value during the experiments was increased from 4.5 to 8 due to the hydrolysis of zeolites.

At lead concentration less than 2.5 mmol l<sup>-1</sup>, removal efficiency was about 90% depending on the treatment of zeolites.

At the same concentration of cadmium, removal efficiency was from 45 to 70%. It was clear that the lead was more selectively removed than cadmium. The effect of temperature on ion-exchange properties was demonstrated. The exchange of the lead and cadmium increased with increasing temperature. Croatian zeolites are recommendable adsorbents and ion exchangers of lead and cadmium from wastewaters.

## REFERENCES

- Barer R. M. (1987) *Zeolites and Clay Minerals as Sorbent and Molecular Sieves*. Academic Press, New York
- Blanchard G., Maunay M. and Martin G. (1984) Removal of heavy metals from waters by means of natural zeolites. *Wat. Res.* **18**, 1501–1507.
- Breck D. W. (1964) Crystalline molecular sieves. *J. Chem. Educ.* **41**, 678–689.
- Cerjan-Stefanović Š., Kaštelan-Macan M. and Filipan T. (1992) Ion exchange of modified zeolite. *Wat. Sci. Technol.* **26**, 1185–1189.
- Cerjan-Stefanović Š., Ćurković L. and Filipan T. (1996) Metal ion exchange by natural zeolites. *Croat. Chem.* **69**, 281–290.
- Corbin D. R., Burgess B. F., Vega A. J. and Farelee R. D. (1987) Comparison of analytical techniques for the determination of silicon and aluminium content in zeolites. *Anal. Chem.* **59**, 2722–2728.
- Hafez M. B., Nazmy A. F., Salem F. and Eldesoki M. (1978) Fixation mechanism between zeolite and some radioactive elements. *J. Radioanal. Chem.* **47**, 115–119.
- Jorgensen S. E., Libor O. and Graber, K. L. (1976) Ammonia removal by use of clinoptilolite. *Wat. res.* **10**, 213–224.
- Joshi M. S. and Mohan Rao P., (1983) Cation sieve properties of natural heulandite. *J. Colloid Interface Sci.* **95**, 131–134.
- Kesraoui-Ouki S., Cheeseman C. R. and Perry R. (1994) Natural zeolite utilization in pollution control: A review of applications to metals' effluents. *J. Chem. Technol. Biotechnol.* **59**, 121–126.
- Malliou E., Loizidou M. and Spyrellis N. (1994) Uptake of lead and cadmium by clinoptilolite. *Sci. Total Environ.* **149**, 139–144.
- Semmens M. J. and Martin W. P. (1988) The influence of pretreatment on capacity and selectivity of clinoptilolite for metal ions. *Wat. Res.* **22**, 537–542.
- Wark M., Lutz W., Schulz-Ekloff G. and Dyer A. (1994) Quantitative monitoring of side products during high loading of zeolites by heavy metals. *Zeolites* **13**, 658–670.
- Zamzow M. J., Eichbaum B. R., Sandgren K. R. and Shanks D. E. (1990) Removal of heavy metals and other cations from wastewater using zeolites. *Sep. Sci. Technol.* **25**, 1555–1569.