

Use of natural clinoptilolite for the removal of lead, copper and zinc in fixed bed column

Marinos A. Stylianou^{*}, Michalis P. Hadjiconstantinou, Vasilis J. Inglezakis,
Konstantinos G. Moustakas, Maria D. Loizidou

*National Technical University of Athens, School of Chemical Engineering, Unit of Environmental Science and Technology,
9 Heron Polytechniou Str., Zographou Campus, 15773 Athens, Greece*

Received 29 May 2006; received in revised form 20 September 2006; accepted 25 September 2006

Available online 18 October 2006

Abstract

This work deals with the removal of lead, copper and zinc from aqueous solutions by using natural zeolite (clinoptilolite). Fixed bed experiments were performed, using three different volumetric flow rates of 5, 7 and 10 bed volume/h, under a total normality of 0.01N, at initial pH of 4 and ambient temperature (25 °C). The removal efficiency increased when decreasing the flow rate and the following selectivity series was found: $Pb^{2+} > Zn^{2+} \geq Cu^{2+}$. Conductivity measurements showed that lead removal follows mainly ion exchange mechanism, while copper and zinc removal follows ion exchange and sorption mechanism as well.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Ion exchange; Copper; Lead; Zinc; Clinoptilolite; Fixed bed

1. Introduction

Industrial wastewater is often characterized by considerable heavy metal content and, therefore, treatment is required prior to disposal in order to avoid water pollution. Heavy metals, such as zinc, lead and copper, are prior toxic pollutants existent in industrial wastewater, while they also constitute common groundwater contaminants [1]. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [2]. Chemical precipitation, oxidation, ultra filtration, reverse osmosis and electro dialysis, membrane filtration, carbon adsorption and ion exchange are the main techniques for treating contaminated wastewater streams containing heavy metals. Ion exchange on natural zeolites seems to be more attractive method due to the large available quantities of the mineral and its low cost. Furthermore, the used zeolite can be disposed or regenerated with low cost [3].

Ion exchange is the exchange of ions between a liquid phase and a porous solid, which may be synthetic or natural. Zeolites are hydrated aluminosilicate minerals with a cage-like struc-

ture that offers large internal and external surface areas for ion exchange. They possess a net negative structural charge due to isomorphic substitution of cations in the mineral lattice. Hence, they have a strong affinity for metal cations, but only little affinity for anions and non-polar organic molecules. Clinoptilolite is the most abundant natural zeolite. Its characteristic tabular morphology includes an open reticular structure of easy access, formed by open channels of 8–10 membered rings. Exchangeable ions, such as Na, K, Ca and Mg, commonly occupy these channels [4].

Among zeolite species, clinoptilolite has received extensive attention due to its attractive selectivity for certain heavy metal cations, such as lead, copper, zinc, cadmium and nickel. Furthermore, it can be used as an ion exchanger for the removal of ammonium ions. Most ion-exchange processes, both at laboratory and plant scale, are performed in columns. A solution is passed through a bed of ion-exchanger material where its composition is modified by ion exchange or sorption. The composition of the effluent and its change with time depends on the properties of the ion exchanger, the composition of the feed and the operating conditions. The curve representing the cation exit concentration versus time (or effluent volume) is called breakthrough curve and is used to characterize the process [5,6].

^{*} Corresponding author. Tel.: +30 2107722334/3154; fax: +30 2107723285.
E-mail address: marstyl@central.ntua.gr (M.A. Stylianou).

Several relevant studies are referred in literature, based on batch or column experiments [1,4,6–12]. More specifically, regarding column studies: Blanchard et al. [13] reported that water containing heavy ions, such as Pb^{2+} , Zn^{2+} and Cu^{2+} ions, can be treated in fixed beds of clinoptilolite. The order of efficiency was found to be $\text{Pb}^{2+} > \text{Cu}^{2+} \geq \text{Zn}^{2+}$. Zamzow et al. [14] reported the following selectivity series $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$. Cincotti et al. [15] examined natural clinoptilolites to evaluate the removal of copper, cadmium, lead, zinc and ammonium. The natural material was either used as received or once converted into the sodium form. Inglezakis and Grigoropoulou [16] investigated the effects of flow rate (5–15 BV/h), particle size, concentration and Na^+ -enrichment of natural clinoptilolite on the removal efficiency of Pb^{2+} , Cu^{2+} , Fe^{3+} and Cr^{2+} in aqueous solutions. The removal efficiency order was $\text{Pb}^{2+} > \text{Cr}^{2+} > \text{Fe}^{3+} \geq \text{Cu}^{2+}$. Mustafa et al. [17] investigated the removal of Pb by zeolite (clinoptilolite) and sepiolite. Medvidovic et al. [18] investigated the removal of lead ions from aqueous solutions using the column method. They concluded that the BV at the breakthrough point decreases with the increase of lead concentration in the initial solution, at the same flow.

The present study aims at investigating the ability of Greek clinoptilolite to treat solutions containing heavy metals, namely, Pb^{2+} , Cu^{2+} and Zn^{2+} , and establish the selectivity series of clinoptilolite for these metals. Furthermore, the evolution conductivity and pH of the samples during the ion exchange process are thoroughly investigated.

2. Experimental

2.1. Heavy metal solutions

All chemicals used were analytical grade reagents. Stock solutions of metals were prepared in a concentration of 0.01N using nitric salts dissolved in deionized water. The pH was initially adjusted at 4 to avoid precipitation during all ion exchange experiments using nitric acid (HNO_3). Initial pH values of the original solution are: Pb = 5.23, Cu = 5.75, Zn = 6.89.

2.2. Ion exchange material

The mineral used was supplied by S&B Industrial Minerals SA and IGME (Institute of Geology & Mineral Exploration). Clinoptilolite 2–5 mm was used in this study. The chemical composition of the material was obtained through XRF and wet chemical analysis (for oxides: XRF on fused beads containing $\text{Li}_2\text{B}_4\text{O}_7$ flux, LOI: mass loss upon firing at 1100°C) (Table 1). XRD analysis for the mineral is shown in Fig. 1. CEC of clinoptilolite is 188.40 mequiv./100 g (NH_4AC method).

2.3. Fixed bed experiments

Fixed bed experiments were conducted in order to examine the Pb^{2+} , Cu^{2+} and Zn^{2+} uptake by natural clinoptilolite, using three different volumetric flow rates of 5–7–10 BV/h [18.05–25.27–36.1 mL/min] (where BV is a volume of liquid equal to the volume of the empty bed), under a total normality

Table 1
Chemical analysis of clinoptilolite

Oxide	% (w/w)
SiO_2	70.08
Al_2O_3	11.72
TiO_2	0.14
Fe_2O_3	0.67
MgO	0.71
CaO	3.18
Na_2O	0.55
K_2O	3.50
LOI	9.45

of 0.01N and initial pH value equal to 4 and ambient temperature (25°C). The ion exchange process was conducted in 0.7 m long plexiglass columns of 0.02 m internal diameter (Fig. 2) [$V_{\text{bed}} = 216.6$ mL, depth of the bed = 0.69 m]. The solution was introduced at a constant volumetric flow rate (Q) and concentration (C), using a peristaltic pump in up-flow mode in order to assure complete wetting of the zeolite particles. Liquid samples were withdrawn at the exit of the bed at specific time intervals, depending on the flow rate, acidified with HNO_3 at pH 2 and analyzed for heavy metal cations. By plotting the exit metal concentration versus time, the breakthrough curves can be obtained.

As the feed passes through the bed, the ion exchange zone moves downstream and, in due course, reaches the exit. When the concentration of the effluent reaches 5–10% of the influent, the flow is stopped. This point is commonly referred in the related literature as “breakthrough point” or “breakpoint”, and is fixed accordingly to the needs of the operation. Since only the last portion of the fluid proceeded has this concentration level, the average fraction of the solute removed from the beginning until the breakpoint is generally very high [16]. In the present study, the “breakpoint” is set at 10% and the total volume of the treated solution until this point (V_{BR} , expressed in terms of bed volumes) is used as a measure of the operation’s removal efficiency.

The samples were analyzed for heavy metal cations by atomic absorption spectrometry (Perkin-Elmer model 2380 spectrophotometer).

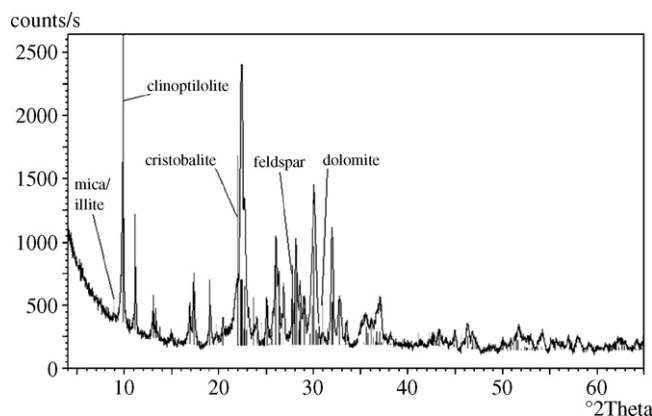


Fig. 1. XRD analysis for zeolite.

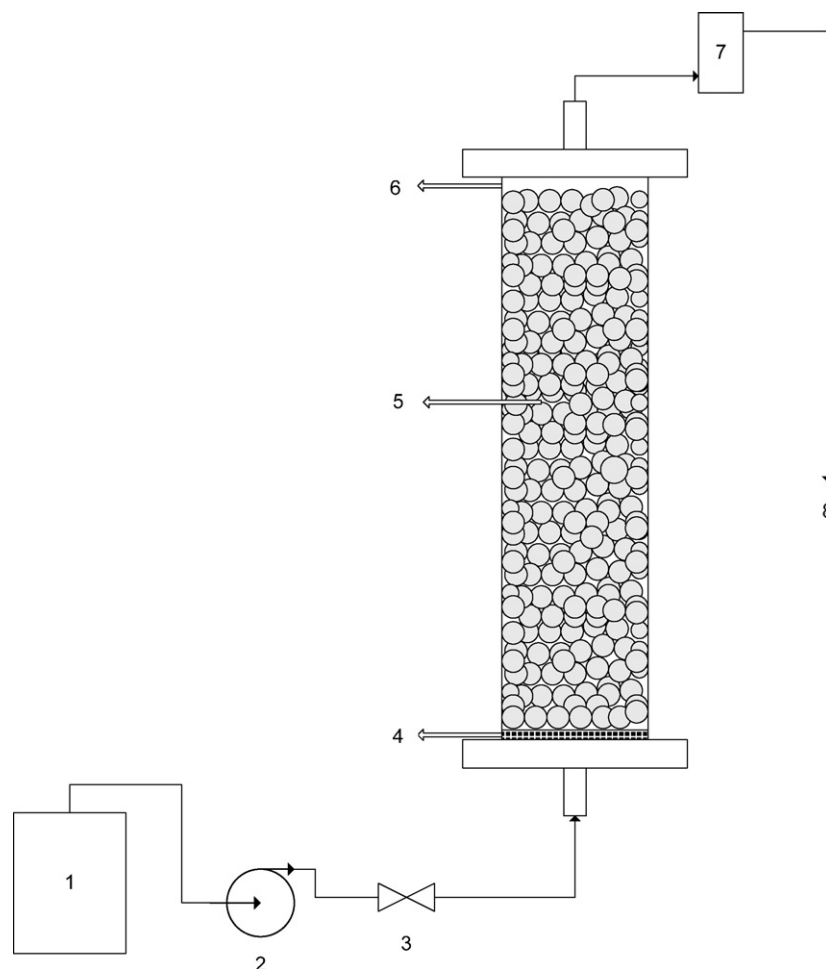


Fig. 2. The experimental setup for adsorption runs: (1) metal solution tank; (2) peristaltic pump; (3) valve; (4) plastic sieve; (5) natural material bed; (6) plexiglass column; (7) samples collector; (8) outlet.

3. Results and discussion

3.1. Effect of volumetric flow rate

The effect of volumetric flow rate is examined for clinoptilolite particles of 2–5 mm and concentration of 0.01N. Typical experimental breakthrough curves are shown in Fig. 3 and the effect of volumetric flow rate on V_{BR} is presented in Fig. 4.

As it can be seen, the removal efficiency is favoured by lower volumetric flow rates in the region of 5–10 BV/h. However, the increment in the removal efficiency is not always directly proportional to the flow rate and, furthermore, depends on the specific cation, a phenomenon which is well known [16].

Lower flow rates result in high residence times in the column. It is well known that, because of the relatively slow loading kinetics of zeolites, relatively long residence times are needed [19]. In actual column operation, any volume element of the solution is in contact with a given layer of the bed for only a limited time period, usually insufficient for the equilibrium attainment. As a result, the failure of attaining local equilibrium causes lower uptake of cations from the incoming solution [5]. However, some side effects of low flow rates may be serious in bench-scale operations. In the present study, upflow operation was chosen in order

to assure complete wetting of the material. In downflow mode, complete wetting of the material is not always possible and specially designed liquid distributors should be used. Generally, by lowering the flow rate, the liquid hold-up of the bed is lowered and liquid maldistribution may have serious effects upon the effectiveness of the process. Liquid maldistribution leads a portion of the flow through preferential paths, a phenomenon called “channelling” while low liquid hold-up values means that a portion bed remains dry: in both cases the net result is that a part of the material is not well wetted or even dry and, thus, it is not active during the process [16].

According to the results of the present study, flow rates higher than 10 BV/h should be avoided, since breakthrough would occur faster and with less sharpened boundaries. Flow rates that are lower than 5 BV/h are expected to be beneficial on removal efficiency, leading, however, to practically too high retention times. Consequently, the value of 5 BV/h is considered to be a reasonable flow rate.

As it can be seen in Fig. 4, the following selectivity series is given: $Pb^{2+} > Zn^{2+} \geq Cu^{2+}$.

In Table 2, for comparison reasons, the breakthrough points found in literature are reported, expressed as BV of treated effluent till breakpoint. It is obvious that V_{BR} depends on var-

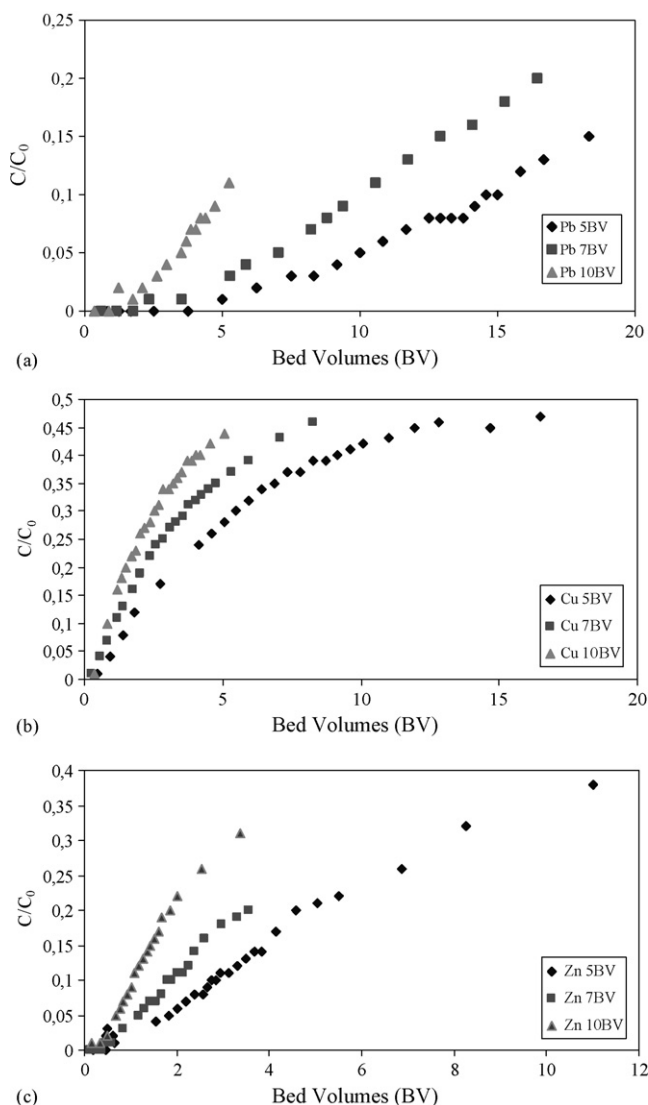


Fig. 3. Typical experimental breakthrough curves for the ion exchange of (a) Pb, (b) Cu and (c) Zn, on natural clinoptilolite ($C=0.01N$, $Q=5-7-10$ BV/h, $d=2-5$ mm).

ious parameters, such as volumetric flow rate, initial solution concentration, particle size, modification of natural sample (pre-treatment) and on different type of raw material. This is the reason why the results cannot be compared directly.

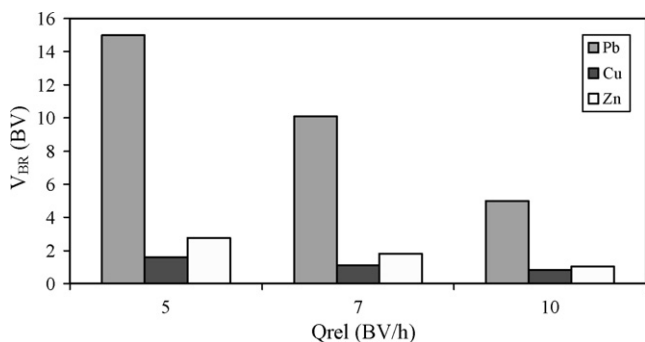


Fig. 4. Effect of volumetric flow rate on breakpoint for the ion exchange of heavy metals on natural clinoptilolite ($C=0.01N$, $d=2-5$ mm). Total volume of treated solution until breakpoint (V_{BR}) is expressed in terms of bed volumes.

The effect of solution concentration on V_{BR} [16,18] showed that the dilution of the solutions is leading to an increase of the total volume treated. Furthermore, particle size effect shows that, by lowering the particle size, V_{BR} increases. It is well known that by decreasing the particle size, the performance of adsorption and ion exchange processes is improved [5]. Finally, the modification of natural sample results in higher breakpoint values. The improvement of the removal efficiency is attributed to the increase of easily removable Na^+ ions in the zeolite structure.

According to Inglezakis and Grigoropoulou [16], who used similar experimental conditions, the study of the effect of volumetric flow rate showed that by lowering the volumetric flow rate from 15 to 5 BV/h, V_{BR} increases by a factor near to 2.5–2.8. Medvidovic et al. [18] reported that by changing the flow rate from 13.9 to 4.6 BV/h, V_{BR} increased by a factor near to 1.2. According to the present study by lowering the flow rate from 10 to 5 BV/h, V_{BR} increased by a factor near to 1.9–3 for all metals studied. Thus, the results of the present study seem to be in general agreement with the already published ones.

3.2. Conductivity and pH studies

Ion exchange resembles sorption in that, in both cases, a dissolved species is taken up by a solid. The characteristic difference between the two phenomena is that ion exchange, in contrast to sorption, is a stoichiometric process. Every ion, which is removed from the solution is replaced by an equivalent amount of another ionic species of the same sign, while in sorption a solute (an electrolyte or non-electrolyte) is taken up without being replaced by another species [5].

Conductivity (k) is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of the ions, on their total concentration, mobility and valence and on the temperature of the measurement. Solutions of most inorganic compounds are relatively good conductors. The equivalent conductivity (Λ) of a solution is the conductivity per unit of concentration (c) [20]:

$$\Lambda = \frac{0.001k}{c} \quad (1)$$

It is found that at constant temperature (Λ) increases as the concentration decreases, and, in many cases, it is quite clear that extrapolation of (Λ) to zero concentration gives a finite value (Λ_0). Kohlrausch deduced the law of independent ionic mobilities, which states that each type of ion in an electrolyte contributes a characteristic amount to the total conductance [21]:

$$\Lambda_0 = \lambda_+^0 + \lambda_-^0 \quad (2)$$

The specific electric conductivity of a solution is essentially given by the concentrations and mobilities of the charge carriers (electrons or ions), which the solution contains. In Table 3, the equivalent conductance (mobilities) of some ions of interest are presented.

The main exchangeable cations of clinoptilolite are Na, K, Ca and Mg (Table 1). As it can be seen (Table 3), the mobilities of these cations are close in value to the mobilities of Pb, Zn and Cu. Thus, it is expected that if ion exchange is the main

Table 2
Breakthrough points data available from zeolite column studies

Metal	Q (BV/h)	d (mm)	C ₀ (mg/L)	Breakpoint (%)	V _{BR} (BV)	References
Pb ²⁺	5	0.8–1	1000	10	21.5	[16]
	5	1.18–1.4	1000	10	14	[16]
	5	1.4–1.7	1000	10	11.5	[16]
	5	1.18–1.4	1000	10(p)	28	[16]
	5	1.18–1.4	500	10	40	[16]
	5.5	2–5	1000	10	15	Present study
	7.1	2–5	1000	10	10.1	Present study
	10.1	2–5	1000	10	5	Present study
	10	1.18–1.4	1000	10	5.5	[16]
	15	1.18–1.4	1000	10	5.1	[16]
	12	1–2	50	10	120	[17]
	25.96	–	65	5	250	[15]
	10	0.4–0.5	0.261	10(p)	290	[13]
	4.6	0.6–0.8	212.5	5	360	[18]
	13.9	0.6–0.8	212.5	5	303	[18]
4.6	0.6–0.8	520.5	5	147	[18]	
Cu ²⁺	5	0.8–1	1000	10	5	[16]
	5	1.18–1.4	1000	10	4.1	[16]
	5	1.4–1.7	1000	10	3	[16]
	5	1.18–1.4	1000	10(p)	7	[16]
	5	1.18–1.4	500	10	12	[16]
	5.5	2–5	1000	10	1.6	Present study
	7.1	2–5	1000	10	1.1	Present study
	10.1	2–5	1000	10	0.84	Present study
	10	1.18–1.4	1000	10	1.2	[16]
	15	1.18–1.4	1000	10	1.1	[16]
	10	0.4–0.5	0.241	10(p)	150	[13]
Zn ²⁺	10	0.4–0.5	0.235	10(p)	190	[13]
	5.5	2–5	1000	10	2.75	Present study
	7.1	2–5	1000	10	1.8	Present study
	10.1	2–5	1000	10	1.05	Present study

(p): Na-form [pretreated clinoptilolites].

uptake mechanism, the solution conductivity remains practically constant. Furthermore better mobility of lead through zeolitic structure is due to lower hydrated ion radius compared to copper and zinc. The later have similar values of ionic radius (Table 3).

As it can be seen from Fig. 5, lead solution conductivity remains practically constant throughout the experiment, in spite of copper and zinc solution conductivity that slightly decreases. This behaviour is a result of two parallel uptake phenomena: ion exchange and adsorption. A constant conductivity value throughout the uptake process could be an indication that ion exchange is the predominant mechanism.

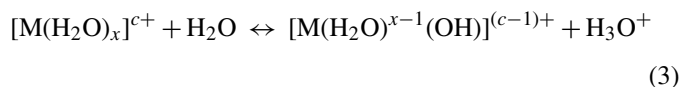
Table 3
Equivalent conductances λ_+^0 and λ_-^0 (mho cm²/equiv.) and ionic radius (Å) for ions in water [20–22]

Cation	λ_+^0	Cation ionic radius (Å)	Anion	λ_-^0
H ⁺	349.80	–	OH [–]	199.18
(1/2)Ca ²⁺	59.50	0.99	NO ₃ [–]	71.44
(1/2)Mg ²⁺	53.06	0.66	HCO ₃ [–]	44.50
Na ⁺	50.11	0.97	(1/2)CO ₃ ^{2–}	72.00
K ⁺	73.50	1.33	(1/2)SO ₄ ^{2–}	80.00
(1/2)Pb ²⁺	70.00	1.20		
(1/2)Cu ²⁺	53.60	0.72		
(1/2)Zn ²⁺	52.80	0.74		

The pH values of the exit solution are shown in Fig. 6. No precipitation was observed during the experiment.

It is well known that natural zeolites tend to elevate the pH in acidic solutions. This is due to the H⁺ exchange with Na⁺, the binding of H⁺ to the Lewis basic sites linked to the framework oxygen atoms of the clinoptilolite and the presence of OH[–] in solution deriving from hydrolysis of some species present in natural zeolite [23,24].

The pH range under which ion exchange takes place should be specified. Several reports tried to determine the optimum pH value of the aqueous solution to be treated with natural zeolite, focusing on copper, lead, zinc [4,6,7,11,12,24–27]. H⁺ cations should be considered as competitive ones in ion-exchange processes and, consequently, ion exchange of metals is favoured by high pH, which should, however, be lower than the minimum pH for precipitation. Another factor that should be taken into account in ion exchange studies is that in metal ion solutions, pH is affected by hydrolysis, according to the following two-way reversible reaction:



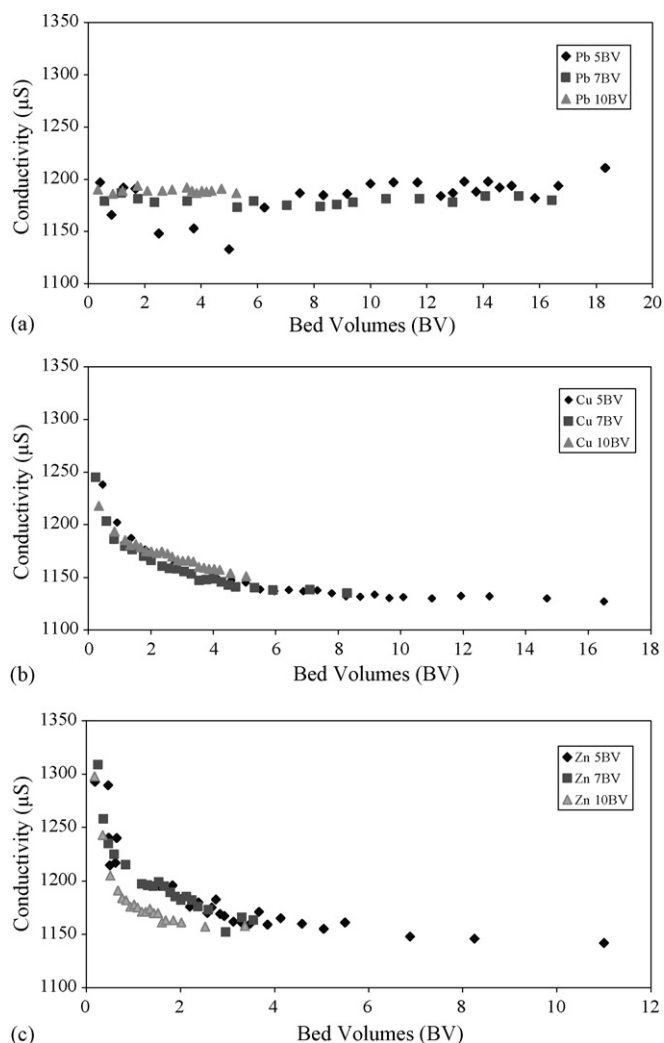


Fig. 5. Conductivity measurement for the ion exchange of (a) Pb, (b) Cu and (c) Zn, on natural clinoptilolite ($C=0.01N$, $d=2-5$ mm).

Consequently, at decreasing pH the above equilibrium is shifted to the left and more highly charged metal complexes are formed, a fact beneficial for the exchange [6].

On the basis of Fig. 6, it is evident that the pH of the exit solution decreases from 6.5–7 to 5–6.5, depending on the metal removed. In the first stages of the ion exchange process, as the solution passes through the zeolite, the metals are totally removed and, thus, the pH in the first layers of the bed increases from its initial value (4) to almost neutral (6.5–7). This is due to the absence of metals in the solution and, thus, the absence of hydrolysis which leads to more acidic solutions. At the same time, the zeolite elevates the pH due to the removal of H^+ ions from the solution. As the zeolite is gradually loaded with metals, the solution concentration increases in the bed and, thus, as the time passes, the pH is decreased (5–6.5) due to hydrolysis. Again, zeolite tends to elevate the solution pH; however, the effect of hydrolysis is stronger, at least in the concentration range that is used in the present study.

Furthermore, measuring the change of the pH value in the effluent of a fixed-bed column can very successfully monitor the progress of the lead service cycle and the zeolite regeneration

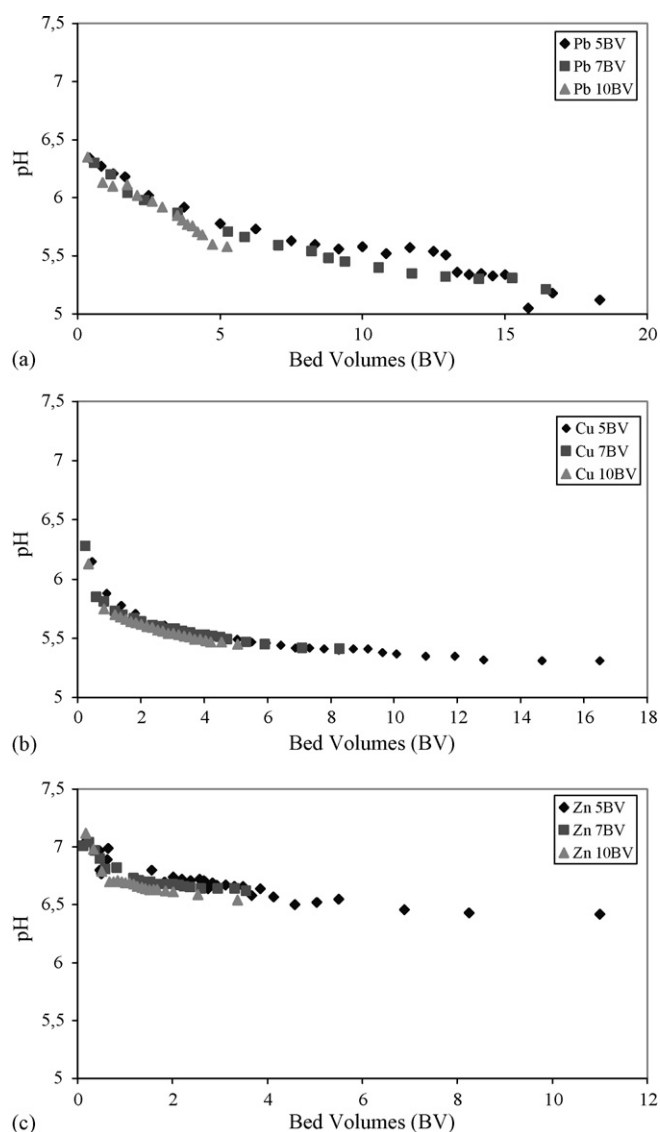


Fig. 6. pH measurement for the ion exchange of (a) Pb, (b) Cu and (c) Zn, on natural clinoptilolite ($C=0.01N$, $d=2-5$ mm).

cycle. This can indicate both the breakthrough point and the completion of the regeneration process, which is very important for achieving practical application [18].

4. Conclusions

Natural clinoptilolite is investigated for the removal of lead, copper and zinc from aqueous solutions in a clinoptilolite fixed bed. The removal efficiency, expressed by the volume treated until breakpoint (V_{BR}), increases when decreasing the flow rate. This is due to the higher contact times achieved by using lower flow rates. Maldistribution and low liquid hold-ups have been avoided by operating the fixed beds under upflow conditions. The obtained selectivity series is: $Pb^{2+} > Zn^{2+} \geq Cu^{2+}$, which is in agreement with other studies. The treated volume until breakpoint for a flow rate of 5 BV/h is found to be around 14 BV for Pb^{2+} , 3 BV for Zn^{2+} and less than 2 BV for Cu^{2+} . This result indicates that under the experimental conditions used in the present

study, zeolite fixed bed is efficient for Pb-containing solutions while for Zn- and Cu-containing solutions modifications should be applied, as for example dilution of the solutions or usage of smaller zeolite particles. Conductivity measurements indicated that lead removal follows ion exchange phenomenon, while copper and zinc removal follows ion exchange–sorption mechanism in parallel. Furthermore, pH measurements showed that pH of the exit solution decreases during operation from 6.5–7 to 5–6.5, depending on the metal removed. This result is a combined effect of the zeolite tendency to raise the pH of an acidic solution and the hydrolysis of the metals.

Acknowledgments

This paper has been prepared in the framework of the EPEAEK II, Pithagoras project entitled “Investigation and optimization of systems using natural zeolites and other mineral materials in environmental applications”. As a result, the authors would like to express thanks to the Ministry of National Education and Religious Affairs of Greece which is financing all EPEAEK II projects. We would also like to thank the Institute of Geology & Mineral Exploration (IGME) and S&B Industrial Minerals SA for supplying the minerals for this work.

References

- [1] J. Peric, M. Trgo, N.V. Medvidovic, Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms, *Water Res.* 38 (2004) 1893–1899.
- [2] A.S.D. Maria Barros, E.A. Silva, P.A. Arroyo, C.R.G. Tavares, R.M. Schneider, M. Suszek, E.F. Sousa-Aguiar, Removal of Cr(III) in fixed bed column and batch reactors using as adsorbent zeolite NaX, *Chem. Eng. Sci.* 59 (2004) 5959–5966.
- [3] S. Bailey, T. Olin, M. Bricka, D. Adrian, A review of potentially low-cost sorbents for heavy metals, *Water Res.* 33 (1999) 2469–2479.
- [4] M.V. Mier, R.P. Callejas, R. Gehr, B.J. Cisneros, P.J.J. Alvarez, Heavy metal removal with Mexican clinoptilolite: multi-component ionic exchange, *Water Res.* 35 (2001) 373–378.
- [5] F. Helfferich, *Ion Exchange*, Dover Publications Inc., New York, 1995.
- [6] V.J. Inglezakis, M.D. Loizidou, H.P. Grigoropoulou, Ion exchange of Pb²⁺, Cu²⁺, Fe³⁺, and Cr³⁺ on natural clinoptilolite: selectivity determination and influence of acidity on metal uptake, *J. Colloid Interf. Sci.* 261 (2003) 49–54.
- [7] M.I. Panayotova, Kinetics and thermodynamics of copper ions removal from wastewater by use of zeolite, *Waste Manage.* 21 (2001) 671–676.
- [8] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, *J. Colloid Interf. Sci.* 280 (2004) 309–314.
- [9] S. Kesraoui-Ouki, M. Kavannagh, Performance of natural zeolites for the treatment of mixed metal–contaminated effluents, *Waste Manage. Res.* 15 (1997) 383–394.
- [10] H. Faghihian, M.G. Marageh, H. Kazemian, The use of clinoptilolite and its sodium form for removal of radioactive cesium and strontium from nuclear wastewater and Pb²⁺, Ni²⁺, Cd²⁺, Ba²⁺ from municipal wastewater, *Appl. Radiat. Isot.* 50 (1999) 655–660.
- [11] U. Wingenfelder, C. Hansen, G. Furrer, R. Schulin, Removal of heavy metals from mine waters by natural zeolites, *Environ. Sci. Technol.* 39 (2005) 4606–4613.
- [12] A.H. Oren, A. Kaya, Factors affecting adsorption characteristics of Zn²⁺ on two natural zeolites, *J. Hazard. Mater. B* 131 (2006) 59–65.
- [13] G. Blanchard, M. Maunaye, G. Martin, Removal of heavy metals from waters by means of natural zeolites, *Water Res.* 18 (12) (1984) 1501–1507.
- [14] M.J. Zamzow, B.R. Eichbaum, K.R. Sandgren, D.E. Shanks, Removal of heavy metal and other cations from wastewater using zeolites, *Sep. Sci. Technol.* 25 (1990) 1555–1569.
- [15] A. Cincotti, N. Lai, R. Orru, G. Cao, Sardinian natural clinoptilolites for heavy metals and ammonium removal: experimental and modeling, *Chem. Eng. J.* 84 (2001) 275–282.
- [16] V.J. Inglezakis, H.P. Grigoropoulou, Effects of operating conditions on the removal of heavy metals by zeolite in fixed bed reactors, *J. Hazard. Mater. B* 112 (2004) 37–43.
- [17] T. Mustafa, U. Mart, B. Yuksel, M.S. Celik, Lead removal in fixed-bed columns by zeolite and sepiolite, *Chemosphere* 60 (2005) 1487–1492.
- [18] N.V. Medvidovic, J. Peric, M. Trgo, Column performance in lead removal from aqueous solutions by fixed bed of natural zeolite–clinoptilolite, *Sep. Purif. Technol.* 49 (2006) 237–244.
- [19] P. Burn, D.K. Ploetz, A.K. Saha, D.C. Grant, M.C. Skriba, Design and testing of natural/blended zeolite ion exchange columns at West Valley, *AIChE Symp. Ser.* 83 (1987) 66–72.
- [20] APHA, AWWA, WEF, *Standard Methods for the Examination of Water and Wastewater*, 20th ed., APHA/AWWA/WEF, 1998.
- [21] Edmund C. Potter, *Electrochemistry Principles and Applications*, Cleaver-Hume Press Ltd., 1999, pp. 20–29.
- [22] *Handbook of Chemistry and Physics*, 53rd ed., The Chemical Rubber Co., 1972, p. F-177.
- [23] A. Rivera, R.G. Fuentes, E. Altshuler, Time evolution of a natural clinoptilolite in aqueous medium: conductivity and pH experiments, *Micropor. Mesopor. Mater.* 40 (2000) 173–179.
- [24] E.A. Kurtoglu, G. Atun, Determination of kinetics and equilibrium of Pb/Na exchange on clinoptilolite, *Sep. Purif. Technol.* 50 (2006) 62–70.
- [25] K. Athanasiadis, B. Helmreich, Influence of chemical conditioning on the ion exchange capacity and on kinetic of zinc uptake by clinoptilolite, *Water Res.* 39 (2005) 1527–1532.
- [26] L. Curkovic, C.S. Stefanovic, T. Filipan, Metal ion exchange by natural and modified zeolites, *Water Res.* 31 (1997) 1379–1382.
- [27] M. Wark, W. Lutz, G. Schultz-Ekloff, A. Dyer, Quantitative monitoring of side products during high loading of zeolites by heavy metals via pH measurements, *Zeolites* 13 (1993) 658–662.