THE EFFECT OF FIXED BED DEPTH OF ZEOLITE ON REMOVAL OF LEAD AND ZINC FROM BINARY AQUEOUS SOLUTIONS

Ivona Nuić, Jelena Perić, Marina Trgo, Nediljka Vukojević Medvidović, Marin Ugrina
Faculty of Chemistry and Technology, University of Split, Teslina 10/V, 21 000 Split, Croatia
E-mail: ivona@ktf-split.hr

ABSTRACT

The column method on the fixed bed of natural zeolite clinoptilolite was applied to remove lead and zinc ions from a binary aqueous solution. The effect of bed depth on the effective capacity has been investigated. It has been found that higher bed depths enhance column efficiency and provide equal binding of both metal ions independently of their affinity to the zeolite.

Keywords**:** zeolite, lead, zinc, column method, binary solution

INTRODUCTION

Natural zeolite tuff containing clinoptilolite is capable of removing heavy metal ions from aqueous solutions by ion exchange. Industrial wastewaters usually contain more than one heavy metal ion and research into their removal from binary solutions is very important [1,2]. This article focuses on the interaction of lead and zinc competing for ion exchange sites in natural clinoptilolite. The effect of fixed bed depth on the capacity of removal of zinc and lead from binary aqueous solutions has been investigated. The breakthrough curves and regeneration curves have been used for characterization of this effect.

EXPERIMENTAL

Sample preparation

The raw zeolite sample originated from the Vranjska Banja (Serbia) deposit. According to the semi quantitative mineralogical analysis zeolite consists up to 80 % of the clinoptilolite. The zeolite was sieved to particle size of 0.6-0.8 mm, rinsed with ultrapure water and dried at 60°C.

Column study

A series of experiments were carried out in glass columns with constant dimensions of inner diameter of 12 mm and height of 500 mm. Columns were filled with the zeolite sample up to 40 mm and 120 mm, to the zeolite bed volume of 4.52 cm^3 and 13.56 cm^3, respectively. The binary feed solution was prepared by dissolving $Pb(NO_3)_2$ and $Zn(NO_3)_2$ x 6 H_2O in ultrapure water. The initial concentration of 1.06 mmol/l contained approximately equimolar amounts of lead and zinc, Pb/Zn=0.95. Column experiments were conducted using the down-flow mode through the fixed bed with a vacuum pump at the constant flow rate of 1 ml/min and at 25°C. After each service cycle, when the fixed bed became exhausted, the regeneration was performed with $NaNO_3$, c=176.5 mmol/l, at the same flow rate. In all experiments, the samples were collected at the bottom of the column and analyzed for heavy metal cations my means of the complexometric method and ion chromatography.

RESULTS AND DISCUSSION

The experimental results for two different bed depths are shown graphically by plotting the c/c_o ratio (c-concentration of metal ions in the effluent and c_o-concentration of metal ions in the influent) versus time or volume solution passed through the zeolite bed expressed as bed volume, BV.

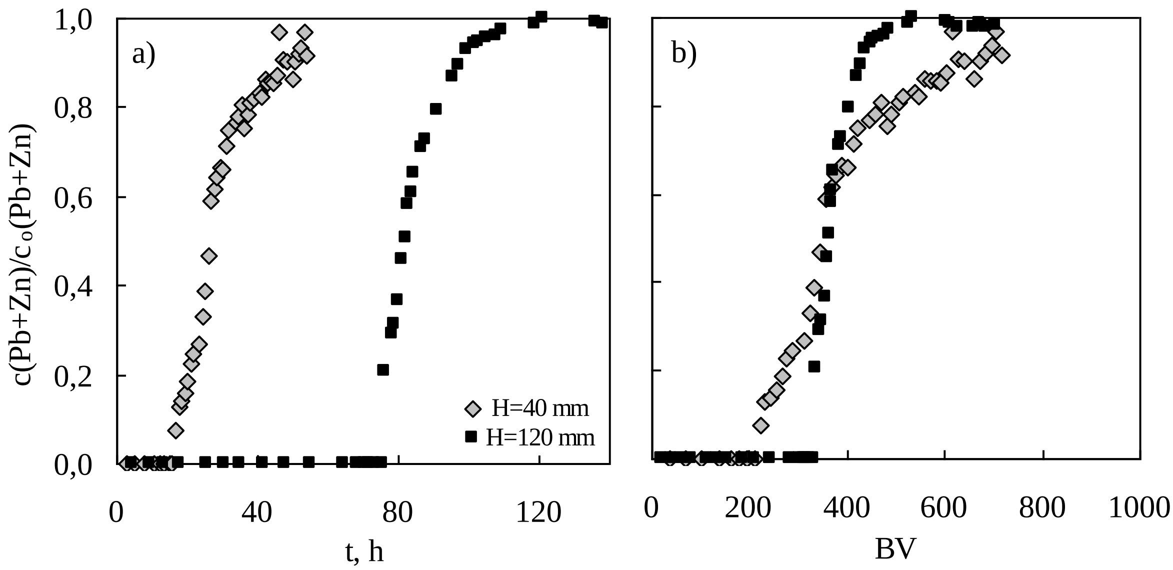

Figure 1. Effect of bed depth of zeolite on breakthrough curves expressed as: a) c/c_o vs. t and b) c/c_o vs. BV.

With increased bed depth, the breakthrough and exhaustion points shift towards higher values of time and volume, and breakthrough curve becomes steeper (Figure 1). The increase of bed depth is reflected in increasing contact time, as well as in the reduction of the effect of dispersion on the overall mass transfer process in the column [3]. Figure 2 shows the experimentally obtained breakthrough curves for each metal ion in the binary solution.

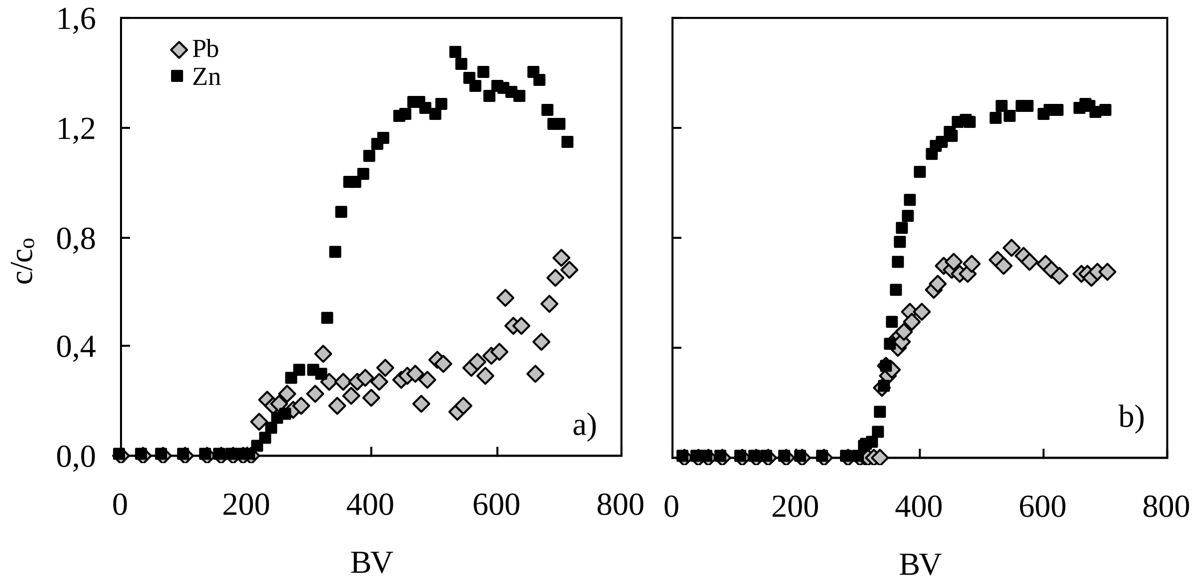

Figure 2. Breakthrough curves for each metal ion in the binary solution for zeolite bed depths: a) 40 mm, b) 120 mm; $c/c_o = c(Pb \text{ or } Zn)/c_o(Pb \text{ or } Zn)$.

Based on the Michaels method [4], the capacity at the breakthrough and exhaustion points for each metal ion in the binary solution has been calculated and is presented in Table 1.

Table 1. Paremeters of the breakthrough curves calculated by graphical integration.

H, mm	V_B, BV	t_B, h		q_B, mmol/g	$q_B(Pb)/q_B(Zn)$	V_E, BV	t_E, h	q_E, mmol/g	$q_E(Pb)/q_E(Zn)$
40	221.2	16.6	Pb+Zn	0.336	0.942	614.8	46.3	0.509	1.980
			Pb	0.163				0.396	
			Zn	0.173				0.200	
120	337.6	76.3	Pb+Zn	0.527	0.905	535.6	121.1	0.587	1.135
			Pb	0.250				0.312	
			Zn	0.276				0.275	

Note: H - bed depth, q_B – capacity at the breakthrough point, q_E – capacity at the exhaustion point, V_B – breakthrough volume, V_E – exhaustion volume, t_B – breakthrough time, t_E – exhaustion time, BV – bed volume.

It is evident from Figure 2 that up to the breakthrough point, lead and zinc ions bind simultaneously. This is confirmed by the ratio of breakthrough capacities for Pb and Zn which are close to the Pb/Zn ratio in the influent (Table 1). As the process progresses, lead ions displace bound zinc ions and finally occupy most of sorption sites, particularly for the bed depth of 40 mm. This is confirmed by significant differences in Pb and Zn exhaustion capacities, where $q_E(Pb)$ is twice higher than $q_E(Zn)$, as well as by a significantly lower quantity of regenerated zinc (Figure 3a). At the bed depth of 120 mm, the zinc ions displacement effect is delayed, resulting in a higher quantity of zinc ions uptake at the exhaustion point. For that reason, the $q_E(Pb)/q_E(Zn)$ ratio is slightly higher than the ratio at breakthrough. This is confirmed by quantities of regenerated lead and zinc ions, shown in Figure 3b.

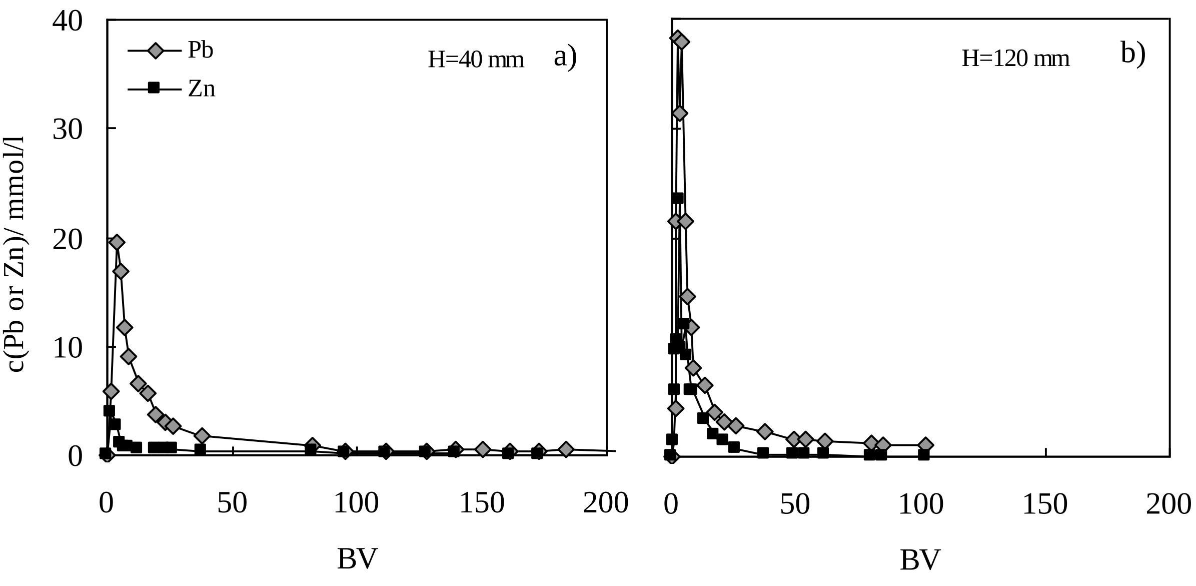

Figure 3. Regeneration curves for each metal ion in the binary solution for zeolite bed depths: a) 40 mm and b) 120 mm.

Although zeolite shows higher selectivity for lead ions after breakthrough, this difference is less expressed at higher bed depths for both bed depths examined.

CONCLUSION

The increase of bed depth prolongs the contact time between the binary solution and the zeolite, which leads to better column efficiency. This is observed in the increase of breakthrough capacities of $q_B(Pb+Zn)=0.527$ for H=120 mm compared to $q_B(Pb+Zn)=0.336$

for H=40 mm. That allows equal binding of both metal ions independently of their affinity to the zeolite. This indicates that bed depth can be used as a main parameter in performance of the column process.

ACKNOWLEDGEMENT

We express our thanks to the Ministry of Science, Education and Sports of the Republic of Croatia, which has been financing a project a part of which is presented in this paper.

REFERENCES

[1] R.P. Han, W.H. Zou, H.K. Li, Y.H. Li and J. Shi, *J. Hazardous Mater.*, 2006, **137**, 934-942.

[2] M.V. Mier, R.L. Callejas, R.Gehr, B.E.J. Cisneros and P.J.J. Alvarez, *Water Res.*, 2001, **35**, 373-378.

[3] T.S. Singh, K.K. Pant, *Sep. Purif. Technol.*, 2006, **48**, 288-296.

[4] N. Vukojević Medvidović, J. Perić and M. Trgo, *Sep. Purif. Technol.*, 2006, **49**, 237-244.