NATURAL ZEOLITES AS MULTIFUNCTIONAL ENVIRONMENTAL FRIENDLY MATERIALS

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INTRODUCTION

Natural zeolites are safe, environmentally friendly, naturally occurring aluminosilicate minerals. Zeolite was discovered 260 years ago by the Swedish mineralogist A.A.F. Cronstedt. He was the first scientist who described the properties of this class of minerals. Since 18th century, more than 50 different natural zeolite minerals have been discovered. Among them, clinoptilolite, chabazite, modernite and philipsite are the most abundant (available). In the last twenty years, properties of these minerals have generated worldwide interest in their research and diverse applications. Due to their physical and chemical properties, natural zeolites have been using as building stone, as lightweight aggregate and pozzolan in cement and concrete, as fillers in paper, as ion exchangers, in uptake of Cs and Sr from nuclear waste and fallout, as molecular sieves, as soil amendments in agronomy and horticulture, as universal adsorbents (gases, liquids), in the removal of metal ions and ammonia from municipal, industrial, and agricultural waste and drinking waters, as energy exchangers in solar refrigerators, as additives in pharmaceutical industry, and for contaminated land remediation [1]. With more than 2000 deposits found globally, natural zeolites are natural plentiful resources, and are inexpensive to mine, since the majority of deposits are found close to the Earth's surface [2]. The most important deposits that are being commercially exploited are in United States, Mexico, Ukraine, Slovakia, Italy, Greece, Turkey, Russia, Serbia, Romania, Bulgaria, Georgia, Armenia, and Cuba.

The charged inner and outer surface of natural zeolites is available for attraction of oppositely charged ions, due to their adsorption properties. They have a crystal framework structure that is occupied by cations and water molecules. These ions and water molecules can move within the inner structure enabling ion exchange and reversible dehydration. This property is used for removal of metal cations from aqueous solutions. Different shapes and sizes of main channels within the three-dimensional zeolite structure result in higher affinity for some cations over others. If the zeolite channel opening is small compared to the radius of the hydrated cation, more energy is required for this cation to migrate into the channel than for another smaller cation. For this reason, ions with smaller hydrated ionic radii bind in higher quantity on the zeolite particle. This effect is also defined as selectivity of ion exchange. This paper discusses the removal of lead and zinc ions from binary aqueous solutions on natural zeolite clinoptilolite.

EXPERIMENTAL

The sample of natural zeolite originated from the Vranjska Banja deposit (Serbia), and contain >80% clinoptilolite. The sample was milled and sieved to obtain particles size 0.6-0.8 mm, dried at $60^{\circ}C$ and analyzed. Binary aqueous solutions of lead and zinc ions have been prepared by dissolving of $Pb(NO_3)_2$ and $Zn(NO_3)_2$ in doubly distilled water. The total concentrations of Zn and Pb in the influent were the same in all experiments, but with a different Pb/Zn concentration ratio. Experiments were performed in glass columns with inner diameters of 12 mm, height of 500 mm, filled with the zeolite sample up to 40 mm. Each service cycle has been performed with a binary solution of different Pb/Zn ratios passing through the fixed zeolite bed using the down-flow mode. After each service cycle, the regeneration cycle was performed using the solution of $NaNO_3$. The flow rate in all

experiments was 1 ml/min. At selected time intervals during service and regeneration cycles, effluents were collected and concentrations of lead and zinc were determined complexometrically and by means of ion chromatography. (Methrom IC 761) [3]. Table 1 shows the concentrations of metal ions used in each service cycle.

Table 1. Concentrations of metal ions in binary aqueous solutions for each service cycle.

Concentration ratio $c_o(Pb)/c_o(Zn)$	$c_o(Pb+Zn)$ mmol/l	$c_o(Pb)$ mmol/l	$c_o(Zn)$ mmol/l
0.19	1.031	0.165	0.866
0.71	1.149	0.478	0.671
0.95	1.062	0.516	0.546
1.37	1.060	0.612	0.448

RESULTS AND DISCUSSION

The experimental results for service cycles are shown by breakthrough curves as dependencies of concentrations of metal ions in the effluent and metal ions in the influent, i.e. c/c_o ratio versus time, volume or bed volume (BV). Number of bed volume is ratio of solution volume (V) and zeolite bed volume (V_S). Figure 1 shows the breakthrough curves for service cycles for different ratios of Pb/Zn in the influent.
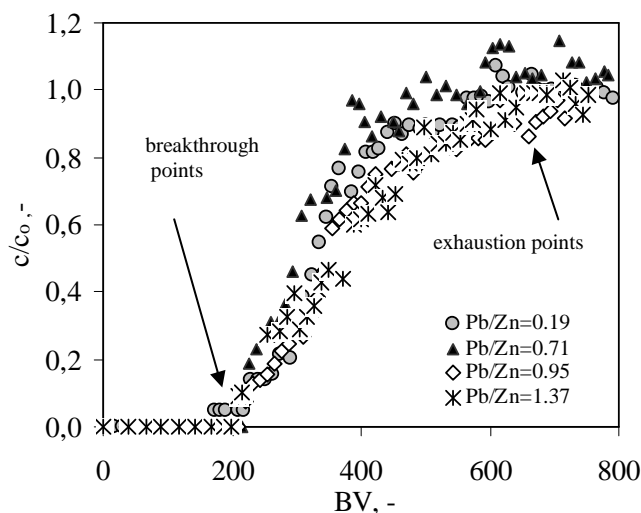

Figure 1. The breakthrough curves for binary aqueous solutions with different Pb/Zn concentration ratios in influents, BV=V/V_S.

All curves have a similar shape and breakthrough points appear at similar volumes of solutions passed through the fixed zeolite bed for all Pb/Zn ratios. Curves are steeper at lower Pb/Zn ratios. The breakthrough point is defined as the point in which metal ions appear in the effluent. The exhaustion point is defined as the point in which the concentration of metal ions in the effluent reaches 95% of the total concentration in the influent binary solution. The values for volumes in exhaustion points are also near for all Pb/Zn ratios, but the total concentration in the effluent exceeds the value of 1 for Pb/Zn ratios = 0.19 and 0.71. This exceeding of value $c/c_o=1$ means that the total concentration of metal ions in the effluent is higher than in the feeding solution. This can be explained by the concentration of each metal ion in the effluent. Figure 2 shows breakthrough curves for Pb and Zn ions in effluents of binary feeding solutions with different Pb/Zn ratios. It is evident that in all breakthroughs, Zn and Pb appear simultaneously, but the increase of the Zn concentration in the effluent is higher and exceeds its concentration in the influent. This is more visible at lower Pb/Zn ratios.
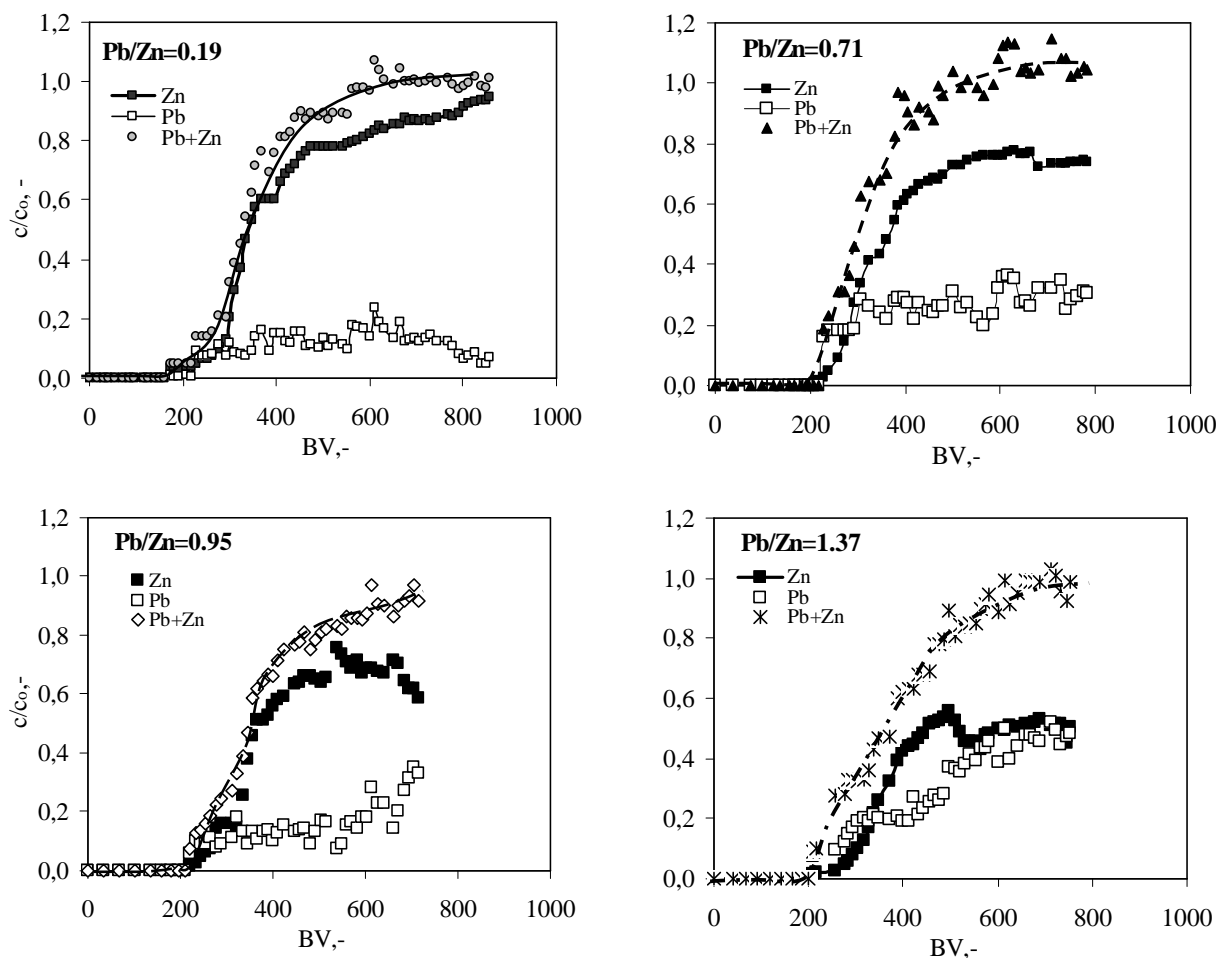
Figure 2. Breakthrough curves for Pb and Zn in binary aqueous solutions of different Pb/Zn ratios in influents.

This indicates that up to the breakthrough, zinc and lead ions bind proportionally to the initial concentration. The concentration of lead ions increases continuously and becomes constant before the exhaustion point except for the Pb/Zn ratio = 1.37. The curves in Figure 1 exceed $c/c_o = 1$ when the concentration of zinc in Figure 2 exceeds the concentration in the feeding solution. As the service cycle progresses and the available sites for binding of metal ions become more saturated, lead ions react with the remaining sites and probably displace a portion of weakly bound zinc ions. Also, during the saturation of the zeolite bed, it becomes less favourable for zinc ions. Therefore the effluent concentration of zinc is greater than in the influent solution. At higher values of Pb/Zn ratios, the distance between the Zn and Pb curves becomes smaller, i.e. concentrations of Zn and Pb in the effluent are nearer. This confirms the assumption that zinc ions are replaced by lead ions during the service cycle. Specifically, at higher initial lead concentrations, lead is bound in higher quantity in the beginning of the process, so zinc cannot be bound and replaced [4,5].

The quantities of metal ions bound in the breakthrough and exhaustion points are expressed as breakthrough capacity q_B and exhaustion capacity q_E, calculated by graphical integration [6]. The results in Table 2 confirm that the breakthrough appears at similar volumes of feeding solutions passed through the bed, while exhaustion appears around the value of 600 BV. The breakthrough capacities are proportional to the Pb/Zn concentration ratio in the influent. Exhaustion capacities are near, but ratios of Pb/Zn bound in the

exhaustion point are greater than the ratio in the influent. This confirms the assumption that zeolite is more selective for lead.

Table 2. The capacities q_B i q_E calculated by graphical integration of the area above breakthrough curves in Figure 2 for different Pb/Zn ratios in the solution.

Concentration ratio Pb/Zn in influent	V_B, BV	V_E, BV		q_B, mmol/g	$q_B(Pb)/q_B(Zn)$	q_E, mmol/g	$q_E(Pb)/q_E(Zn)$
0.19	218.9	564.0	Pb+Zn	0.336	0.189	0.545	0.174
			Pb	0.053		0.080	
			Zn	0.281		0.460	
0.71	206.8	583.9	Pb+Zn	0.337	0.714	0.521	1.012
			Pb	0.140		0.260	
			Zn	0.196		0.257	
0.95	221.2	614.8	Pb+Zn	0.336	0.942	0.509	1.980
			Pb	0.163		0.396	
			Zn	0.173		0.200	
1.37	209.0	572.8	Pb+Zn	0.312	1.364	0.581	2.010
			Pb	0.180		0.388	
			Zn	0.132		0.193	

$Disagreement\ q(Pb+Zn) \neq q(Pb) + q\,(Zn)$ is due to imperfections of graphical integration.

After each service cycle, regeneration is performed, where ions bound in the fixed bed are eluted and their concentrations are determined in the regeneration effluent. These results are shown graphically as regeneration curves in Figure 3. All curves in Figure 3 first show a rapid increase in the total concentration (Pb+Zn), followed by a decrease down to a constant value of ≈0.5 mmol/l.

In order to determine the contribution of zinc and lead in the regeneration effluent, their concentrations have been determined and are shown in Figure 4. The concentration of lead ions is higher in all service cycles except for Pb/Zn=0.19. The regeneration effluents contain mostly lead because it was bound on the fixed zeolite bed. The only exception is the binary solution with a small Pb/Zn ratio. The quantity of metal ions eluted during regeneration has been calculated by graphical integration of the area below the curves in Figure 4 [6].
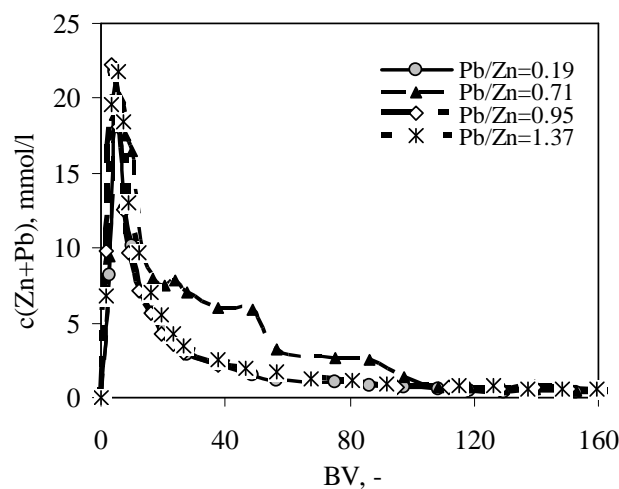

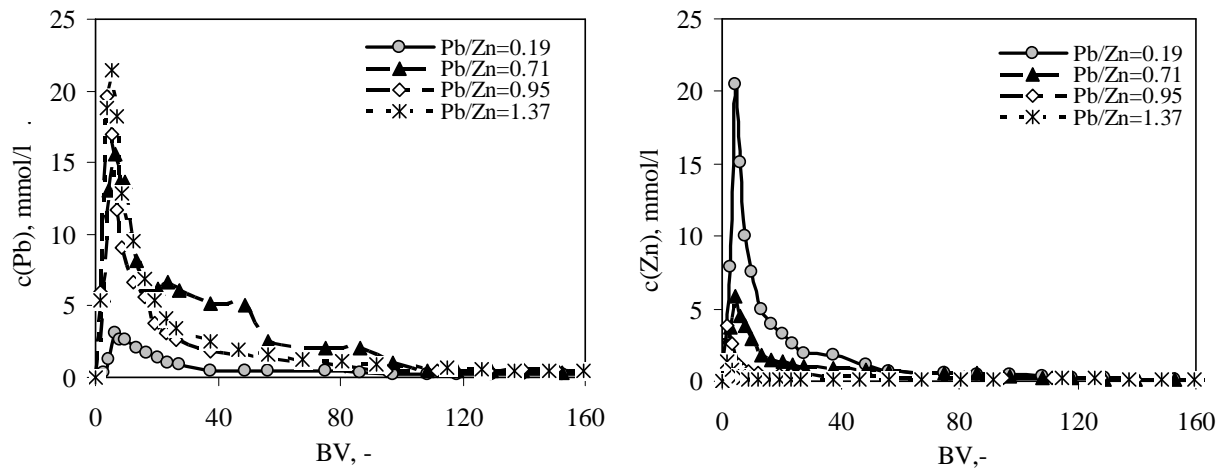Figure 3. Regeneration curves for binary aqueous solutions with different Pb/Zn ratios in the service cycle.

Figure 4. Content of lead and zinc in the regeneration effluent for binary aqueous solutions with different Pb/Zn ratios.
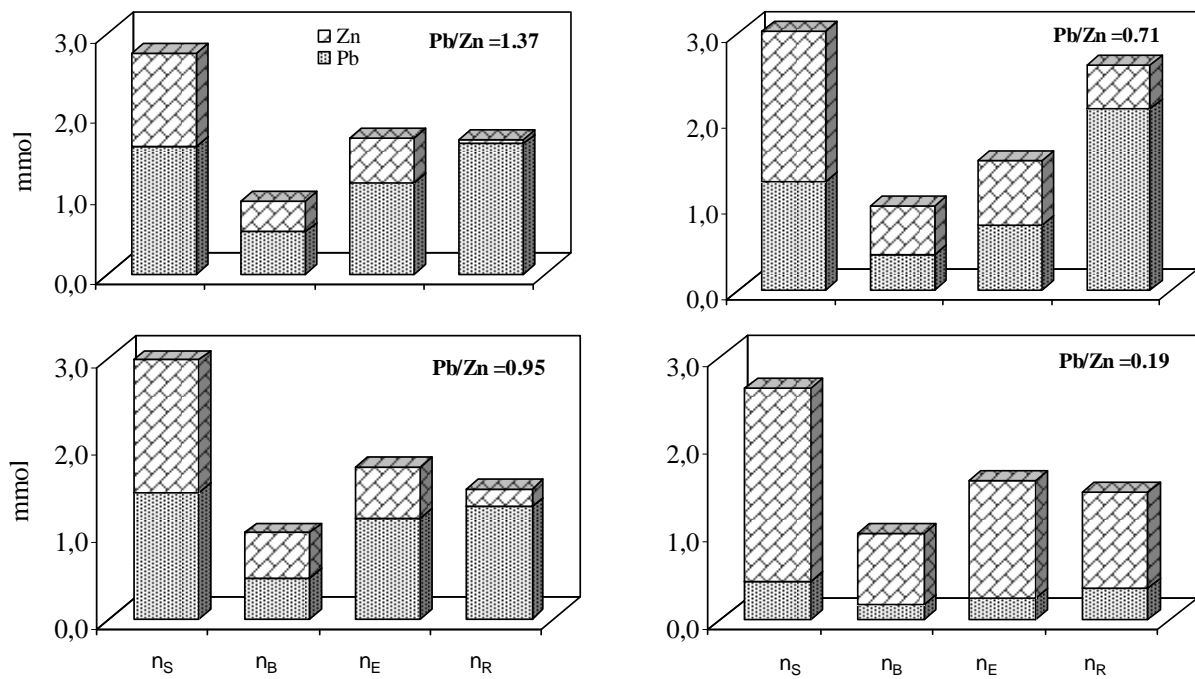

Figure 5. Comparison of n_S, n_B, n_E and n_R for Pb and Zn for different Pb/Zn ratios in the influent binary aqueous solution.

The quantity of each metal ion eluted during the regeneration n_R is compared to the quantity of ion loaded to the fixed bed during the service cycle n_S, and quantity of ion bound onto the fixed bed until the breakthrough point n_B, and quantity of ion bound onto the fixed bed until the exhaustion point n_E. Their comparison is shown in Figure 5. It is evident that molar ratios of Pb and Zn bound on zeolite in the breakthrough n_B are proportional to ratios in the influent n_S.

CONCLUSION

The quantity of lead bound on zeolite at exhaustion is higher than its portion in the feeding solution (n_S). The quantity of regenerated zinc is significantly lower compared to the loaded quantity and the bound quantity in the exhaustion point. This confirms that lead was mostly bound onto zeolite due to replacement of zinc ions with lead ions during the service cycle. This replacement is due to higher selectivity of natural zeolite for lead ions. Namely, the lower radius of the hydrated Pb^{2+} ion in comparison to Zn^{2+} provides for its better mobility through the framework structure.

ACKNOWLEDGEMENT

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