Zeolites and Related Materials: Trends, Targets and Challenges
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Competitive removal of lead(II) and zinc(II) from a binary aqueous solution on a fixed bed of natural zeolite

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Abstract

The column method using a fixed bed of zeolite clinoptilolite was applied to remove lead and zinc ions from binary metal ions solutions. The raw zeolite sample used in this study was obtained from the Vranjska Banja deposit (Serbia) and contained more than 80% of clinoptilolite. The breakthrough curves have an S-shape for the total as well as for the single metal ions in binary solution. Lead and zinc ions bind simultaneously on the zeolite bed, and as the service cycle progresses lead ions displace a great portion of bound zinc. During the regeneration cycle, the quantity of lead desorbed is ≈15 times higher than the quantity of zinc, which means that mostly lead ions were bound on the zeolite. Breakthrough curves have been interpreted quantitatively by means of the Michaels method, and the results calculated have been compared with the results for single metal ions solutions.

Keywords: zeolite, lead, zinc, column method, binary solutions.

1. Introduction

Investigations of removal of heavy metals from wastewaters before their discharge have received considerable attention in development of technology that includes wastewater treatment. It is well known that natural zeolites have excellent adsorption and ion exchange properties for removal of heavy metals from aqueous solutions, and examinations were mainly carried out with single-component heavy metal ion solutions [1-3]. A relatively small number of studies have examined the removal from two- or three-component solutions of heavy metals. Most of them have used solid waste as an adsorbent, but examinations of competitive removal of heavy metals on natural zeolites are quite poor [4-7]. The contribution of this paper is the investigation of competitive removal of lead and zinc ions from binary metal ions solutions on a fixed bed of zeolite clinoptilolite.

2. Experimental

The raw zeolite sample used in this study was obtained from the Vranjska Banja deposit (Serbia) and contained more than 80% of clinoptilolite. The sample was milled, sieved to the particle size fraction of 0.6-0.8 mm, dried at 60°C, and analysed. A binary solution of lead and zinc ions with the total concentration of 1.145 mmol/l (concentrations of lead and zinc are 0.557 mmol/l and 0.588 mmol/l respectively) was prepared by dissolving $Pb(NO_3)_2$ and $Zn(NO_3)_2$ in doubly distilled water. Experiments were carried out in a glass column with the inner diameter of 12 mm and a height of 500 mm, filled with 2.9 g of the zeolite sample to the bed depth of 40 mm. Experiments were performed using the down-flow mode at the constant initial concentration, bed

depth and constant flow through the fixed bed of 1 ml/min. After the service cycle, the regeneration was performed with the solution of $NaNO_3$ at the concentration of 176.5 mmol/l and flow of 1 ml/min.

3. Results and Discussion

The experimental results are shown as the total or single ion concentration in the effluent versus time or volume solution passed through the zeolite bed (expressed as bed volume, BV). The breakthrough curve on figure 1 has S-shape with the breakthrough point at ≈177 BV(after 800 min). After breakthrough, the total concentration rapidly increases and reaches its maximum at 1.263 mmol/l, which corresponds to the maximum value $c/c_o = 1.126$. Contrary to expectations, the total concentration is higher than the total initial concentration and further on, it slowly decreases and becomes constant at ≈900 BV. The explanation for this behaviour is provided by the analysis of the breakthrough curves of each metal ion in the effluent of the binary solution (Figure 2).

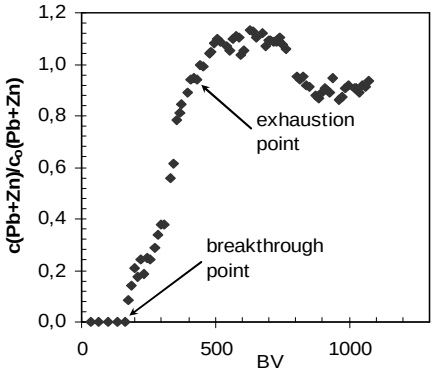

Figure1. The breakthrough curve for the total concentration in the binary solution during the service cycle.

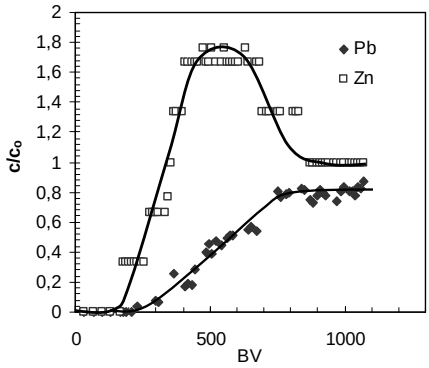

Figure 2. The breakthrough curves for each metal ion in the binary solution during the service cycle.

The breakthrough point of zinc ions appears first with the increase of concentration up to values significantly higher than the initial one. Then the maximum value c/c_o exceeds the usually expected value of 1. The breakthrough of lead ions in the effluent appears after 1400 minutes (≈310 BV), the concentration has a tendency of continuous increase up to relatively constant values. The extended S-shape of the breakthrough curve for lead is due to continuous replacement of bound zinc ions by lead ions. Namely, as the service cycle progresses, lead ions react with the remaining sorption sites and probably displace a great portion of weaker bound zinc. For this reason the value c/c_o for zinc ions reaches 1.67. At the time that corresponds to the constant total concentration of metal ions in the binary solution (≈3600 min, 800 BV), zinc ions are mostly displaced. The breakthrough curve in figure 1 is quantitatively interpreted using the method proposed by Michaels [1,8]. Based on this method, the capacity in the breakthrough point C_B is defined as the amount of ions bound on zeolite when the total concentration of ions in the effluent reaches ≈5% of the initial concentration [8]:

$$C_B = \frac{\int_0^{V_B} (c_o - c)dV}{\rho HA} = \frac{n_B}{m} = \frac{c_o V_B}{m} \qquad (1)$$

c_o – influent concentration, mmol/l; c – effluent concentration, mmol/l; V_B - volume of solution passed up to breakthrough point, ml; ρ – packing density of the bed, g/cm^3; H – bed depth, cm; A – bed cross-sectional area, cm^2; n_B - total amount of ions removed up to breakthrough point, mmol; m – mass of the zeolite, g. The capacity in the exhaustion point C_E corresponds to the amount of ions bound on zeolite when the total concentration of ions in the effluent reaches ≈95% of the initial value:

$$C_E = \frac{\int_0^{V_E} (c_o - c)\,dV}{\rho HA} = \frac{n_E}{m} \qquad (2)$$

n_E - amount of lead removed up to exhaustion point, mmol; V_E - volume of solution passed up to the exhaustion point, ml. The breakthrough and exhaustion points in figure 1 are evaluated at 177 BV and 420 BV respectively. The values of total capacity and capacities of particular ions in breakthrough and exhaustion points are calculated using equations (1) and (2), and their values are shown in table 1.

Table 1. Corresponding capacities of Pb and Zn, as well as quantities of Zn and Pb loaded and exchanged on the zeolite bed, and quantities displaced during regeneration.

	*C_B, mmol/g zeolite	*C_E, mmol/g zeolite	n_S mmol	n_E mmol	$n_E/n_S \times 100$ % bound	n_R mmol
Pb+Zn	0.315	0.544	2.174	1.580	73	1.598
Pb	0.139	0.319	1.057	0.924	87	1.485
Zn	0.146	0.192	1.118	0.570	51	0.113

* Note: A slight disagreement between values is due graphical integration.

The breakthrough capacities of Pb and Zn have close values, which indicates their simultaneous removal. The exhaustion capacity of Pb is significantly higher than that of Zn in the same point, indicating their different ion exchange abilities in the range from breakthrough and exhaustion points in figure 1. Their different exchange ability is due to higher selectivity of zeolite for lead ions compared to zinc ions. This can be explained as higher exchange efficiency of lead, due its higher degree of coordination to the framework oxygen and effective neutralization of the negative charge through aluminosilicate framework. For that reason the quantity of bound Pb (n_E) is 87% of the value loaded into the column (n_S), while the corresponding amount for Zn is only 51 %. The total breakthrough capacity (Pb+Zn) (table 1) is lower than for single heavy metal solutions, and the total exhaustion capacity is close to results for single heavy metal solutions in our previous paper. [1].

The experimental results for the regeneration cycle are shown with curves in figures 3 and 4. Figure 3 shows the plots of the total ions concentrations (Pb+Zn) and pH in the effluent during regeneration, and figure 4 shows the plots of concentrations of each metal ion in the same effluent. The results exhibit a sharp increase of the total concentration at the beginning with the maximum total concentration at 35 mmol/l.

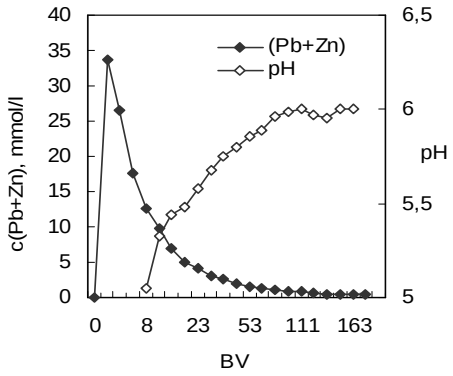

Figure 3. Total concentration of lead and zinc and pH in the effluent of the regeneration cycle.

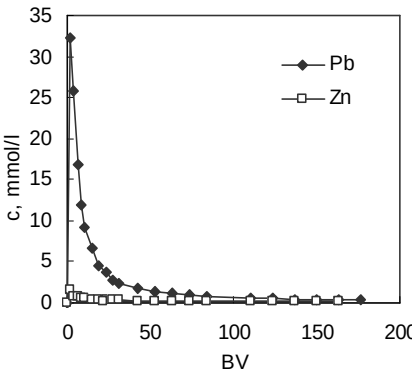

Figure 4. Concentrations of each metal ion in the effluent of the regeneration cycle.

The quantities of lead and zinc ions displaced during regeneration, i.e. n_R(Pb) and n_R(Zn), are calculated by graphical integration of the area under the regeneration curves in figure 4. The values from table 1 indicate that the regenerate solution contains mainly lead. The quantity of lead ions regenerated is ≈15 times higher than that of regenerated zinc ions, which means that almost all lead was bound. These results confirm displacement of bound zinc ions with lead ions from the solution, which probably takes place after the breakthrough point in figure 1.

4. Conclusions

The fixed bed of natural zeolite clinoptilolite can be successfully used for continuous removal of lead and zinc ions from binary aqueous solutions. During the service cycle, binding of zinc and lead ions probably takes place simultaneously, but after the exhaustion point bound zinc ions are replaced with lead ions from the solution. This has been confirmed by ≈15 times higher quantity of lead regenerated from the column compared to zinc. In practical application of this process, the most sensitive point is the decision when it is necessary to break the service cycle and perform regeneration. The results in table 1 suggest regeneration after the breakthrough point of the total (Pb+Zn) breakthrough curve. Up to this point the removal of both ions is not competitive; they are exchanged simultaneously with close values of experimental capacities.

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