THE INFLUENCE OF IONIC INTERACTION ON REMOVAL OF METAL IONS FROM A BINARY SOLUTION ONTO ZEOLITES

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ABSTRACT

The competitive equilibrium removal of metal ions from three equimolar binary aqueous solutions (Pb+Cd, Pb+Zn, Zn+Cd) onto natural (NZ) and iron-modified zeolite (IMZ) have been investigated by the batch method. The influence of ionic interaction on the removal of metal ions from the binary solution onto zeolite samples was evaluated by calculation of the q_{binar}/q_{single} ratio. The results confirm the competitive effect of metal ions in the binary solution, in which Pb is removed in the predominant amount.

Keywords: binary solution, zinc, cadmium, lead, competition effect

INTRODUCTION

Large deposits of natural zeolite in many countries provide some promising benefits in wastewater treatment to local industries. However, as contaminated water usually contains more than one heavy metal, for their efficient removal by natural zeolite it is necessary to understand their affinity towards zeolites. Metal uptake from a binary or multi-component solution onto the sorbent material is more complex due to the involvement of the solution-solid surface interaction and metal ions competition. In this paper, batch experiments were performed to examine the competition effect among the Zn, Cd and Pb to natural zeolite and its modified form. The influence of ionic interaction on the removal of metal ions from the binary solution onto zeolite samples was evaluated.

EXPERIMENTAL

Sample preparation: The natural zeolite (NZ), originating from the Zlatokop deposit, Vranjska Banja, Serbia, was milled and sieved to particle size fractions of 0.6-0.8 mm. The iron-modified zeolite (IMZ) sample was prepared from the natural sample according to the procedure published previously [1].

Metal uptake experiments from the binary aqueous solution: 1g of zeolite sample was shaken with 100 ml of binary equimolar aqueous solutions of Pb+Cd, Pb+Zn, Zn+Cd, with total initial concentrations ranging up to 16.137 mmol/l, using the incubator shaker. After equilibration (48 h) at room temperature, the concentrations of remaining metal ions in supernatants were determined by atomic absorption spectroscopy (AAS) and ion chromatography (IC).

RESULTS AND DISCUSSION

The total equilibrium quantity of metal ions uptake per unit mass of NZ and IMZ (q_{total}) from the binary solution has been calculated and plotted in relation to the initial total metal ion concentration in Fig 1. For the NZ sample, the results show that values of q_{total} increase with the increase of the total initial concentration of metal ions and reach a plateau. The maximum removal quantities are as follows:

$q_{max(Zn+Pb)}$ = 0.227 mmol/g; $q_{max\ (Pb+Cd)}$ = 0.189 mmol/g; $q_{max\ (Zn+Cd)}$ = 0.110 mmol/g.

It is evident that the highest values of q_{max} are achieved for the binary solution of Zn+Pb, followed by the solution of Pb+Cd, and the smallest values in the solution of Zn+Cd.

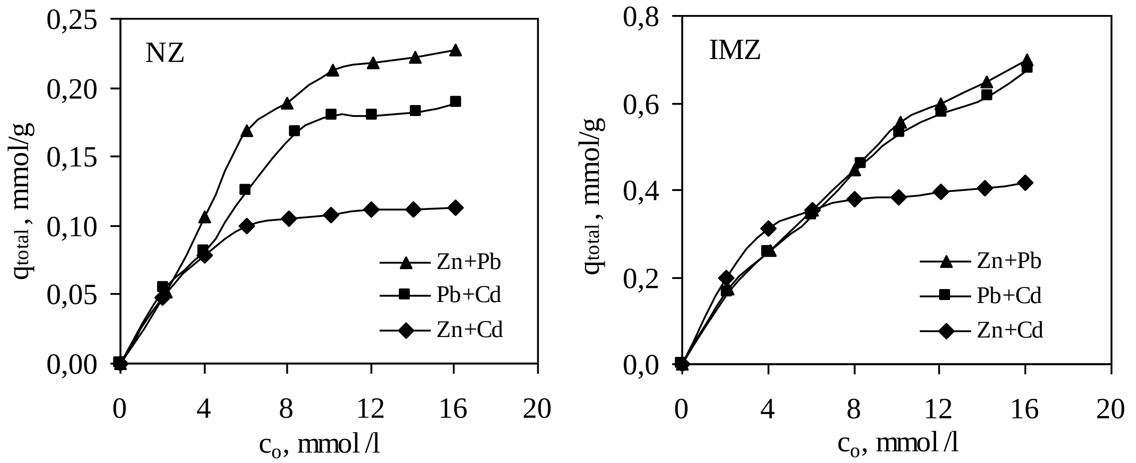

Fig 1. Total equilibrium quantity of metal ion uptake per unit mass of NZ and IMZ from the binary solution vs. the initial metal ion concentration.

For the IMZ sample, the values of q_{total} are significantly higher than for NZ, and for binary solutions of Zn+Pb and Pb+Cd, the plateau did not occur. The maximum removal quantities are as follows:

$q_{max(Zn+Pb)}$ = 0.699 mmol/g; $q_{max(Pb+Cd)}$ = 0.678 mmol/g; $q_{max(Zn+Cd)}$ = 0.410 mmol/g.

It can be observed that the q_{max} value obtained from binary solutions Zn+Pb and Pb+Cd is similar, whereas this value is significantly reduced for Zn+Cd. Figs. 2 - 4 indicate the quantity of total metal ions and particulate metal ion removal in each examined system.

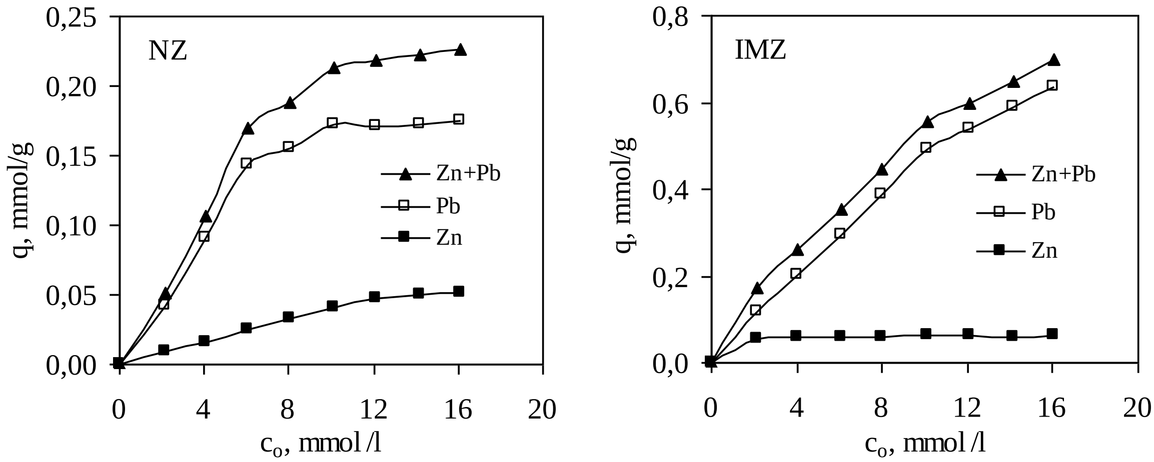

Fig 2. The amount of removed metal ions (particulate and total) per gram of NZ and IMZ from the equimolar binary solution of Zn+Pb.

For Pb+Cd and Zn+Pb systems, Figs. 2 and 3 show the dominant removal of Pb compared to Zn and Cd for both samples. For the Zn+Cd system presented in Fig. 4, both metals bind equally on NZ and IMZ.

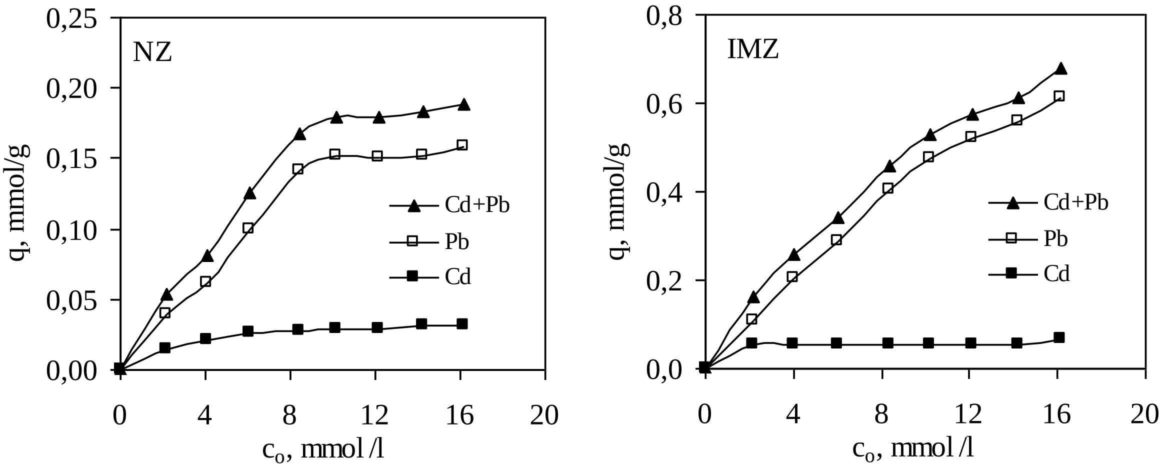

Fig 3. The amount of removed metal ions (particulate and total) per gram of NZ and IMZ from the equimolar binary solution of Cd+Pb.

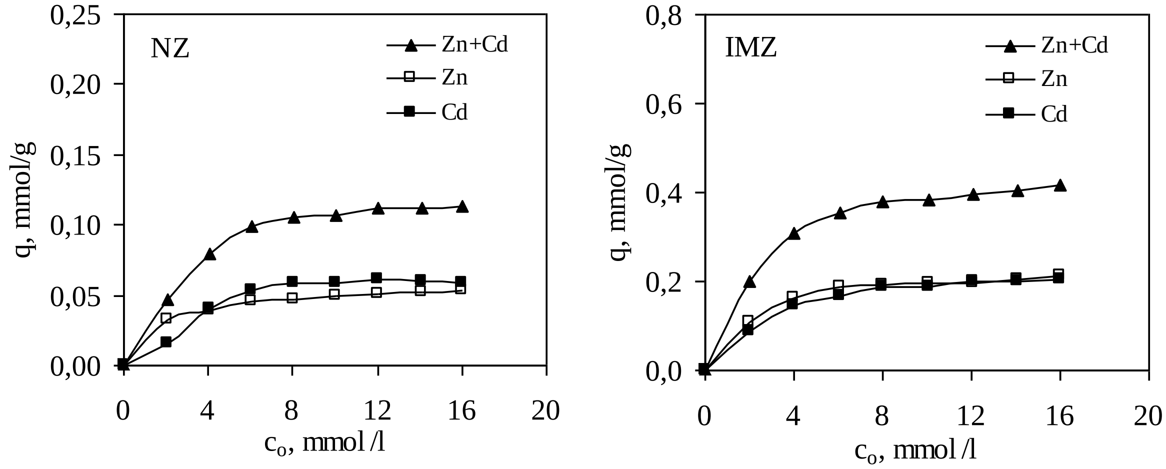

Fig 4. The amount of removed metal ions (particulate and total) per gram of NZ and IMZ from the equimolar binary solution of Zn+Cd.

According to literature [2, 3] the influence of ionic interaction on the removal of metal ions present in the binary solution can be evaluated from the following ratio:

$$q_{binar}/q_{single} \quad (1)$$

where:

q_{binar} - the amount of removed metal ion per gram of NZ or IMZ from the binary solution

q_{single} - the amount of removed metal ion per gram of NZ or IMZ from the single solution.

The results of the q_{binar}/q_{single} ratio for NZ and IMZ are presented in Tables 2 and 3.

Table 2. Evaluation of the q_{binar}/q_{single} ratio for NZ.

q_{single}		q_{binar}				q_{binar}/q_{single}		
		System	Zn	Pb	Cd	Zn	Pb	Cd
Pb	0.286	Zn+Pb	0.052	0.175	-	0.477	0.611	-
Zn	0.109[a]	Pb+Cd	-	0.158	0.031	-	0.547	0.262
Cd	0.118[a]	Zn+Cd	0.054	-	0.059	0.495	-	0.500

Note[a]: results of q_{single} for zinc and cadmium are taken from reference [4].

Table 3. Evaluation of the q_{binar}/q_{single} ratio for IMZ.

q_{single}		q_{binar}				q_{binar}/q_{single}		
		System	Zn	Pb	Cd	Zn	Pb	Cd
Pb	0.727	Zn+Pb	0.063	0.637	-	0.145	0.876	-
Zn	0.433[a]	Pb+Cd	-	0.614	0.065	-	0.844	0.171
Cd	0.381[a]	Zn+Cd	0.213	-	0.203	0.492	-	0.638

It is evident that in all cases the ratio q_{binar}/q_{single} is lower than 1, confirming the competitive interaction of metal ions from the binary solution towards the same active sites on both zeolite samples.

CONCLUSION

The results of evaluation of ionic interaction confirmed the competitive effect of metal ions in examined binary solutions. In the case of Pb+Zn and Cd+Pb solutions, the removal of Zn or Cd is suppressed by the presence of Pb, and this effect is more pronounced for the IMZ sample. In the binary solution of Zn+Cd, the removal achieved is almost equal for both metal ions. The reason for this behaviour is a consequence of the solution-zeolite surface interaction and physical properties of metal ions such as hydrated ionic radius, electronegativity and energy of hydration. These values are very similar for Zn and Cd, while Pb is characterized with smaller hydrated ionic radius leading to its higher mobility and easier reaching of active sites in the zeolite structure. The obtained selectivity sequence of zeolite samples for metal ions from single and binary solutions is: Pb>Cd≈Zn.

ACKNOWLEDGEMENT

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