SORPTION EDGE CURVES FOR Pb(II), Zn(II) and Cd(II) REMOVAL BY NATURAL AND IRON-MODIFIED ZEOLITE

Marin Ugrina*, Nediljka Vukojević Medvidović, Ina Baletić, Jelena Perić, Ivona Nuić
Faculty of Chemistry and Technology, University of Split, Teslina 10/V, 2100 Split, Croatia
*E-mail: mugrin@ktf-split.hr

ABSTRACT

Sorption edge curves for Pb(II), Zn(II) and Cd(II) removal on natural (NZ) and iron-modified zeolite (IMZ) were constructed. A sharp shape of sorption edge curves was observed for the IMZ sample at pH=2-3, and for NZ in the range of pH=2-4. The equilibrium pH_e of the solution is recognized as a simple indicator for determination of the sorption edge and optimal pH range with highest metal removal efficiency.

Keywords: heavy metals, natural zeolite, iron-modified zeolite, sorption edge.

INTRODUCTION

The pH of the solution has a significant impact on efficiency of removal of heavy metals on zeolite influencing on the zeolite surface charge as well as the degree of ionization and speciation of heavy metals. Depending on the solution pH, the mechanism of metal binding on zeolite can change from ion exchange and/or adsorption in the acid region to adsorption and/or complexation and possible precipitation in the basic region [1,2]. Thus, in practical application it is very useful to know which pH range is optimal for removal of each heavy metal. Metal cations exhibit a relatively narrow pH range (about 2 pH units) over which the sorption increases from 0% to almost 100%. This pH region is termed the "sorption edge" and its position is characteristic for a particular metal cation, type and quantity of sorbent as well as of the solution-sorbent interaction (Figure 1). The increase in the amount of sorbent shifts down the pH of the sorption edge, while the increase in the concentration of metal cations shifts the sorption edge to a higher pH value [3].
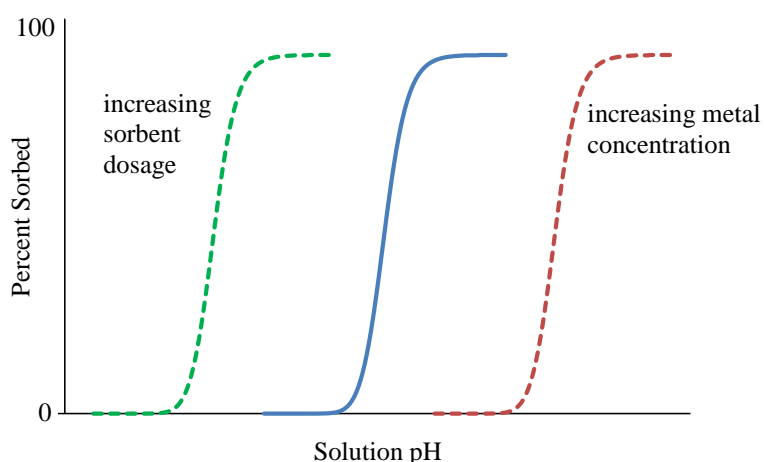

Figure 1. Generalized sorption edge curve for cation sorption on zeolite.

EXPERIMENTAL

Samples: The natural zeolite, clinoptilolite (NZ) used in this study came from the Vranjska Banja deposit (Serbia). The sample was milled and sieved to the particle size of 0.6-0.8 mm.

The iron-modified zeolite (IMZ) was prepared from NZ according to the procedure previously published [4].

Batch experiments: The aqueous solution of lead, $c_o=4.006$ mmol/l and zinc, $c_o=3.054$ mmol/l was prepared by dissolving $Pb(NO_3)_2$ or $Zn(NO_3)_2 \times 6H_2O$ in ultrapure water. The initial pH of the lead solution was adjusted to the range of $pH_o=2.43-5.01$ and for zinc to $pH_o=2.14-6.01$. The removal of lead and zinc by NZ and IMZ was examined at the solid/liquid ratio of 10 g/l during the period of 48 hours at room temperature, using the incubator shaker. pH values of suspensions were measured during equilibration and concentrations of remaining lead and zinc ions were determined by the atomic absorption spectroscopy method. The results for cadmium removal with the same experimental procedure have been previously published and used for comparison [4].

RESULTS AND DISCUSSION

Depending on the pH in the aqueous solution, lead, zinc and cadmium form the following species: M^{2+}, $M(OH)^+$, $M(OH)_2$, $M(OH)^{3-}$ and $M(OH)_4^{2-}$. According to the speciation diagram for each metal cation [5], lead is mainly present as Pb^{2+} at pH<6.5, zinc as Zn^{2+} at pH<7 and cadmium as Cd^{2+} at pH<7.5. Lead starts to precipitate at pH>6.5, zinc at pH>7 and cadmium at pH>8. To avoid precipitation, the removal of metal ions was performed below these pH values. Also, at pH<2, the degradation of zeolite particles occurs and experiments were not carried out. In order to observe a narrow range in which sorption suddenly increases, the sorption edge curves have been constructed. They represent the graphical dependence of the metal removal efficiency vs. the initial pH_o of metal solutions on NZ and IMZ and are presented in Figure 2.
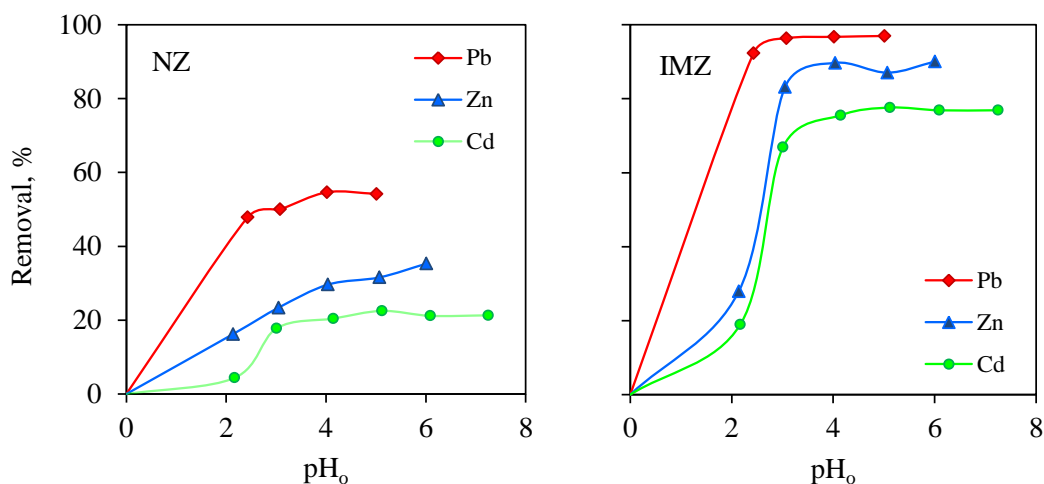

Figure 2. Sorption edge curves for Pb(II), Zn(II) and Cd(II) ions on NZ and IMZ.

For both zeolite samples, the removal efficiency increased as the initial pH_o increased and at a specific pH_o reached the maximum removal efficiency. The IMZ sample shows a sharp sorption edge at pH=2-3, while the NZ sample has the sorption edge at pH=2-4. After the sorption edge region, the removal efficiency becomes constant. These results suggest three pH ranges in which the binding of metal cations takes place: zone I (sorption edge area, below the optimal pH range), zone II (maximum sorption efficiency, the optimal pH range), and zone III (precipitation area, above the optimal pH range). These zones are presented in Figure 3.
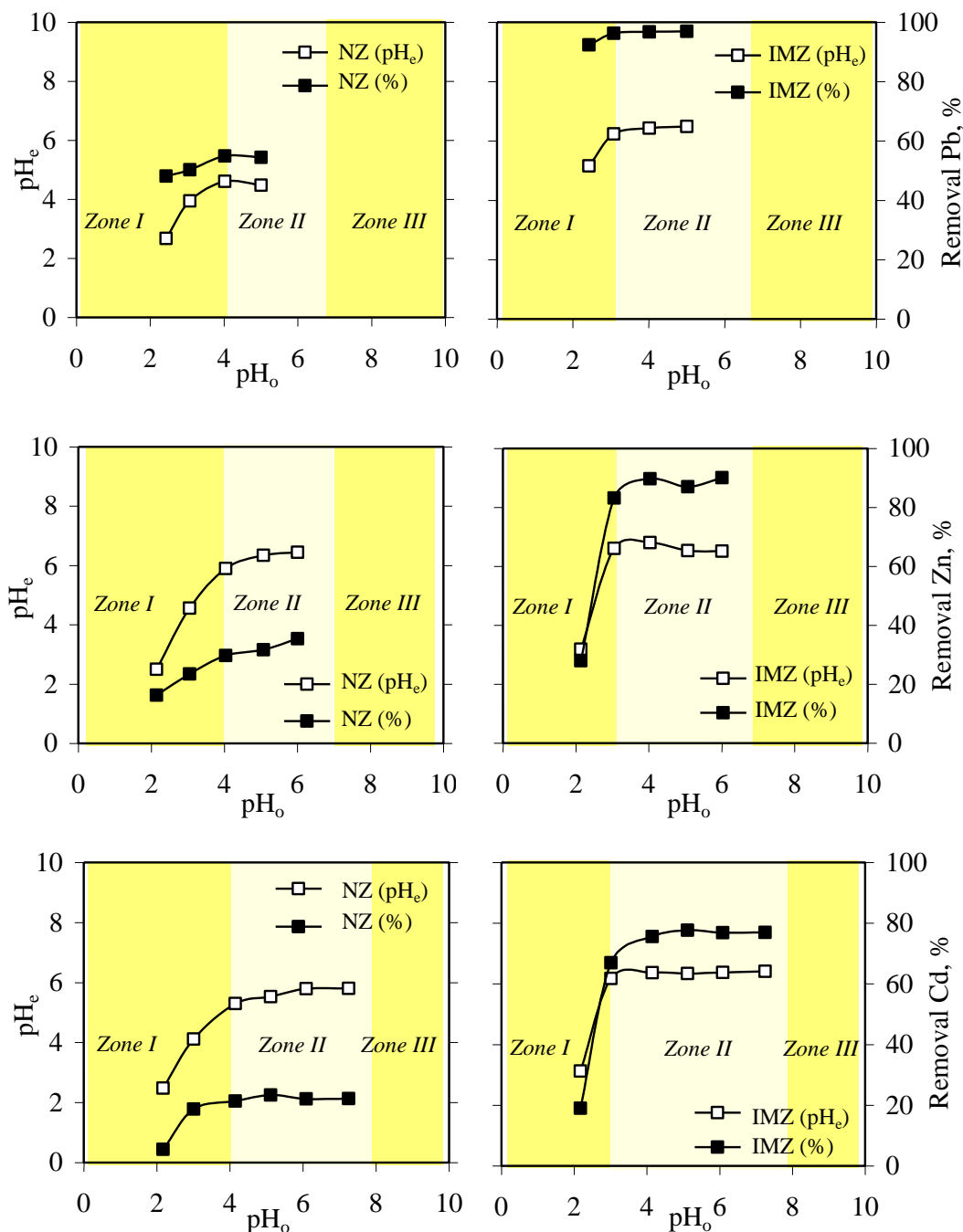
Figure 3. Dependence of pH_e and removal efficiency (%) of Pb, Zn and Cd on NZ and IMZ vs. initial pH_o.

In zone I, the minimum removal efficiency is observed, partially due to the competition effect between H^+ and metal cations. However, this competition is not significant for Pb(II), resulting in higher removal efficiency compared to Zn(II) and Cd(II). Also, this effect is more pronounced for IMZ due to higher amounts of the outgoing exchangeable cation (Na, K, Ca, Mg) which participates in the ion exchange process. As a consequence of the solution-zeolite interaction, the equilibrium pH_e increases with the increasing pH_o. In Zone II, the constant pH_e and maximal removal efficiency is achieved and represents the zone of the optimum pH range. Figure 3 clearly shows that the width of zone II depends on the type of metal cation and zeolite characteristics. Zone II begins at pH=4 for NZ and at pH=3 for IMZ. The end-point of zone II

depends on the solubility constant of metal cations in the aqueous solution. Results show that the removal of metal ions on NZ should be performed in the range of pH=4-6.5 for Pb(II), pH=4-7 for Zn(II) and pH=4-8 for Cd(II), and on IMZ in the range of pH=3-6.5 for Pb(II), pH=3-7 for Zn(II) and pH=3-8 for Cd(II). Due to the solution-zeolite surface interaction, it is evident that the equilibrium pH of the solution can be used as a simple indicator for determining the sorption edge area and the optimal pH range for the removal process. However, systems with IMZ reach a higher pH_e, so it is important to control the zeolite/solution ratio in order to avoid precipitation.

ACKNOWLEDGEMENT

CONCLUSION

This study has provided valuable information on Pb(II), Zn(II) and Cd(II) sorption on NZ and IMZ indicating that the pH is an important parameter which influences the removal efficiency. For both zeolite samples, the region of the adsorption edge is reached at pH=2-4 for Zn(II) and Cd(II) while shifted towards lower pH values for Pb(II). The width of the zone where the maximum removal efficiency is observed depends on the type of metal cation and zeolite sample characteristics.

REFERENCES

[1] M. Minceva, R. Fajgar, L. Markovska and V. Meshko, *Sep. Sci. Technol*, 2008, **43**, 2117-2143.

[2] D.L. Sparks, "*Sorption/Metals*" in *Encyclopedia of Soils in the Environment*, p. 532-537. D. Hillel, J.L. Hatfield, D.S. Powlson, C. Rosenweig, K.M. Scow, M.J. Singer and D.L. Sparks (Eds.), Elsevier Ltd., Oxford UK, 2005, 532-537.

[3] K.S. Smith, 1999, "*Metal sorption on mineral surfaces: an overview with examples relating to mineral deposits*", Chapter 7, in *The environmental geochemistry of mineral deposits, Part A: Processes, techniques, and health issues*, Reviews in Economic Geology, Vol. 6A, G.S. Plumlee and M.J. Logsdon (Eds.) Littleton, Colorado, Society of Economic Geologists, Inc., 1999, 161-182.

[4] J. M. Ugrina, N. Vukojević Medvidović, I. Penava, *Influence of initial pH of suspension on cadmium removal by natural and iron-modified zeolite*, in *Proceedings of the 5th Serbian-Croatian-Slovenian Symposium on Zeolites*, N. Rajić, J. Bronić, N. Zabukovec-Logar (Eds.). Beograd: Serbian Zeolite Association, 2013, 76-79.

[5] V.A. Nazarenko, V.P. Antonovich, E.M. Nevskaya, *Gidroliz ionov metallow v razbavlennikh rastorakh*, Atomizdat, Moskva, 1979.