

THE NATURAL ZEOLITE CLINOPTILOLITE AS EFFICIENT COST-EFFECTIVE SORBENT FOR COMPETITIVE HEAVY METAL REMOVAL FROM MULTICOMPONENT SYSTEMS

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ABSTRACT

The low-cost natural zeolite clinoptilolite was successfully applied for competitive removal of Pb or Cd together with Zn from binary (Pb+Zn) and (Cd+Zn) systems, at different flow rates and Pb/Zn and Cd/Zn concentration ratios. In both systems, the competition between the ions occurs leading to displacement of bound Zn with Pb and Cd from the feeding solutions. The competition results in “overshooting” of the Zn initial concentration up to 2.3 times in the presence of Pb, and up to 1.2 times in the presence of Cd. The obtained results indicate that removal of metal ion with lower affinity can be enhanced by experimental conditions such as flow rates and the initial concentrations. The eco-friendly natural zeolite clinoptilolite proved to be high efficient sorbent for heavy metal removal from multicomponent systems.

Keywords: binary systems, lead, cadmium, zinc, competition, overshooting.

INTRODUCTION

Increased levels of different heavy metals have been found widely in various environmental media due to their presence in municipal, industrial, mining and agricultural runoff [1]. Since they easily can reach the surface and groundwater by rainfall, their removal from wastewaters is mandatory for the purpose of preserving the environment and human health [2]. Dynamic sorption in the packed bed seems the most appropriate design for treatment of a large quantity of heavy metal polluted waters. Using of easy available and eco-friendly sorbents such as natural zeolites is very desirable for these purposes. Industrial effluents are commonly multi-metal systems where interferences between metal ions occur as well as competition for sorption sites [3]. Namely, the exceeding in effluent concentration over the influent concentration (“overshooting”) affects more the metal ions with lower affinity, causing their weaker binding. In order to improve the accuracy of prediction of sorbent efficiency in simultaneous removal of two or more metal ions, the experiments in multi-metal systems are required. The intention of present study was to clarify the behaviour and interactions of Pb or Cd together with Zn in two binary systems, (Pb+Zn) and (Cd+Zn), depending on solutions flow rates [4] and initial metal ions concentrations.

EXPERIMENTAL

Experiments were conducted isothermally at the ambient temperature (23 ± 2 °C) in a glass column (1.2 cm inner diameter; 50 cm length) packed with natural zeolite clinoptilolite (Zlatokop deposit, Vranjska Banja, Serbia) of particle size 0.6-0.8 mm up to height of 8 cm. The sorption was performed by feeding the binary solutions of (Pb+Zn) or (Cd+Zn) of total initial concentration ≈ 1 mmol/L in the down-flow mode at different flow rates Q - 1, 2, 3 or 4 mL/min. The process was continuously monitored by analysis of metals concentrations by ionic chromatography (IC) in the effluents at the column outlet. Each time the same zeolite sample was used due to successful regeneration of exhausted zeolite bed with NaNO₃ solution with concentration of 176.5 mmol/L.

RESULTS AND DISCUSSION

The breakthrough curves of effluent (c) and influent (c_0) Zn concentration ratios vs. volume (V) of the treated solution were plotted in Figures 1a and 1b.

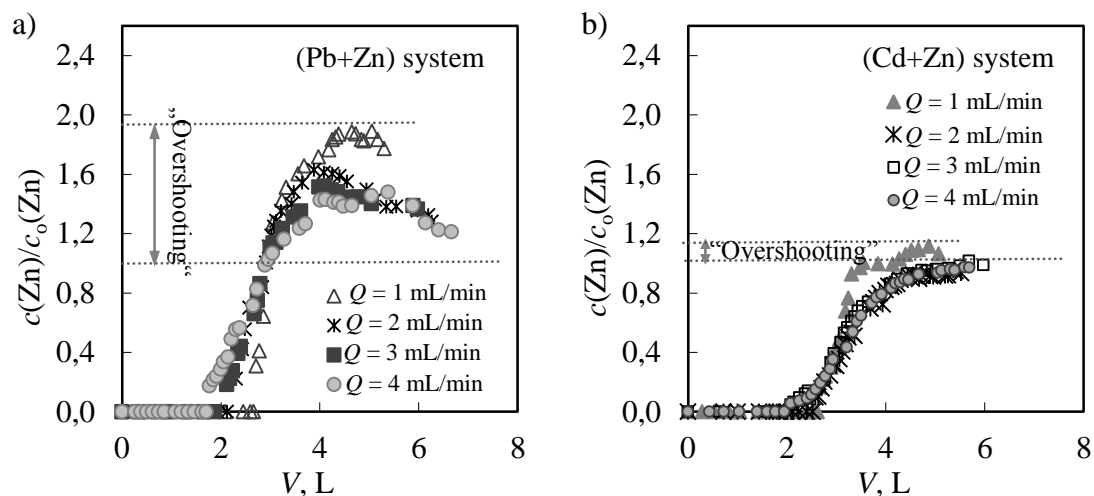


Figure 1. Comparison of Zn breakthrough curves in: a) (Pb+Zn) and b) (Cd+Zn) systems depending on flow rates in equimolar solutions.

The “overshooting” (Figure 1) in Zn effluent concentration over its influent concentration ($c/c_0 > 1$) is evident in both binary systems. This excess in Zn effluent concentration indicates displacement of already bound Zn from zeolite structure by Pb or Cd from the feeding solutions. In (Pb+Zn) system (Figure 1a) it happens for all flow rates, where despite reduced contact time Pb was still able to displace the bound Zn due to much smaller hydrated ionic radius [5]. In (Cd+Zn) system (Figure 1b) “overshooting” happens only for the lowest flow rate of 1 mL/min. Namely, with increasing in flow rate, due to shorter contact time the diffusion of Cd and Zn ions from the solution to the zeolite particle is weaker, leading to reduced competition and consequently lower “overshooting” phenomenon. The similar physicochemical properties of Cd and Zn ions also contribute to this phenomenon [5]. The obtained results have been compared (Figure 2) with previous findings [6] for different Pb/Zn and Cd/Zn initial concentration ratios, for both binary systems.

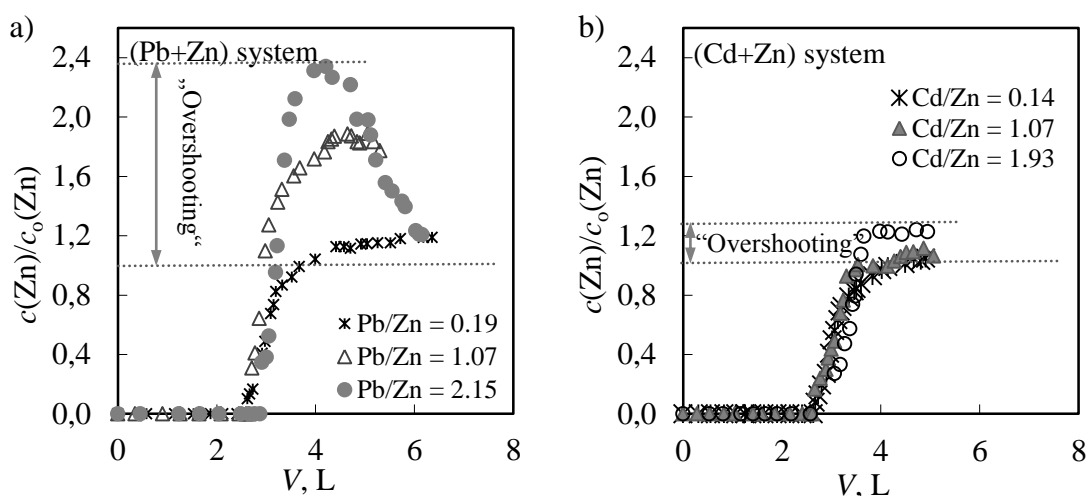


Figure 2. Comparison of Zn breakthrough curves in: a) (Pb+Zn) and b) (Cd+Zn) systems depending on Pb/Zn and Cd/Zn initial concentration ratios at $Q = 1$ mL/min [6].

In (Pb+Zn) system (Figure 2a), Zn exceeds its influent concentration for all Pb/Zn ratios especially for the highest one (Pb/Zn = 2.15). In (Cd+Zn) system (Figure 2b), the displacement effect is obtained for Cd/Zn of 1.07 and 1.93. Although it is less pronounced than in (Pb+Zn) system, it was quite surprising due to very similar physicochemical properties of Cd and Zn, unlike Pb and Zn [5]. The “overshooting” phenomenon suggests competition between ions for the common binding sites, when the metal with the lower affinity is being displaced from the sorbent structure by the metal with the higher affinity. This phenomenon happens after breakthrough point (the first appearance of the ions in the column effluent) due to the absence of the free binding sites in the zeolite structure. From the breakthrough curves, the capacities in breakthrough, q_B , and exhaustion (zeolite saturated with Pb, Cd and Zn ions), q_E , have been calculated for each ion using Michael’s method [3] and compared in Figures 3 and 4.

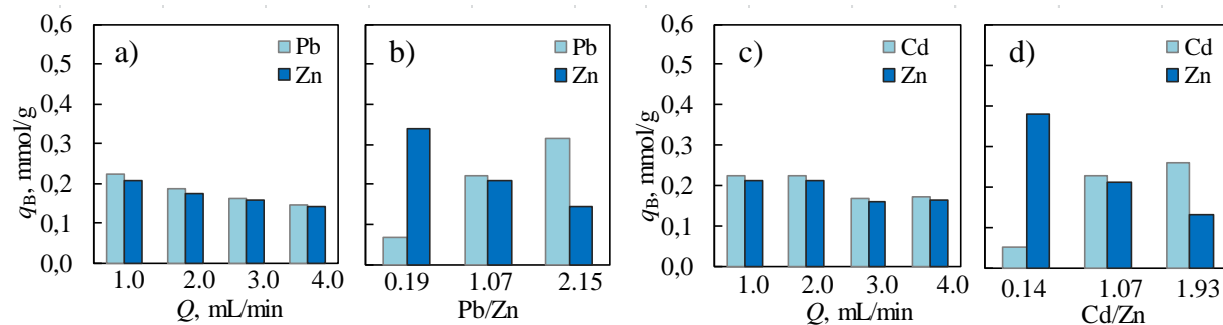


Figure 3. Comparison of breakthrough capacities for each ion in (Pb+Zn) and (Cd+Zn) systems depending on: (a,c) flow rates in equimolar solutions and (b,d) initial concentration ratios at $Q = 1$ mL/min.

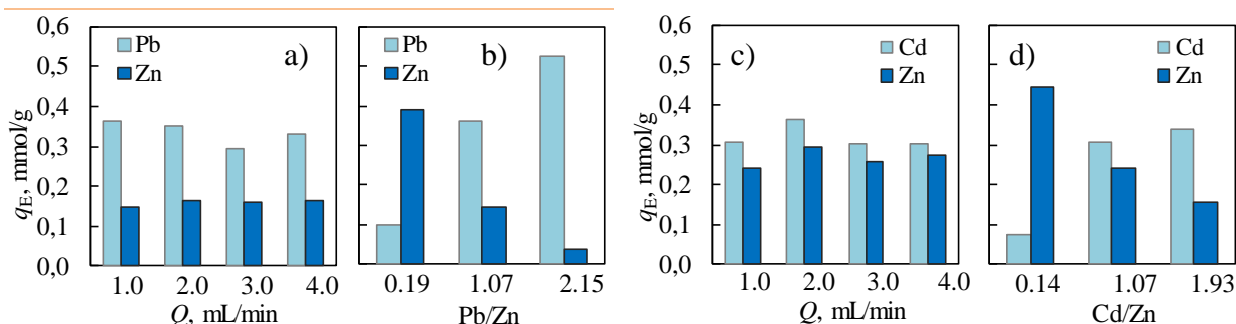


Figure 4. Comparison of exhaustion capacities for each ion in a) (Pb+Zn) and b) (Cd+Zn) systems depending on: (a,c) flow rates in equimolar solutions and (b,d) initial concentration ratios at $Q = 1$ mL/min.

From Figures 3 and 4 it is obvious that ions in both binary systems showed mostly similar sorption behaviour. In Figures 3a and 3c, until the breakthrough point Zn was bound in slightly smaller amount compared to Pb and Cd, but these differences decrease with increasing in flow rate, as a result of the shorter contact time. For different initial ions concentrations in Figures 3b and 3d, the Zn was bound in a higher amount compared to Pb and Cd only for the lowest Pb/Zn and Cd/Zn ratios. From the capacities in the exhaustion (Figures 4a and 4c) Zn was less bound in the presence of Pb than the Cd, for all flow rates indicating much more pronounced displacement effect in (Pb+Zn) than in (Cd+Zn) system. Regarding the initial ions concentrations (Figures 4b and 4d), although the Zn was bound in higher amount for the lowest Pb/Zn and Cd/Zn ratios, still, even for the significantly lower initial Pb concentration, Zn was displaced by Pb (Figure 2a), which confirms much higher affinity of Pb toward zeolite.

CONCLUSION

In both binary systems the presence of Pb and Cd disrupted the binding of the Zn, but it was found that the competitive effect of Pb in (Pb+Zn) system is stronger than of Cd in (Cd+Zn) system. The absence of “overshooting” in Zn concentration for the lowest Cd/Zn ratio and for the higher flow rates of 2, 3 and 4 mL/min shows that preferential removal of ions with higher affinities can be affected and controlled by solutions flow rates and initial ions concentrations. These findings point to unpredictability and complexity of metal behaviour in multi-metal systems. The detail research of each system is necessary in order to reliably predict the sorption efficiency. However, Pb, Cd and Zn were successfully removed onto eco-friendly natural zeolite clinoptilolite making it an excellent efficient sorbent in treatment of wastewaters polluted with heavy metals.

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REFERENCES

- [1] C.S. Qu, Z.W. Ma, J. Yang, Y. Liu, J. Bi, and L. Huang, *PLoS ONE*, 2012, **7**, e46793.
- [2] I.P. Ejidike, and P.C. Onianwa, *J. Anal. Methods Chem.*, **2015**, 2015.
- [3] I. Nuić, M. Trgo, J. Perić, and N. Vukojević Medvidović, *Micropor. Mesopor. Mat.*, 2013, **167**, 55-61.
- [4] M. Šušnjara, Influence of flow rate on competitive binding of cadmium and zinc from binary aqueous solution on natural zeolite by column process, Bachelor thesis, Faculty of Chemistry and Technology, University of Split, 2018.
- [5] M. Minčeva, R. Fajgar, L. Markovska, and V. Meshko, *Sep. Sci. Technol.*, 2008, **43**, 2117-2143.
- [6] I. Nuić, M. Trgo, N. Vukojević Medvidović and M. Ugrina, *Int. J. Environ. Res. Public Health*, 2019, **16**, 426-447.