INFLUENCE OF INITIAL pH OF SOLUTION ON CADMIUM REMOVAL BY NATURAL AND IRON-MODIFIED ZEOLITE

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ABSTRACT

The uptake of cadmium ions on natural zeolite (NZ) and iron-modified zeolite (IMZ) has been examined from aqueous cadmium solutions of different initial pH values. For both samples, the initial pH from acidic and slightly alkaline solutions tends to become neutral after cadmium uptake. The optimum pH range for cadmium uptake for both samples is pH=4-7. Up to pH=4, the competitive effect of H^+ with Cd^{2+} is dominant, while at pH>7 the precipitation of cadmium hydroxide takes place. The obtained removal capacity for IMZ is three-to-four times higher then for NZ.

Keywords: zeolite, iron-modified zeolite, cadmium removal, ion exchange.

INTRODUCTION

Among a large number of harmful substances released into the environment, heavy metals represent a major problem [1]. Due to their toxicity, heavy metals have to be removed from wastewater before their discharge into the recipient. Higher concentrations are usually removed by precipitation as metal hydroxides, while lower concentrations can be removed by adsorption, ion exchange, and different membrane techniques [2]. Among these methods, adsorption and ion exchange processes are probably the most attractive due to their high efficiency, and possibility of using low-cost sorbents such as natural zeolite. This study has examined the influence of the initial pH value of the cadmium solution on its removal using natural and iron-modified zeolite.

EXPERIMENTAL
Samples

The natural zeolite (NZ) originated from the Zlatokop deposit, Vranjska Banja, 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 described in a previous paper [3].

Batch experiments

Cadmium aqueous solution of initial concentration of 2.942 mmol/l was prepared by dissolving $Cd(NO_3)_2 \times 4H_2O$ in ultrapure water. The prepared solution was divided into six parts and in each of them the initial pH of solution in the range of pH=2.17-8.07 was adjusted by small additions of 0.1 mol/l HNO_3 or 0.1 mol/l KOH. The removal of cadmium by NZ and IMZ relative to the pH of solution was examined using the incubator shaker, in the period of 48 hours at room temperature, with the solid/liquid ratio of 10 g/l. The pH values of suspensions were measured during equilibration. After equilibration, the concentrations of cadmium as well as released Na, K, Ca and Mg ions in supernatants were determined by ion chromatography and the complexometric method [4].

RESULTS AND DISCUSSION

Monitoring of pH during experiments

Fig 1 shows the results of measurements of pH during cadmium uptake on NZ and IMZ samples from cadmium aqueous solutions of different initial pH values.
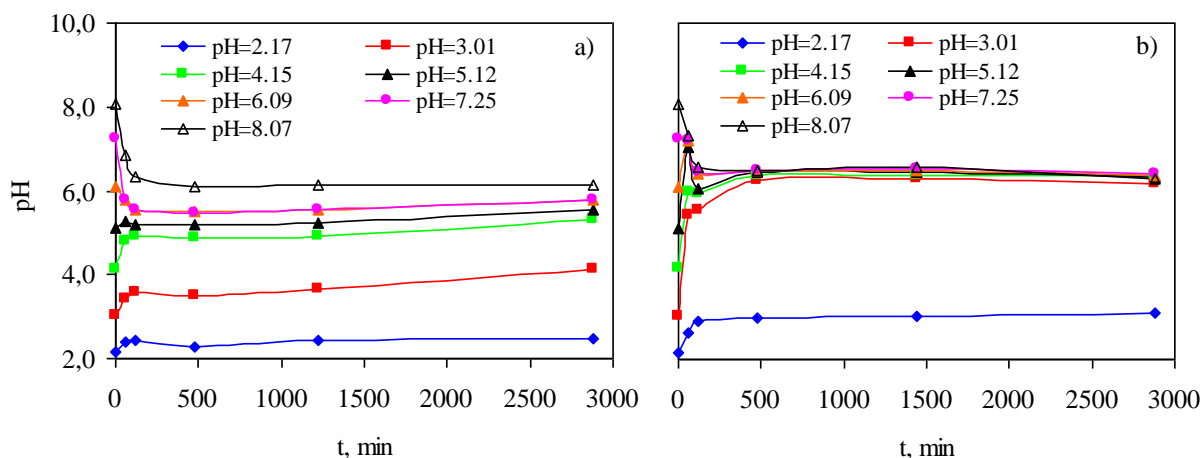

Figure 1. Change of pH during cadmium uptake for different initial pH values for: a) NZ, b) IMZ.

For the NZ sample, the increase of pH in the range of 2-3 is negligible, while at pH 3-6 a slight increase of pH is observed. At pH=7-8, a slight decrease in the pH is evident (Figure 1a). For the IMZ sample, at initial pH=2 a slight increase in pH is noticed, while at all other pH values a tendency is observed towards pH=6.

The increase and decrease of pH values is the consequence of interactions in the zeolite-aqueous cadmium solution system of different initial pH values. For both samples, the initial pH from acidic and slightly alkaline solutions tends to become neutral after cadmium uptake. This neutralizing effect is particularly pronounced for the IMZ sample. It is very important for zeolite applications in treatment of wastewater of different initial pH values.

Influence of pH on cadmium uptake on zeolites

Figure 2 shows the experimental results after equilibration in aqueous solution-zeolite samples systems depending on their initial pH value. For both zeolite samples, the results show that equilibrium cadmium concentration, c_e, decrease with increases of pH=2-4, and remained unchanged at pH range 4-7. At pH>7 a slight decrease of c_e is observed for both zeolite samples, which can be attributed to the formation of cadmium hydroxide.
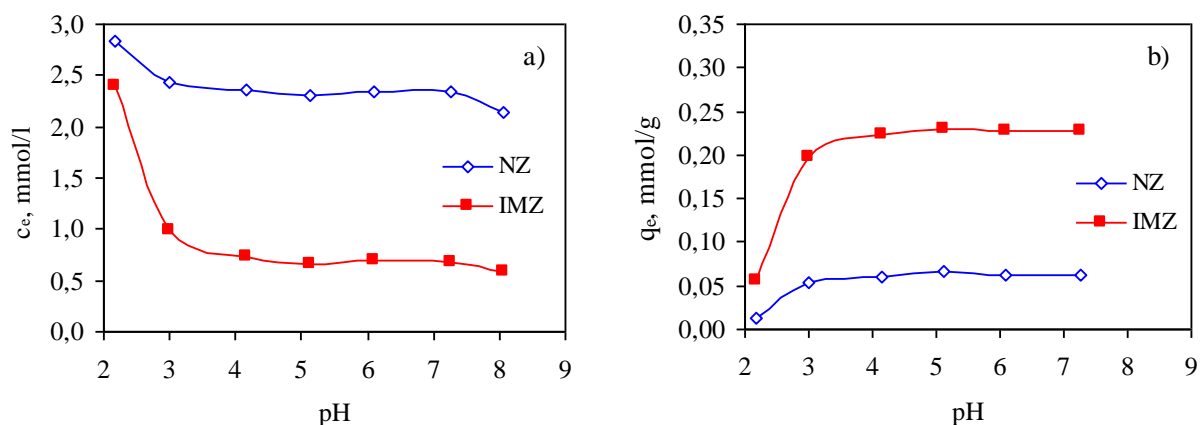

Figure 2. Influence of initial pH value of the solution on: a) residual cadmium concentration after equilibration; b) quantity of cadmium uptake onto NZ and IMZ samples.

The equilibrium concentration per gram of zeolite, q_e is calculated by considering initial concentration and residual concentration and shown in Fig 2b. At pH=4-7, the value of q_e assumes constant values and is equal to 0.062 mmol Cd/g NZ and 0.226 mmol Cd/g IMZ. These results indicate that the optimum pH range for cadmium uptake for both samples is 4-7.

Figures 3a and 3b show the dependence of pH_e and q_e for different initial pH values of cadmium aqueous solutions.
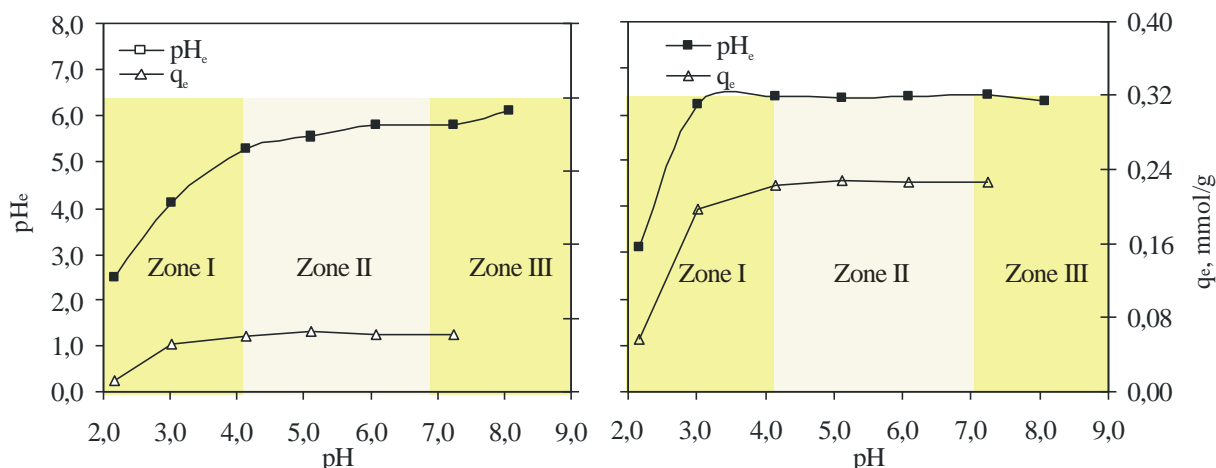

Figure 3. Dependence of the equilibrium pH of the suspension (pH_e) and equilibrium quantity cadmium uptake per gram of zeolite sample (q_e) vs. initial pH of solutions for: a) NZ b) IMZ.

From the results shown in Figure 3, three zones are observed: Zone I (pH range 2-4), zone II (pH range 4-7), Zone III (range pH> 7).

In Zone I the increase of q_e is observed with increases of the solution pH for both zeolite samples. The minimum value of q_e for both samples was obtained at pH=2, which is probably due to the competition effect of H^+ with Cd^{2+}. At pH=3, a sudden increase in q_e is noticed, resulting in a lower concentration of cadmium in the solution and the higher equilibrium pH.

In Zone II (pH 4-7) q_e and pH_e are seen to assume a constant value for each sample. In Zone III (pH>7), the effect of chemical precipitation of cadmium hydroxide on the surface of zeolite is observed.

The competitive effect in Zone I is confirmed by analyzing the relation between the concentrations of Na, K, Ca, Mg ions leaving the zeolite structure and the concentrations of Cd ions entering the zeolite structure for different initial pH values of cadmium solutions, and is presented in Figure 4.
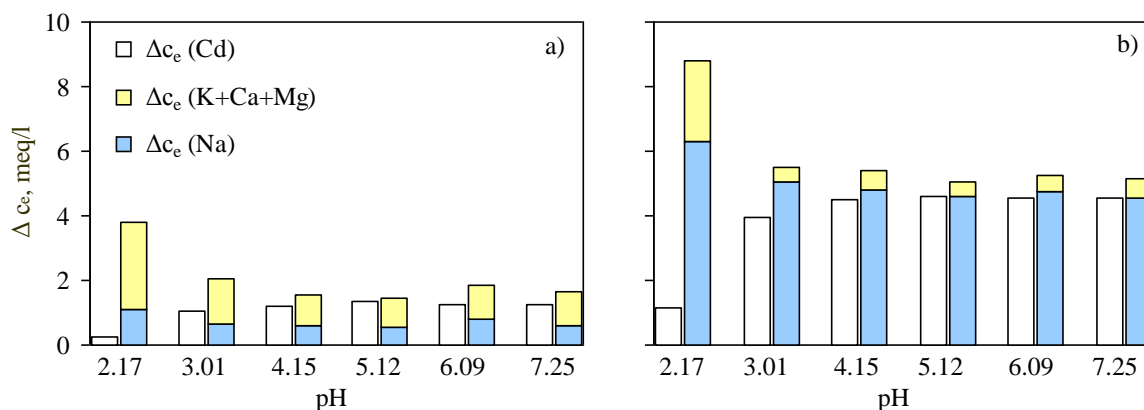

Figure 4. Relationship between the concentrations of Cd bound and released exchangeable cations in the solution as a function of initial pH of the solution for: a) NZ and b) IMZ sample.

The results show that in Zone I, the amount of released exchangeable cations overcomes the amount of Cd^{2+} bound on both zeolites, which is due to the competitive effect of H^+ with Cd^{2+}. In the range of pH=4-7, an almost complete stoichiometric relation for NZ and IMZ is observed, indicating ion exchange as the main mechanism responsible for Cd uptake.

CONCLUSION

The optimum pH range for cadmium uptake for both zeolite samples is 4-7, where the obtained values for q_e was 0.062 mmol Cd/l for NZ, and 0.226 mmol Cd/l for IMZ, respectively. Continuous monitoring of pH from acidic and slightly alkaline solutions has revealed a tendency to neutralize the equilibrium pH values for both samples. From the correlation between q_e and pH_e versus pH_i, three zones were identified: Zone I (pH 2-4), Zone II (pH 4-7) and Zone III (pH>7). The obtained results indicate that the pH value is one of crucial parameters which influence the efficiency of the process of cadmium uptake on natural and modified zeolite.

Acknowledgement

REFERENCES

[1] G. Purna Chandra Rao, S. Satyaveni, A. Ramesh, K. Seshaiah, K. S. N. Murthy, and N. V. Choudary, *J. Environ. Manage.* 2006, **81**, 265-272.

[2] F. Fenglian and W. Qi, *J. Environ. Manage.* 2011, **92**, 407-418.

[3] M. Ugrina, N. Vukojević Medvidović, J. Perić, M. Trgo, A. Daković, and M. Kragović, in *Proceedings of the 4th Slovenian-Croatian Symposium on Zeolites*, T. Antonić Jelić, N. Vukojević Medvidović, N. Novak Tušar and J. Bronić (Eds.), Zagreb: Croatian Zeolite Association, 2011, 53-57.

[4] "*Complexometric Assay Methods with Triplex*", E. Merck (Ed.), Darmstadt, 1982, 24-25.