MERCURY IONS CAPTURE BY NATURAL AND IRON-MODIFIED ZEOLITE - INFLUENCE OF SOLID/LIQUID RATIO

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ABSTRACT

Mercury capture by natural (NZ) and iron-modified (IMZ) zeolites has been investigated in the batch mode at S/L ratios in the range of 4-140 g/l. The results show that the S/L ratio should not exceed the value of 12 g/l for the IMZ sample. Increased S/L ratio induces increasing amounts of exchangeable cations and pH values in solutions, which may lead to possible precipitation of HgO. At the S/L ratio > 20 g/l, the equilibrium amount of mercury capture (q_e) reaches the values of up to 1.8 mg/g for NZ. In case of the IMZ sample, at the S/L ratio < 12 g/l, the value of q_e reaches 28.6 mg/g.

Keywords: zeolite, iron-modified zeolite, mercury capture, S/L ratio

INTRODUCTION

Anthropogenic emission of mercury is of great environmental concern because Hg is highly toxic, persistent and tends to bio-accumulate in the food chain [1,2]. The effluents from chlorine and chlor-alkali manufacturing processes, which use mercury cells in the electrolysis process, represent one of the most important sources of mercury pollution. The removal of mercury from industrial wastewater before its discharge into the environment is therefore necessary. Commonly adopted methods for removal of mercury from effluents include sulphide precipitation, membrane filtration, ion exchange and adsorption on activated carbon [3]. In order to reduce utilisation costs, recent investigations have been steered towards the use of natural abundant and industrial wastes as ion exchangers or adsorbents for mercury removal [4]. The present paper reports on an experimental study of mercury capture by natural and iron-modified natural zeolite.

MATERIALS AND METHODS

Zeolite samples preparation

The natural zeolite originated from the Zlatokop deposit (Serbia) was milled and sieved to the particle size fraction of 0.6-0.8 mm. After rinsing and drying at 60°C, the material was stored in the desiccator. The iron-modified zeolite (IMZ) was prepared from natural zeolite according to the procedure published previously [5].

Solution preparation

Reagent−grade chemicals and deionised water were used in all experiments. The initial mercury solution of 777.15 mg Hg/l (3.87 mmol/l) was prepared by dissolving $HgCl_2$. The initial value of pH=3.19 was adjusted with HNO_3.

Isothermal batch experiments

Examinations of mercury sorption on NZ and IMZ were performed using an incubator shaker in the period of 24 h at the room temperature. Different amounts of zeolite, in the range from 0.2 g to 7 g, were shaken with 50 ml of mercury aqueous solution (S/L= 4-140 g/l). During equilibration, the pH values were measured in suspension using a Mettler Toledo pH meter. After equilibration, the concentrations of remaining mercury in supernatants were

determined by Automated Mercury Analyzer MA-2 (Nippon Instruments Corporation). Concentrations of released Na, Ca, K and Mg ions in supernatants were determined by ion chromatography, and the concentration of Fe was checked by complexometric method.

RESULTS AND DISCUSSION

Figure 1 shows measured pH values in the suspension during equilibration of mercury ions with NZ and IMZ samples at different S/L ratios.
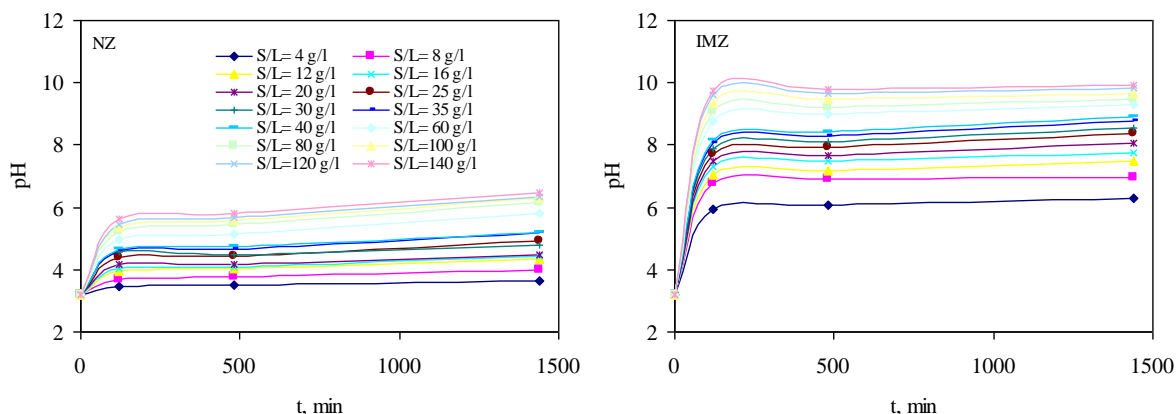

Fig. 1. pH values in suspensions during equilibration of mercury ions with NZ and IMZ samples at different S/L ratios.

As can be seen from Fig. 1, pH values rapidly increase within the first 60 min, and reach plateaus. A rapid increase of pH values is more evident with increasing S/L ratio, and reaches the values of 5.62 and 9.75 for NZ and IMZ, respectively. It is evident that the increase in pH values is more pronounced for IMZ.

Fig. 2 shows the mercury equilibrium concentration (γ_e) and equilibrium pH_e values in solutions versus S/L ratios for NZ and IMZ. Both zeolites samples reduce the mercury concentration in suspensions with increasing S/L ratios. The sharp decrease of γ_e is evident for IMZ, indicating significantly higher amounts of removed mercury ions. At higher S/L ratios, the equilibrium pH_e values significantly increase for IMZ, while this increase is less pronounced for the NZ sample.
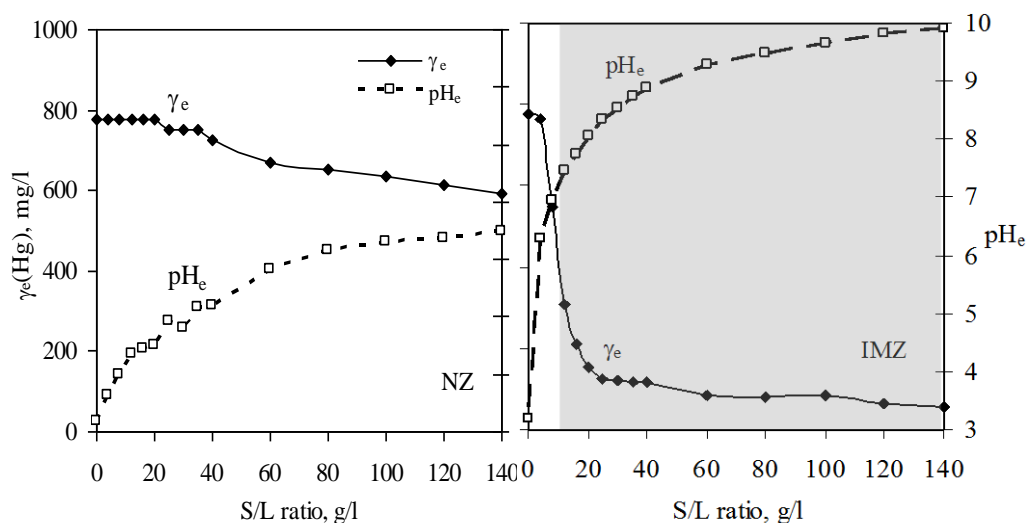

Fig. 2. Mercury equilibrium concentration (γ_e) and equilibrium pH value (pH_e) in the solution relative to the S/L ratio for the NZ and IMZ samples.

At the S/L ratios > 12 g/l (the shaded area in Fig. 2), a yellow precipitate is produced, which we presume corresponds to HgO, which is produced at high pH according to the following reaction [6]:

$$Hg^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} --> HgO_{(s)} + H_2O \; . \tag{1}$$

The relation between the concentrations of Na, K, Ca, Mg ions released from the zeolite structure and concentrations of Hg ions remaining in the solution for different S/L ratio is presented in Fig. 3.
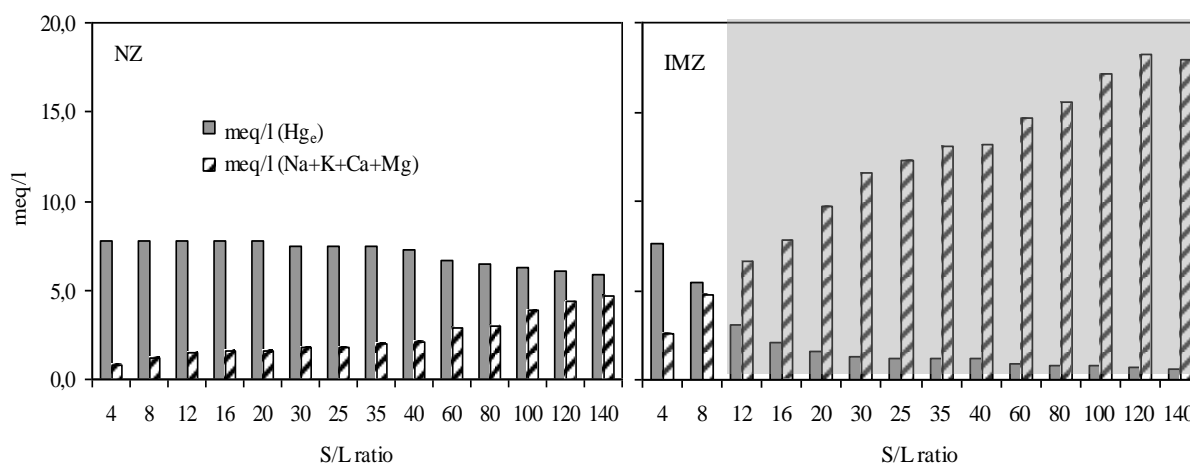

Fig. 3. Relations between equilibrium concentrations of Hg and released exchangeable cations in the solution as a function of the S/L ratio.

The results shown in Figs. 2 and 3 clearly indicate that a sharp increase of pH values for the IMZ sample is related to increased concentration of exchangeable cations (Na, K, Ca and Mg) and decrease of Hg ions remaining in solutions. At S/L = 12 g/l, the amount of released exchangeable cations (mainly Na ions) exceeds the concentration of Hg ions in the solution, inducing production of a yellow precipitate which probably corresponds to HgO (indicated by the shaded area in Fig. 3).

The results show that during removal of Hg species on IMZ, the S/L ratio should not exceed the value of 12 g/l, and the pH values should be kept slightly acid to neutral. At a low pH, there is a competitive adsorption between H^+ and Hg^{2+} at the binding sites on zeolite, while at higher pH values, precipitation of HgO may occur.

In case of the NZ sample, the precipitation of HgO did not occur and Hg species were removed by ion-exchange and adsorption processes. Fig. 3 shows that the lowest values of Hg ions remaining in the solution are obtained at the S/L ratio of 140 g/l.

Based on results for equilibrium concentrations, the equilibrium amounts of mercury uptake per gram of zeolite (q_e) and the removal efficiency (α) have been calculated for S/L ratios ranging from 4-140 g/l for NZ and for S/L ratios less than 12 g/l for IMZ, according to the following equations:

$$q_e = (\gamma_o\text{-}\gamma_e) \cdot V / m \; , \qquad \alpha = (\gamma_o\text{-}\gamma_e) \cdot 100 / \gamma_o \tag{2}$$

where γ_o is the initial mercury concentration in mg/l, γ_e is the equilibrium concentration in mg/l, V is the solution volume in l, m is the zeolite weight in g, and Fig. 4 shows the results.

At the S/L ratio < 20 g/l for the NZ sample, mercury removal was not detected due to a small amount of zeolite. With increasing S/L ratios, the q_e increased up to 1.8 mg/g for NZ,

while removal efficiency reached (α) 23 %. In case of the IMZ sample for S/L ratios < 12 g/l, q_e and α show a sudden increase up to 28.6 mg/g and 29 %, respectively.
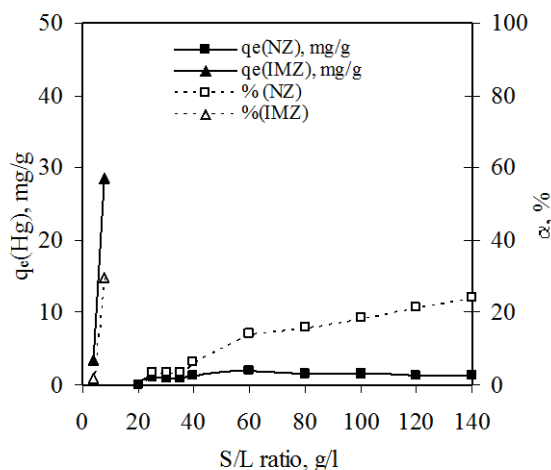

Fig. 4. The equilibrium amount of mercury uptake per gram of zeolite (q_e) and removal efficiency (α) versus S/L ratios for NZ and IMZ zeolites.

CONCLUSION

During removal of Hg ions on IMZ, the S/L ratio should not exceed the value of 12 g/l, due to possible precipitation of HgO at a higher pH. In case of the NZ sample, the precipitation of HgO did not occur and the percentage of mercury removal on NZ increases with increasing S/L ratio. The equilibrium amount of mercury uptake per gram of IMZ zeolite is 15 times higher compared to the NZ.

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REFERENCES

[1] Y. Xiaohong, Z. Lijan, G. Baiwei, and H. Shouyang, *J Environ Sci.* 2008, **20**, 1328-1334.

[2] M. Madhava Rao, D.H.K. Kumar Reddy, P. Venkateswarlu, and K. Seshaiah, *J. Environ. Manag.* 2009, **90**, 634-643.

[3] F.D. Natale, A. Lancia. A. Molino, M.D. Nalate, and D. Karatza, D. Musmarra, *J. Hazard Mater.* 2006, **B132**, 220-225.

A. Chojnacki, K. Chojnacka, J. Hoffman, and H. Gorecki, *Mineral. Eng.* 2004, **17**, 933-937.

[4] M. Ugrina, N. Vukojević Medvidović, J. Perić, M. Trgo, A. Daković, M. Kragović: "*Uptake of cadmium ions from aqueous solution by natural and iron modified zeolite*" in: *"Proceedings of the 4th Slovenian-Croatian Symposium on Zeolites"*, T. Antonić Jelić, N. Vukojević Medvidović, N. Novak Tušar, J. Bronić (Eds.), Croatian Zeolite Association, Zagreb, 2011, 53-57.

[5] S. Donatello, A. Fernandez-Jimenez, and A. Palomo, *J Hazard Mater.* 2012, **213-214**, 207-215.