

THE ASSESSMENT OF NATURAL ZEOLITE AS A MATERIAL FOR REMEDIATION OF MERCURY CONTAMINATED WATER BODIES

*Ivona Nuić¹, Ivona Miličević¹, Tamara Teršič², Marina Trgo¹, Miloš Miler², Marin Ugrina¹,
Nediljka Vukojević Medvidović¹, Mateja Gosar²*

¹Faculty of Chemistry and Technology, Department of Environmental Engineering, University of Split,
Ruđera Boškovića 35, 21 000 Split, Croatia

²Geological Survey of Slovenia, Dimičeva ulica 14, 1000 Ljubljana, Slovenia
E-mail: ivona@ktf-split.hr

ABSTRACT

The sorption ability of natural zeolite clinoptilolite for total mercury leached from contaminated soil of Idrija district in Slovenia has been investigated. The satisfactory removal of total mercury on two particle sizes of zeolite sample has been observed. The pH value is a key factor for leaching and uptake of mercury from natural soil systems. It was established that natural zeolite clinoptilolite has a potential to be used as a material for remediation of mercury contaminated waters.

Keywords: Idrija mine, mercury contaminated soil, leachate, natural zeolite, remediation

INTRODUCTION

The Idrija mine in Slovenia, as the second largest mercury mine in the world, was a significant anthropogenic source of mercury. As many as 107,692 tons of mercury were extracted in the entire period of the mine's operation. However, due to primitive ore processing methods such as burning in piles and later in clay retorts, more than 37 tons of mercury was lost. Besides, most roasting remains were dumped directly into the Idrijca River, which carried the material into the Soča River and further to the Adriatic Sea. Consequently, the environment from Idrija to the Gulf of Trieste has been polluted with mercury.^[1] The soil in Idrija area contains from 10 to even 10,000 mg Hg/kg at ancient roasting sites. Since Idrija is situated in karst area, surface and rain waters can leach Hg from contaminated soil to deeper soil layers and then into groundwater. For developing effective mercury control technologies in protection/remediation of water bodies, there is a need for evaluation of the capacity of different solid sorbents. In an attempt to produce an economic and cost-effective sorbent for controlling the mobility of mercury in contaminated soil of Idrija district, the sorption ability of natural zeolite clinoptilolite for leached mercury has been investigated. The excellent adsorption and ionic exchange properties of natural zeolite for heavy metals^[2], as well as its environmental compatibility and cost-effectiveness were the reasons for selection of this material for remediation of mercury contaminated waters.

EXPERIMENTAL

Leachate of mercury contaminated soil: The mercury contaminated water has been obtained by leaching of contaminated soil (fine-grain size < 0.075 mm, containing 1347 mg Hg/kg) of Idrija district in ultrapure water of different pH values (pH₀ = 3.00 - 10.04), by standard batch method according to DIN 38414 S4. The total mercury concentrations in obtained leachates were in the range $c_0 = 0.33 - 9.02 \mu\text{g/l}$.

The natural zeolite sample - The raw zeolite sample (two particle sizes, d_p of 0.6 - 0.8 mm and < 0.04 mm) originates from the Zlatokop deposit in Serbia and contains up to 80% of clinoptilolite as the major mineralogical component.^[2]

Sorption study - The sorption study was performed by shaking the leachates and zeolite samples in solid/liquid ratio S/L = 1/100 in an incubator shaker at 25 °C and 25 rpm. The pH values of leachates before sorption were in the range pH_S = 3.83 - 6.83. After 24 h the suspensions have been filtered and centrifuged. The pH values have been monitored during sorption experiment. The mercury concentrations have been analysed by an atomic absorption spectrometry analyser.

RESULTS AND DISCUSSION

The results of sorption study of mercury removal from leachates onto natural zeolite of two particle sizes are given in Table 1 in dependence of initial pH values (pH₀) of ultrapure water, pH values of leachates (pH_S) before sorption and mercury concentration (c_0) in leachates.

Table 1. Experimental results of total mercury sorption onto natural zeolite samples of two particle sizes.

pH ₀	pH _S	c_0 (Hg), µg/l	c_e (Hg), µg/l		q , µg/g		η , %	
			0.6 - 0.8	< 0.04	0.6 - 0.8	< 0.04	0.6 - 0.8	< 0.04
Natural zeolite particle size d_p , mm								
3.00	3.83	2.4	0.28	0.14	0.212	0.226	88.3	94.2
4.03	6.83	9.0	1.19	1.22	0.781	0.778	86.8	86.4
5.09	6.16	2.49	1.42	1.81	0.107	0.068	43.0	27.3
6.32	5.77	6.77	3.69	4.74	0.308	0.203	45.5	30.0
7.21	5.83	4.91	3.72	3.57	0.119	0.134	24.2	27.3
8.11	5.94	8.98	5.08	3.56	0.390	0.542	43.4	60.4
9.18	5.03	0.33	0.23	0.09	0.010	0.024	30.3	72.7
10.04	5.53	9.02	2.69	1.89	0.633	0.713	70.2	79.0

The correlation between pH₀, pH_S and c_0 is not evident. Moreover, the values of pH_S and c_0 in relation to pH₀ show irregular increase and decrease. This is probably a consequence of soil characteristics and presence of mercury in different forms. The results of sorption experiments are expressed as zeolite sorption capacity, q , and removal efficiency, η , calculated according to Equations 1 and 2:

$$q = (c_0 - c_e) \cdot V / m_Z \quad (1)$$

$$\eta = [(c_0 - c_e) / c_0] \cdot 100 \quad (2)$$

where: c_e is total mercury concentration remaining after equilibration in sorption process, V is the volume of leachate and m_Z is the mass of zeolite sample. From Table 1 and Figure 1 it can be seen that q and η are generally higher for the lower zeolite particle size. This can be attributed to the increase in the specific surface area of the zeolite.

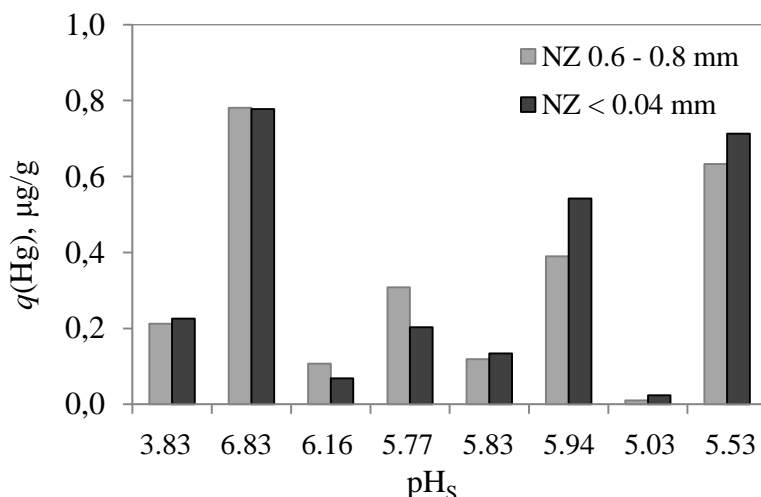


Figure 1. Sorption capacities of zeolite samples depending on pH_s values.

The quantity of total mercury bound on zeolite increases with the increase in total leached mercury concentration (Figure 2).

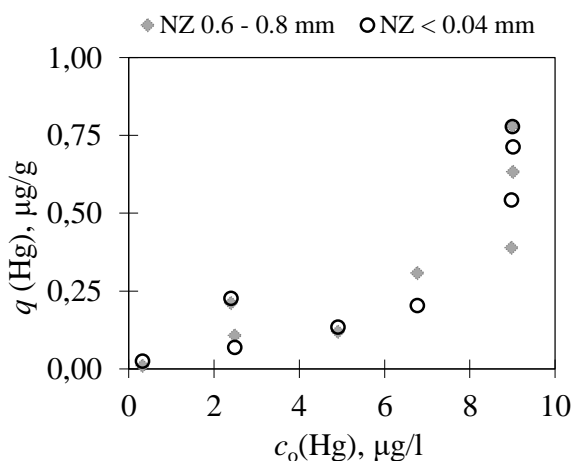


Figure 2. Capture of total mercury by natural zeolite clinoptilolite vs. total leached mercury concentration.

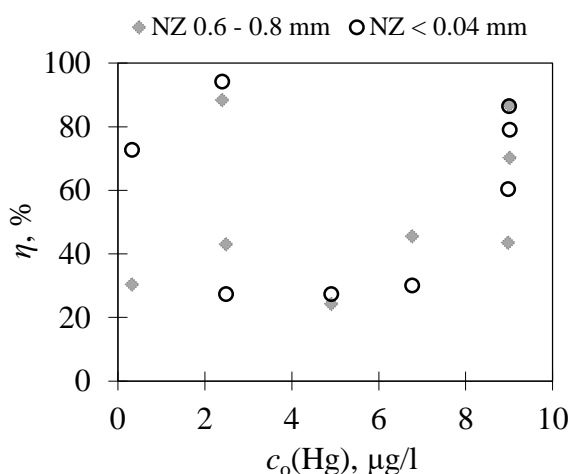


Figure 3. The removal efficiency vs. total leached mercury concentration.

Extremely higher removal efficiencies (Figure 3) have been obtained for c_0 values of 2.4 and 9.0 µg/l, which means for low and high concentration of leached mercury. This is probably due to significant difference in pH_s values that may affect the number of available sites in zeolite structure. Continuous measuring of pH values during sorption study is presented in Figures 4a and b. During binding of mercury species onto zeolite, the pH values of suspensions show neutralization for $d_p = 0.6 - 0.8$ mm, while for $d_p < 0.04$ mm the equilibrium pH values are low alkaline. Investigations presented in this paper are performed in real system and mercury occurs in the leachates in different organic and inorganic compounds^[3], which strongly affects the sorption ability of zeolite. However, in all samples the satisfactory removal of total mercury has been obtained.

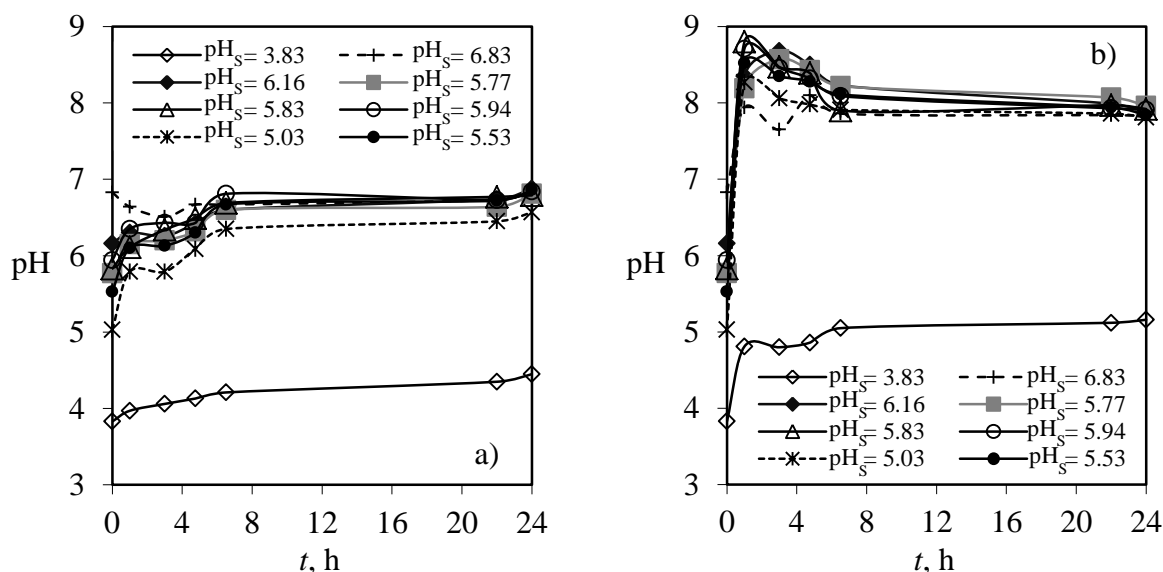


Figure 4. Changes in pH values in suspensions during sorption process on zeolite samples: a) $d_p = 0.6 - 0.8$ mm and b) $d_p < 0.04$ mm.

CONCLUSION

The mercury removal depends on pH value in the liquid phase since it determines the mobility and solubility of mercury compounds. The satisfactory removal of total mercury has been obtained on both zeolite particle sizes. The quantity of total mercury removed as well as the removal efficiency is generally higher for the zeolite with the smaller particle size. The obtained results indicate that natural zeolite clinoptilolite has a potential to be used as a material for groundwater remediation and treatment of mercury contaminated soil.

ACKNOWLEDGEMENT

This study has been financially supported by Ministry of Science and Education of the Republic of Croatia under the bilateral Croatian-Slovenian project *Application of Natural Zeolite for Remediation of Mercury Contaminated Soil*.

REFERENCES

- [1] M. Gosar, T. Teršič, *Environ. Geochem. Health* **2012**, *34*, 27–41.
- [2] I. Nuić, M. Trgo, J. Perić, N. Vukojević Medvidović, *Microporous Mesoporous Mater.* **2013**, *167*, 55–61.
- [3] I. Nuić, T. Teršič, M. Trgo, M. Miler, M. Ugrina, N. Vukojević Medvidović, M. Gosar, in *B. Abstr. 4th Int. Symp. Environ. Manag. - Towar. Circ. Econ.* (Eds.: Z. Katančić, N. Koprivanac, A. Lončarić Božić, H. Kušić, Z. Hrnjak Murgić), Zagreb, Croatia, **2016**, pp. 45–45.