

## APPLICATION OF NATURAL ZEOLITE CLINOPTILOLITE FOR REMEDIATION OF MERCURY CONTAMINATED SOIL AND WATER

*Ivona Nuić<sup>1</sup>, Ivona Jukić<sup>1</sup>, Mariusz Macherzyński<sup>2</sup>, Marin Ugrina<sup>1</sup>*

<sup>1</sup>Faculty of Chemistry and Technology, Department of Environmental Engineering, University of Split, Rudera Boškovića 35, 21 000 Split, Croatia

<sup>2</sup>AGH University of Science and Technology, Faculty of Energy and Fuels, Department of Coal Chemistry and Environmental Sciences, al. Mickiewicza 30, 30-059 Krakow, Poland  
E-mail: ivona@ktf-split.hr

### ABSTRACT

The possibility of using the natural zeolite clinoptilolite as filler in permeable reactive barriers for the remediation of mercury contaminated soil and water has been investigated. The leaching of mercury from surrounding soil of Idrija mine in Slovenia was carried out in ultrapure water of different initial pH<sub>0</sub> values, without and with addition of natural zeolite. A significantly lower concentration of total mercury was determined in leachates in the presence of natural zeolite indicating its potential use in the remediation of mercury contaminated soil and water.

Keywords: mercury contaminated soil and water, remediation, natural zeolite, permeable reactive barrier.

### INTRODUCTION

The Idrija mine in Slovenia, as the second largest mercury mine in the world, has been a significant anthropogenic source of mercury. The mining methods resulted in a huge amount of waste from which the mercury reached the surrounding environment [1]. In the karst area, mercury from the surface infiltrates into the deeper soil layers and reaches groundwater, which is most commonly used for water supply. One of the most promising alternative remediation technology for the contaminated groundwater are permeable reactive barriers (PRB), where natural zeolite (NZ) can be used as a filler for retaining the harmful substances by sorption process [2]. The aim of this research was to evaluate the efficiency of NZ in preventing of mercury leaching, and thus its possible use in mercury contaminated soil and water remediation.

### EXPERIMENTAL

*Materials:* The experiments were carried out on a sample of the contaminated soil (fine-grain size of 0.075 mm) with mercury content of 1347 mg/kg, taken from the Idrija district in Slovenia. The natural zeolite (particle size 0.09 - 0.56 mm) used in this study originates from the Zlatokop deposit in Serbia and contains up to 80 % of clinoptilolite as the main mineralogical component.

*The leaching of mercury from contaminated soil according to the standard batch method (DIN 38414 S4) [3]:* The experiments were performed by shaking the mercury contaminated soil with ultrapure water of different initial pH<sub>0</sub> values (3.00 - 11.46) in the solid/liquid (S/L) ratio of 1/10, in a batch incubator shaker during 24 h, at ambient temperature (23 ± 2 °C) and at 25 rpm.

*The leaching of mercury from contaminated soil without and with addition of natural zeolite:* The leaching of mercury was carried out by stirring the 3 L of ultrapure water with adjusted initial pH<sub>0</sub> values of 4.11; 5.09 and 6.04 and 300 g of mercury contaminated soil, at ambient temperature (23 ± 2 °C) for 24 h at ≈ 800 rpm. Afterwards, the new experiments were performed under the same conditions, but with addition of 30 g of NZ to the soil.

The separation of solid from the liquid phase was carried out by double centrifugation (Centric 322 A Technica) for 15 min at 4000 rpm and filtration through a membrane filter ( $\phi = 0.45 \mu\text{m}$ ). All experiments were monitored by measuring the concentration of total mercury in leachates or supernatants by Mercury Analyser MA - 3000 (NIC).

## RESULTS AND DISCUSSION

### The total leached mercury concentration according to the standard batch method

The total leached mercury concentration (TLMC) after 24 h (Figure 1) was very low but still exceeded the maximum permissible concentrations (MPC) in water according to the Croatian and Slovenian legislations and to the Council Directive of the European Community [4]. The highest concentration was obtained at  $\text{pH}_0 = 11.46$ , since alkaline conditions probably effects on dissolving the humic substances in the soil and thus higher leachability of mercury.

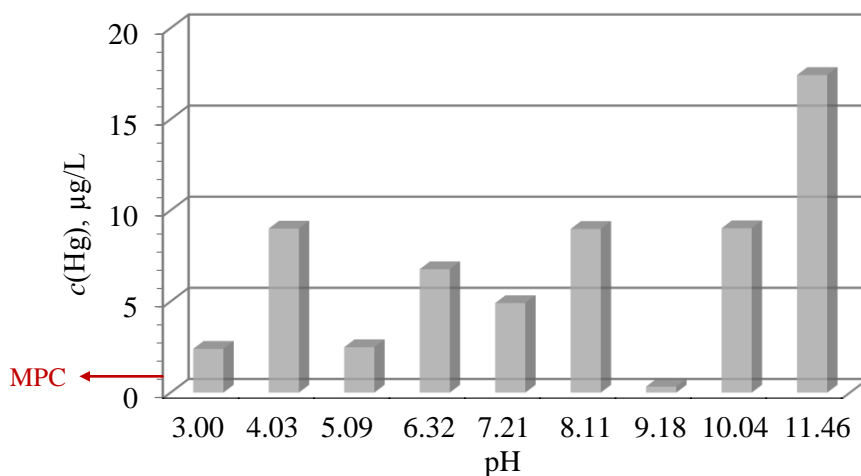


Figure 1. The TLMC in ultrapure water of different  $\text{pH}_0$  values after 24 h.

Although the standard prescribes a contact time of 24 h, the TLMC at time intervals within 24 h (Figure 2) has been monitored in order to get insight into mercury leaching behaviour over time.

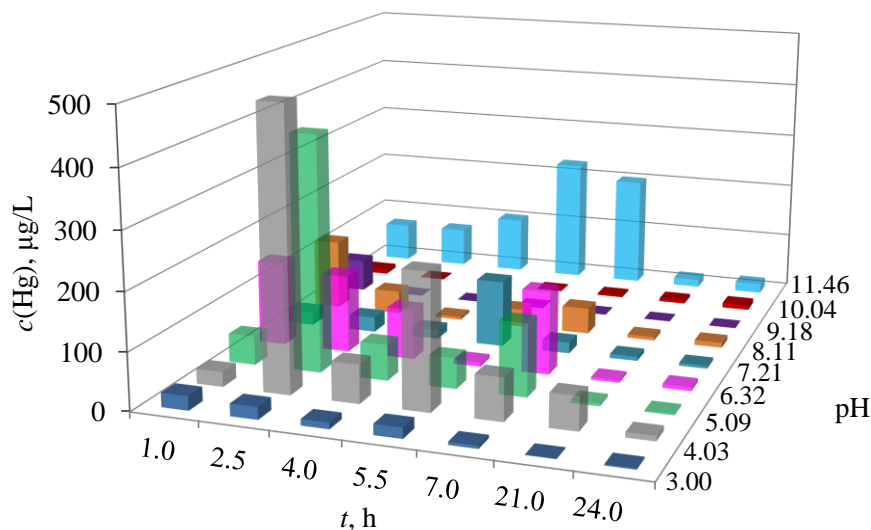


Figure 2. The TLMC in ultrapure water of different  $\text{pH}_0$  values in time intervals within 24 h.

In the first few hours of the experiment, the concentration of leached mercury is considerably higher than that after 24 h. It reaches even  $\approx 488 \mu\text{g/L}$  after 2.5 h from the beginning of the experiment. More importantly, these high concentrations were obtained for  $\text{pH}_0$  values of 4.03; 5.09 and 6.32, which are more likely to occur in nature. The reason for so high mercury leached concentrations can be attributed to its complexation with organic matter from the soil (mostly humic and fulvic acids), which is considered to be the most dominant processes controlling its mobility. These findings indicate the necessity for further studying of mercury leachability at ancient roasting sites of the Idrija district. Therefore, this research has been continued with an emphasis on the first few hours of the experiment for  $\text{pH}_0$  ranging from  $\approx 4$  to  $\approx 6$ .

**The total leached mercury concentration without and with the addition of natural zeolite**

The TLMC in the time intervals within 24 h without and with the addition of NZ for initial  $\text{pH}_0$  values of 4.11; 5.09 and 6.04, is graphically shown in Figure 3 [5].

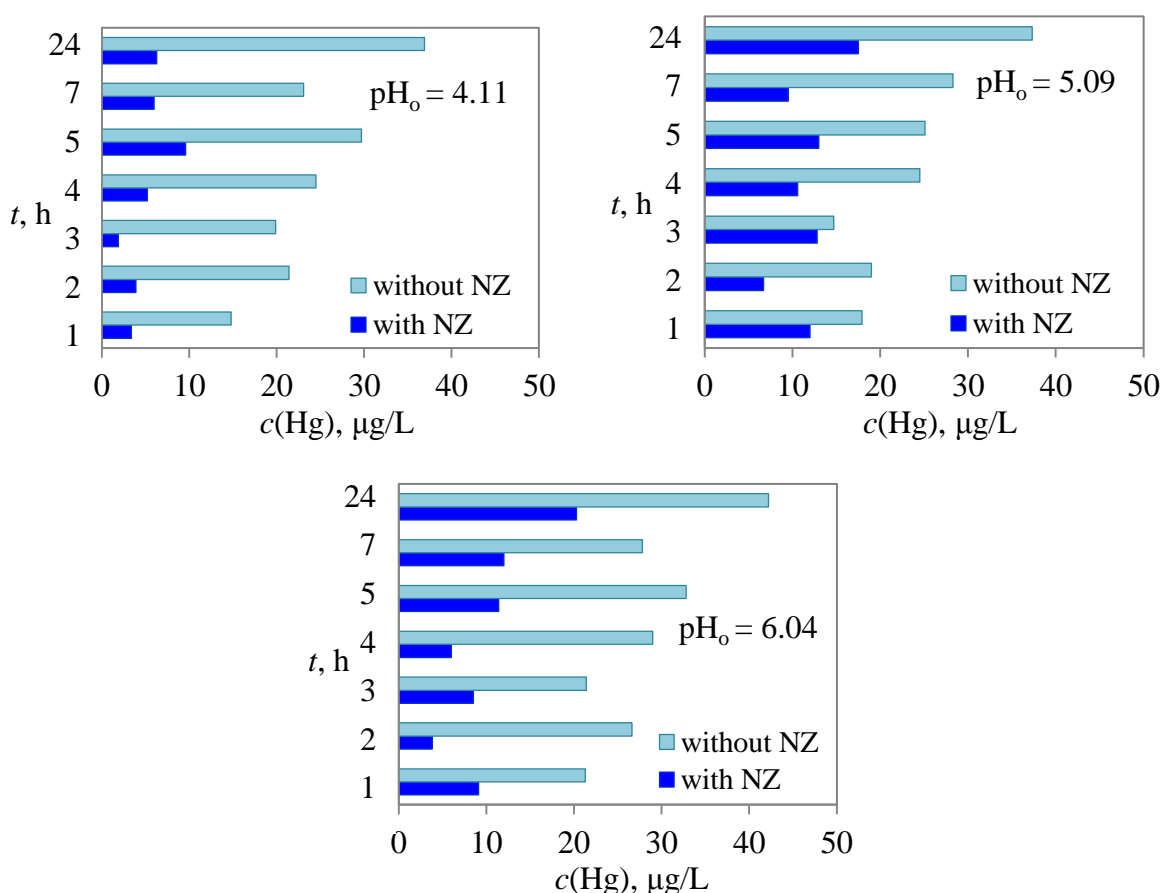


Figure 3. The TLMC in ultrapure water of different  $\text{pH}_0$  values at time intervals within 24 h without and with addition of NZ.

The TLMC in suspensions without presence of the NZ was in range  $14.7 - 42.2 \mu\text{g/L}$ , with the maximum concentration achieved after 24 h, for all  $\text{pH}_0$  values. The lower remaining concentration of total mercury ( $1.9 - 20.3 \mu\text{g/L}$ ) is determined in all leachates in the presence of NZ indicating the sorption of the mercury ionic species and their retention in NZ structure. The TLMC was irregular and did not exhibit a clear pattern as function of time. Continuous changes in concentrations of the leached mercury within 24 h is most likely due to changes in the mobility of mercury and its species [6], both in soil and

suspensions. The removal efficiency,  $\alpha$  (%), of the total leached mercury in ultrapure water of different  $\text{pH}_0$  values by NZ was calculated according to the following equation:

$$\alpha = \frac{c_{\text{WZ}}(\text{Hg}) - c_{\text{NZ}}(\text{Hg})}{c_{\text{WZ}}(\text{Hg})} \cdot 100 \quad (1)$$

Where  $c_{\text{WZ}}(\text{Hg})$  and  $c_{\text{NZ}}(\text{Hg})$  are concentrations of total leached mercury in supernatants without and with the presence of NZ,  $\mu\text{g/L}$ . The obtained results are presented in Figure 4.

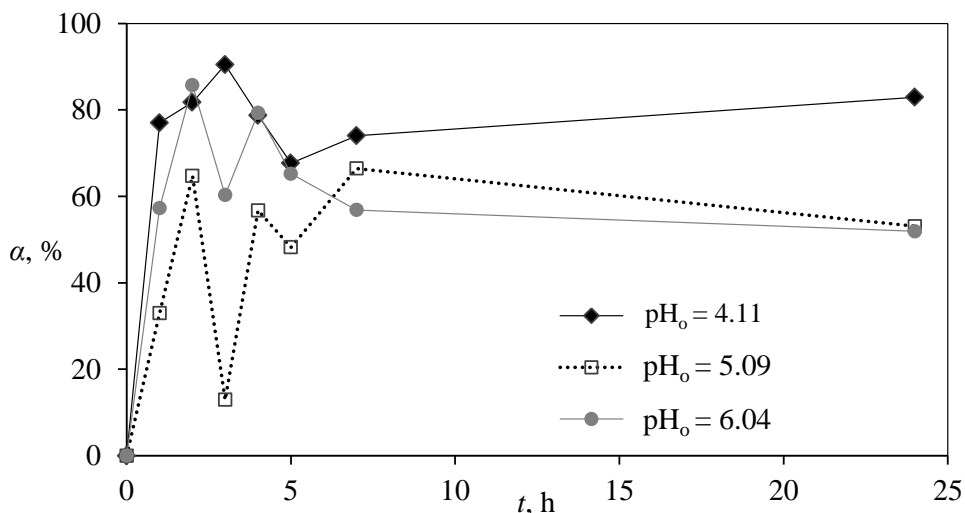


Figure 4. The removal efficiency of NZ at different initial  $\text{pH}_0$  values.

The removal efficiency (Figure 4) was in the range from 12.9 % to even 90.5 %, with the best removal at the lowest  $\text{pH}_0$  value of 4.11. Moreover, at this  $\text{pH}_0$  the value  $\alpha$  in range from 77 % to 90.5 % was achieved up to first 3 h. The same tendency, although less pronounced, is observed for  $\text{pH}_0$  of 5.09 and 6.04 up to first 2 h from the beginning of the experiment. Reduction of mercury concentration below the maximum permissible level could be performed with the new stage of sorption onto fresh natural zeolite.

## CONCLUSION

The very low concentration of leached mercury indicates a strong affinity of mercury to the soil constituents. However, the concentrations still exceeded the maximum permissible levels, due to further research and monitoring of the soil quality at the Idrija district is required. According to the obtained removal efficiencies (up to 90.5 %), the natural zeolite clinoptilolite could be applied as filler in PRB for the remediation of mercury contaminated soil and water. To obtain the better removal efficiency and to reduce the concentration of total mercury below the maximum permissible levels, the multi-stage sorption process onto natural zeolite should be performed. The hydrophilic/hydrophobic surface properties of the zeolite, the affinity for organic and anionic species and higher removal efficiency could be improved by modification. Moreover, the knowledge about the exact form in which mercury is present in the soil and water could give a better insight into its mobility and leaching behaviour as well as in its bioavailability.

## ACKNOWLEDGEMENT

This work was partially supported by bilateral Croatian-Slovenian project *Application of Natural Zeolite for Remediation of Mercury Contaminated Soil* (2016-2018), by the Erasmus

Staff Training Mobility in academic year 2017/2018, and by the AGH UST grants No. 16.16.210.476.

We would like to thank the colleagues from the Geological Survey of Slovenia in Ljubljana for their cooperation and collection of contaminated soil samples.

## REFERENCES

- [1] M. Gosar and T. Teršič, *Environ. Geochem. Health*, 2012, **34/1**, 27-41.
- [2] P. Misaelides, *Micropor. Mesopor. Mat.*, 2011, **144**, 15-18.
- [3] G. Kocasoy, and Z. M. Murat, *J. Environ. Sci. Health A*, 2009, **44**, 605-614.
- [4] Uredba o standard kakvoće voda (NN 73/13, 151/14, 78/15, 61/16 i 80/18); Pravilnik o pitni vodi (Uradni list RS, št. 19/04, 35/04, 26/06, 92/06, 25/09 in 74/15); Council Directive 98/83/EC on the quality of water intended for human consumption.
- [5] I. Jukić, Investigation of remediation of mercury contaminated environment by application of natural zeolite clinoptilolite, Bachelor thesis, Faculty of Chemistry and Technology, University of Split, 2018.
- [6] I. Nuić, I. Milićević, T. Teršič, M. Trgo, M. Miler, M. Ugrina, N. Vukojević Medvidović, and M. Gosar, in *Proceedings of 7th Slovenian-Serbian-Croatian Symposium on Zeolites* (eds. N. ZabukoveLogar, N. Rajić, J. Bronić) 2017, 79-82.