ENVIRONMENTAL-FRIENDLY MODIFIED NATURAL ZEOLITES AS SORBENTS FOR *IN SITU* REMEDIATION OF MERCURY-CONTAMINATED SOIL IN IDRIJA REGION, SLOVENIA

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ABSTRACT

Toxicity Characteristic Leaching Procedure (TCLP) was applied to mercury-contaminated soil from the Idrija region, Slovenia to evaluate the potential soil toxicity. The TCLP test was performed with and without the addition of natural zeolite, iron(III)-modified zeolite or sulphur-impregnated zeolite. Results showed that the soil is extremely polluted and represents hazardous waste. The addition of zeolites significantly reduces the concentration of leached Hg, whereby the most satisfactory results being achieved with sulphur-impregnated zeolite, making it as a potential sorbent for *in situ* remediation of mercury-contaminated soil.

Key words: natural zeolite, iron-modified zeolite, sulphur-impregnated zeolite, leaching, mercury-contaminated soil.

INTRODUCTION

The remediation of soil in surrounding area of the Idrija mine in Slovenia is of significant interest in order to prevent spreading of pollution and negative impacts on the entire ecosystem. Investigations have shown that mentioned area is extremely polluted with mercury which is transported through watersheds to more distant areas and even to the Gulf of Trieste via the Idrijca and Soča-Isonzo rivers [1]. Although mercury is present mainly in inorganic form, it can also make complexes with organic matter which increases its mobility, or can abiotically or biotically transform into organic form. Among organic mercury compounds, methylmercury is the most toxic because it can be easily uptaken to phytoplankton, representing the starting point for its bioaccumulation and biomagnification within the food web. Therefore, there is a clear necessity to remediate this area to prevent or reduce the formation of methylmercury. For this purpose, different *in situ* and *ex situ* methods could be applied, whereby first ones based on sorption processes are more easily feasible [2]. Materials impregnated with sulfur species are most commonly used as mercury-binding sorbents due to a high affinity of sulphur for mercury, forming sparingly soluble HgS ($K_{sp} = 3.9\cdot10^{-53}$). It seems that natural zeolites could be good carriers for coating with iron or sulphur species due to their porous structure. Moreover, these materials are environmentally compatible since they are natural constituents of the environment. Therefore, in this paper, natural zeolites and their modified forms, iron-modified zeolite and sulphur-impregnated zeolite, are investigated as sorbents for *in situ* remediation of mercury-contaminated soils in Idrija, Slovenia.

EXPERIMENTAL

Zeolite sample preparation

Natural zeolite (NZ) clinoptilolite was collected from the Zlatokop deposit (Vranjska Banja, Serbia). The sample was milled and sieved, and a particle size fraction of 0.6 to 0.8 mm was separated. The sample was then washed in ultrapure water and dried at 60 °C. Iron-modified zeolite (FeZ) was prepared by treating NZ according to the previously published procedure [3].

Briefly, the NZ is treated separately with a 1 M $Fe(NO_3)_3 \cdot 9H_2O$ at pH = 3.6, followed with 1 M NaOH and 4% $NaNO_3$ solutions. Sulphur-impregnated zeolite (SZ) was prepared by immersing NZ in 1 M Na_2S during 4 hours at 150 °C according to a previously published procedure [4]. Systematic physico-chemical characterization of NZ, FeZ and SZ samples is described in detail in the previously published papers [3,4].

Soil sample preparation

The soil sample was taken in the area of the Idrija mine, at location of the Frbejžene trate. The sample was dried at 35 °C to a constant mass, and then ground in a ceramic mortar, homogenized and sieved through a 2 mm pore size mesh. Thereafter, the sample was additionally pulverized in an agate mill to fine grain size (< 0.075 mm) and stored in a polyethylene bag. Total Hg content in homogenized soil sample was measured after aqua regia digestion for 3h at 160 °C by using Inductively Coupled Plasma Emission Spectrometry (ICP-ES) method.

Leaching experiments according to the Toxicity Characteristic Leaching Procedure

Toxicity Characteristic Leaching Procedure (TCLP) is the most commonly used single extraction test [5]. The TCLP test involves the extraction of harmful substances from a milled sample with an extraction solution of pH values of 2.88 and 4.93 prepared according to the detailed procedure described, by mixing 1 M NaOH and/or 0.1 M glacial acetic acid. A mass of 2.5 g of a mercury-contaminated soil was leached with 50 mL of extraction solutions with and without addition of zeolites in an amount of 10–40% (w/w) relative to the mass of the soil (solid/liquid ratio is 1:20) during 18 h ± 2 h at 30 rpm. After extraction/sorption time, soil suspensions were centrifuged, the liquid phase was separated, and then the concentration of total leached soluble Hg was immediately analyzed by LECO's AMA254 Mercury Analyzer. If the concentration of leached Hg exceeds the limit value prescribed by this method (> 0.2 mg/L), waste material is classified as hazardous.

RESULTS AND DISCUSSION

The total Hg content determined in the soil sample was 1347 mg/kg, indicating that the Idrija mine site is extremely polluted and requires appropriate remediation. Therefore, the addition of different portions (10–40%) of natural or modified zeolites on the reduction of Hg mobility from the soil was compared with the raw soil at pH = 2.88 and pH = 4.93 according to the performed TCLP test.

The results of the TCLP test at two examined pHs for raw soil and treated soil with different amounts of NZ, FeZ or SZ are shown at Figure 1. From Figure 1, higher concentration of total soluble leached Hg from raw soil at pH = 4.93 (3.345 mg/L) compared to pH = 2.88 (2.178 mg/L) is observed. This finding differs from the expected, since usually at lower pH, the solubility of the metal increases. However, in a soil sample, presence of mineral components as well as organic matter, especially humic and fulvic acids, could affect the solubility of bound Hg. Unlike fulvic acids that are soluble under all pH condition, co-precipitation of humic acids at pH < 3 occurs, while increase of pH facilitates their dissolution. At pH = 2.88, dissolution of eventually present soil mineral components should also take place. However, a higher concentration of total leached Hg at pH = 4.93 indicates that dissolution of Hg from humic acids dominates. Therefore, it could be assumed that the binding of Hg to humic substances is predominant in investigated soil. This further suggests that humic acids should be the most responsible for the higher Hg retention by this soil at pH = 2.88.

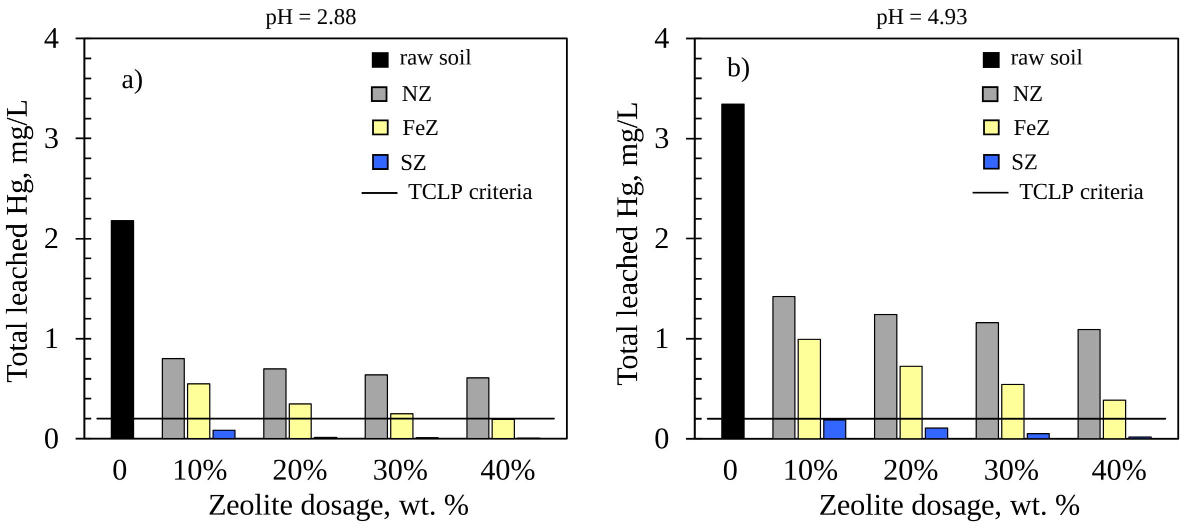

Figure 1. TCLP results of total leached Hg concentration at: a) pH=2.88 and b) pH=4.93.

In soil samples with addition of zeolites, the total soluble leached Hg concentrations not exceed 1.42 mg/L (Fig. 1a and b). With an increase in zeolite dosage, a decrease in total leached Hg is observed, which is more pronounced for the FeZ and especially for the SZ compared to the NZ. The removal efficiency of leached Hg in the zeolite-treated soil samples was calculated according to the Eq. (1) and is shown in Figure 2:

$$\text{Removal efficiency }(\%) = \frac{\left(c_{\text{Hg,raw soil}} - c_{\text{Hg,treatedsoil}}\right)}{c_{\text{Hg,raw soil}}} \cdot 100 \qquad (1)$$

where: $c_{\text{Hg, raw soil}}$ is the concentration of total leached Hg at equilibrium in raw soil sample (mg/L) while $c_{\text{Hg, treated soil}}$ is the concentration of total leached Hg at equilibrium in the soil sample treated with zeolites (mg/L).

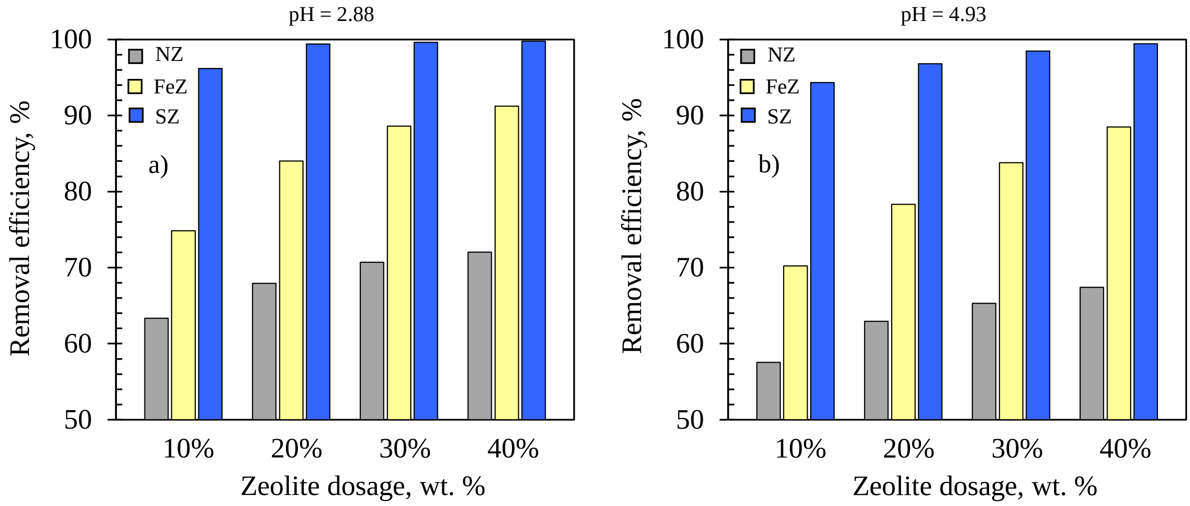

Figure 2. Removal efficiency of leached Hg by addition of different quantities of zeolites at: a) pH=2.88 and b) pH=4.93.

The removal efficiency increased with increasing in zeolite dosage at both pH values. The removal efficiency of leached Hg of 57–72% for NZ, 70–91% for FeZ and over 94% for SZ at both pHs is achieved. The most significant increase in removal efficiency with increasing zeolite dosage was observed for the FeZ, the smallest for the NZ while the SZ sample immediately achieved high efficiency even with the lowest dosage. This behavior could be attributed to the number of available active sites that differ among the zeolite samples due to the modification method.

The sorption of soluble mercury species from soil onto zeolites is presumably very complex and involves multi-sorption mechanism. The most pronounced decrease in total leached Hg in the presence of the SZ can be a consequence of the formation of sparingly soluble HgS on SZ surface, since it is well known that Hg exhibit strong affinity for sulfur species. Moreover, the formation of HgS is desirable since it is the least toxic form of mercury due to its stability, low solubility, relative immobility, which thus reduces the bioavailability of Hg for methylation in deeper soil layers. Furthermore, TCLP requires that the concentration of Hg leached from the waste material is less than 0.2 mg/L (line in Fig. 1a and b). According to the TCLP test, raw soil is an extremely hazardous waste with the concentrations of total leached Hg of 3.345 mg/L at pH = 4.93 and 2.178 mg/L at pH = 2.88. The addition of natural and especially modified zeolites significantly reduces Hg leaching by its stabilization in zeolite. At pH = 2.88, the leached Hg concentrations below the prescribed value of 0.2 mg/L, were achieved by the addition of all dosages of SZ (10–40%), and only with the highest dosage of FeZ (40%). At pH = 4.93 prescribed values was achieved only with SZ even with the smallest dosage of 10%. The stated values were not achieved with the NZ sample at both pHs. The obtained results indicate that SZ is a promising material for *in situ* remediation of contaminated soil, since its minimal dose significantly reduces Hg leaching from contaminated soil at both examined pH values.

CONCLUSION

The results clearly showed that higher pH favors Hg leaching from contaminated soil. Moreover, the tested pH of 4.93 corresponds to the real pH of rainwater, indicating that leaching of Hg in real conditions takes place continuously. Therefore, the need for topsoil remediation is necessary in order to reduce/prevent this phenomenon, and this could be achieved by applying the SZ sample.

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REFERENCES

[1] T. Teršič, H. Biester and M. Gosar, *Geoderma*, 2014, **226-227**, 213–222.

[2] L. Wang, D. Hou, Y. Cao, Y. Sik Ok, F.M.G. Tack, J. Rinklebe and D. O'Connor, *Environ. Int.*, 2020, **134**, 105281.

[3] M. Ugrina, N. Vukojević Medvidović and A. Daković, *Desalin. Water Treat*. 2015, **53**, 3557–3569.

[4] M. Ugrina, M. Gaberšek, A. Daković and I. Nuić, *Processes*, 2021, **9**, 217.

[5] USEPA, Method 1311: *Toxicity Characteristic Leaching Procedure*, US Environmental Protection Agency, Washington, D.C., 2004.