Latvian Journal of Chemistry, No 4, 2012, 336–341
DOI: 10.2478/v10161-012-0019-6

REMEDIATION OF SOIL CONTAMINATION WITH HEAVY METALS BY USING ZEOLITE AND HUMIC ACID ADDITIVES

J. Burlakovs, M. Klavins, A. Karklina

University of Latvia, Raina bulv. 19, LV-1586, Riga, Latvia
E-mail: maris.klavins@lu.lv

Soil remediation at contaminated sites very often needs customized approach, because of the different content of pollutants. Various technologies from simple soil excavation and transporting to hazardous waste landfills to different kinds of remediation by vitrification and the use of additives can be used for the treatment of soil. A series of remediation experiments using zeolites and humic acids were applied to soil contaminated with copper. Remediation can be performed with easily available additive materials of natural origin found near the place of application, in order to diminish the leaching of contaminants. Soils contaminated and spiked with copper were mixed with additives, and ion selective electrode potentiometry was used in order to establish the stability constants of humic-metal complexes. Thus the study provides an opportunity to gain information on the fate of copper variously mixed with potential remediation agents – zeolites and humic acids – as additives to contaminated soils.

Key words: *soil additives, heavy metals, remediation, potentiometry.*

INTRODUCTION

Soil is a variable mixture of minerals, organic matter and water, capable of supporting the most fundamental requirements for sustainable land use. Therefore the quality of soil is essential, and various technologies are used for the remediation of industrial contamination. The development of soil and groundwater remediation technologies is of great importance for recovering historically and currently contaminated sites, because the ongoing pollution deteriorates the environmental quality, the possibilities of site utilization, and prevents full value use of land. Contamination causes both the loss of land as a resource and the loss of property [1]. Remediation means actions taken to clean up, mitigate, correct, abate, minimize, eliminate, control and contain, or prevent a release of contaminants into the environment, in order to protect human health and the environment, including actions to investigate, study or assess any actual or suspected release [2]. Soil pollution with heavy metals is an increasingly urgent problem all over the industrialized world. Excessive concentrations of heavy metals in soils often result from anthropogenic activities, such as the mining industry and processing of metal ores, waste incineration, road transport, and the use of fertilizers and agrochemicals [3]. Remediation technologies can be divided into two categories: *in-situ* [4] and *ex-situ* remediation methods [5], as well as on site and off site technologies. Soil additives can often be used as one of *in-situ* technologies for the rehabilitation process of contaminated soil.

Zeolite and humic acids (HA) are considered as important remediation agents for the immobilization of heavy metals in soils [6, 7]. Any of these remediation agents can decrease bioavailability of heavy metals in soils. It means that locally available resources such as natural clays and organic substances can be used effectively for the treatment.

Zeolites are a class of alkaline porous alumosilicates with a negatively charged crystal lattice, neutralized by the presence of exchanged cations in the structural cavities [8–11]. Zeolites are being developed as an improvement of soil quality – they diminish the solubility and thus the biological availability of metals: salts, complexes, as well as oxides and metal-carbonate precipitates are formed with zeolites [12, 13]. Soil organic matter has been of particular interest due to its ability to form stable complexes with metal ions [14, 15].

Metal ion complex formation is one of the most prominent interactions in nature, and metal complexation is of widespread interest. The strength of the interaction between organic ligands and metals is usually expressed in terms of stability constants of the formed complexes. The knowledge of stability constants enables the behaviour of a metal ion with one or more ligands to be modelled as a function of pH and reactant concentration [16].

The aim of this work was to evaluate the utility of natural zeolites mined in Latvia and humic acids (HAs), which can be produced in Latvia, in order to assist remediation of copper-contaminated soils. The difference in the treatment of spiked soils was studied using both agents, each agent separately, and without these agents.

EXPERIMENTAL

Mineral soil samples were collected during geotechnical field works from different depths (3–12 m) at 10 sites, mainly of sandy soil granulometric composition. Sampling sites were chosen near the estuaries of rivers Daugava and Gauja, in the floodplain areas.

Air-dried soil samples were sifted through a 2 mm sieve, and fractions finer than 0.05 mm were determined by pipette analysis [2]. On the basis of the USDA soil texture classes, the fractions from 0.063 to 2.0 mm were classified as sand, 0.002–0.063 mm – as silt, and finer than 0.002 mm – as clay [17] (see Table 1). The percentage of sand, silt and clay was calculated from fine earth (<2 mm fraction). Soil pH_{KCl} was measured with a glass electrode in 1 *M* KCl (1:2.5 mass-to-volume ratio) in triplicate.

For the determination of the cation exchange capacity for each of the 10 samples, 0.1 *M* $BaCl_2$ was used, samples were batch treated, filtered and analyzed by atomic absorption spectrometry with PerkinElmer Instrument Analyst 200. Granulometric parameters and other properties for the pH (KCl), Fe content and cationic exchange capacity (CEC) are given in Table 1.

Afterwards, all 10 samples were sieved again, and 10 g of each sample were weighed for five different series. All the 50 samples were spiked with copper sulphate in order to apply to them the known contamination of 500 mg/kg, 10 samples were left untreated, 10 – mixed with the zeolite (the red Lode clay of the Devonian Gauja Formation), 10 – with the light gray clays of the same formation, 10 samples were amended with HAs at the rate of 1:100, and the last 10 were treated with HAs and zeolites. All the 50 samples were incubated at

room temperature for 1 month. Before the measurement series all samples were filtered; measurements were done in triplicate.

Table 1. **The main properties of analyzed soil samples**

No	Sand, %	Silt, %	pH_{KCl}	Na, $mg \cdot kg^{-1}$	Mg, $mg \cdot kg^{-1}$	K, $mg \cdot kg^{-1}$	Ca, $mg \cdot kg^{-1}$	CEC, mEq/100 g soil
1–2	87.7	12.3	5.82	187	99	16.2	806	5.7
1–3	93.7	6.3	3.94	186	80	15.3	397	3.5
1–4	94.6	5.4	7.09	184	79	15.8	357	3.3
2–2	20.4	79.6	6.85	193	153	28.5	1046	7.4
2–3	91.6	8.4	8.00	186	70	22.2	903	6.0
D1–1	87.5	12.5	6.81	243	136	45.7	550	5.1
D1–2	64.5	35.5	6.84	270	163	44.7	709	6.2
D1–3	86.6	13.4	6.73	217	91	21.9	557	4.5
D3–1	93.0	7.0	6.80	207	70	24.9	333	3.2
D3–2	87.4	12.6	–-	215	104	20.5	409	3.9

Zeolite (clay) additives were taken from the Lode quarry in the northern part of Latvia. This clay consists of illite with a significant content of kaolinite.

HAs produced by Tehum was used, with known basic characteristics. This product is extracted from Bohemian (Czech) oxyhumolite and by elemental composition contains 60.7% of carbon, 34.1% of oxygen, 3.7% of hydrogen and 1.5% of nitrogen (Eglīte, 2007).

Copper(II) ion selective electrode, manufactured by pHoenix Electrode Co., was used to detect the amount of free copper ions, which can be related to biologically available forms [18]. At first the electrode was calibrated in order to correctly determine the amount of free copper ions in the solution. All the measurements for samples were done with the pH value adjusted to 6.

The potentiometry results were recalculated by using calibration data to the concentration of metal ions in the solution, as well as to the ability of metals to bind with HAs and zeolites according to formulas (1) and (2):

$$Cu + HS = CuHS, \tag{1}$$

where Cu – the number of Cu^{2+} moles in the solution;
HS – the number of HAs moles in the solution,

and

$$Ko = \frac{CuHS}{[Cu] \cdot (HS - CuHS)}, \tag{2}$$

where $[Cu]$ – the concentration of hydrated Cu^{2+} in the solution;
Ko – the stability constant of the copper-humic acid complex;
$CuHS$ – the number of moles for copper ions included in the complexes [19].

RESULTS AND DISCUSSION

Stability constants are well known tools for analytical chemists, biochemists and chemists in general to help determine the properties of metal–ligand

reactions in chemical and biological systems. Stability constants of copper in various forms increase when various complexing agents are added. This trend of an increasing stability constant is obvious for zeolites, which were chosen for this study from two types of Lode quarry clays.

Table 2. **The calculated stability constants for soils spiked with copper at 500 mg/kg concentration and different types of additives applied: no additives, humic acids, red Lode clay, gray Lode clay and both clay and humic acids together***

No.	No additives	Humic acid 1:100	Red Lode clay 1:100	Gray Lode clay 1:100	Both Lode clay and humic acids 1:100 each
1–2	6.18	–	7.92	7.86	4.89
1–3	4.52	4.21	6.59	7.91	4.37
1–4	5.53	4.13	6.73	7.74	4.67
2–2	5.87	6.24	8.53	7.26	7.02
2–3	3.68	5.54	7.04	7.84	5.13
D1–1	6.58	6.46	8.28	7.03	6.29
D1–2	6.52	6.38	8.48	8.12	6.72
D1–3	6.34	6.48	8.17	7.18	6.09
D3–1	3.56	5.87	7.56	7.19	6.30
D3–2	6.26	6.19	7.54	8.37	5.14

* pH values during the electrode potentiometry measurements were adjusted to 6.0±0.2.

The results of already calculated Cu stability constants for 49 samples are shown in Table 2. Ion selective electrode measurements were used in this study to determine the conditional stability constants of a number of Cu^{2+} complexes with zeolites (alumosilicates) and organic ligands (HAs in this case).

Comparing the stability constant results for 9 samples without any additives to samples with added HAs, the stability constants increased only in three cases, decreased in two, and remained relatively the same in other cases. Significant changes of stability constants were detected when zeolites alone were added. The results were inconclusive with respect to which of the clay types is more effective, because the red and gray clays were approximately equal. After adding both zeolites and HAs, the stability constants increased in three cases, decreased in three, but in four cases remained approximately the same.

The logarithmic values of stability constants in spiked soils without additives varied from 3.68 to 6.52 (5.50 on average), for spiked soils with only HA additives between 4.13 and 6.48 (5.70 on average), for samples with the red and gray clay addition – between 6.59 and 8.53 (7.65 on average), but with both agents added, the interval was between 4.37 and 6.72 (5.70 on average). The stability constants did not change significantly due to adding HAs; also the combined use of zeolites and HAs at the same time did not effectively diminish the free copper ion amount, and thus the contamination remained biologically available, and the soil was still dangerous for the environment. However, the addition of the clay mined from Gauja Formation Lode quarry in a concentration of 1:100 significantly diminished the biologically available copper within the soil pH at 6. Zeolite addition considerably reduced the biological availa-

bility of copper, and thus could be used for the remediation purposes as a soil additive.

This experiment showed that copper in the presence of zeolite additives has a much lower availability for leaching out and being mobile in the biogeochemical cycle: the stability constant of copper complexes was higher in soils with a zeolite additive.

CONCLUSIONS

The availability of trace elements as demonstrated with the example of copper, was lower in soils with Devonian clay additive. At the same time, treatment of contaminated soils with humic substances may even increase the trace element availability. Further studies for different soil types spiked with trace elements must be performed in order to find better additives for soil remediation. The increase of stability constant was clearly seen in the samples with both clay and HAs additives. This effect could be used to increase the biological availability of heavy metals if the phytoremediation method is applied.

Acknowledgements

This research was carried out with the help of the European Social Fund (ESF).

REFERENCES

1. Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008 concerning integrated pollution prevention and control. Text with EEA relevance. *Official Journal of the European Union*, *L 24/8.*
2. 9VAC20-160-10. Definitions. (2002). *Virginia Register* Volume **13**, Issue 18, eff. June 26, 1997; amended, *Virginia Register* Volume **18**, Issue 18, available: http://leg1.state.va.us/cgi-bin/legp504.exe?000+reg+9VAC20-160-10, accessed: 11.08.2012.
3. Lado, L.R., Hengl, T., Reuter, H.I. (2008). Heavy metals in European soils: a geostatistical analysis of the FOREGS Geochemical database. *Geoderma, 148,* 189–199.
4. Breck, D. W. (1974). Zeolite Molecular Sieves: Structure, Chemistry and Use. New York: John Wiley & Sons.
5. Reddy, K.R., Adams, J.F., Richardson, C. (1999). Potential technologies for remediation of Brownfield. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, *3* (2), 61–68.
6. Dercova, K., Sejakova, Z., Skokanova, M., Barancikova, G., Makovnikova, J. (2007). Bioremediation of soil contaminated with pentachlorophenol using humic acids bound on zeolite. *Chemosphere, 66*, 783–790.
7. Indianara, C.O., Maria, A.S.D.B., Edson, A.S., Joao, H.D., Pedro, A.A., Osxaldo, C.M.L. (2009). A comparative study for the ion exchange of Fe(III) and Zn(II) on zeolite NaY, *J. Hazard. Mater*., *161*, 1404–1412.
8. Joshi, U.D., Joshi, P.N., Tamhankar, S.S., Joshi, V.P., Idage, B.B., Joshi, V.V., Shiraljar, V.P. (2002). Influence of the size of extra framework monovalent cations in X-types zeolite on their thermal behaviour. *Thermochim. Acta, 373*, 121–130.
9. Mohamed, M.M. (2001). Heat capacities, phase transitions and structural properties of cation-exchanged H-mordenite zeolites. *Thermochim. Acta, 372*, 75–83.
10. Van Reeuwijk, L.P. (1995). *Procedures for Soil Analysis*. 5th edition, Wageningen: International Soil analysis and Reference Centre.
11. Mondales, K.D., Carland, R.M., Aplan, F.F. (1995). The comparative ion exchange capacities of natural sedimentary and synthetic zeolites. *Miner. Eng*., *8*, 535–548.
12. Chlopecka, A., Adriano, D.C. (1996). Mimicked in-situ stabilization of metals in a cropped soil: bioavailability and chemical form of zinc. *Environ. Sci. Technol., 30*, 3294–3303.
13. Querol, X., Alastuey, A., Moreno, N., Alvarez-Ayuso, E., Garcia-Sanchez, A., Cama, J., Ayora, C., Simon, M. (2006). Immobilization of heavy metals in polluted soils by the addition of zeolite material synthesized from coal fly ash. *Chemosphere, 62*, 171–180.

14. Chen, Y. (1996). Organic matter reactions involving micronutrients in soils and their effect on plants. In A. Piccolo (Ed.). *Humic Substances in Terrestrial Ecosystems* (pp. 507–530). Elsevier.
15. Havelcava, M., Mizera, J., Sykorova, I., Pekar, M. (2009). Sorption of metal ions on lignite and the derived humic substances. *J. Hazard. Mater., 161,* 559–564.
16. Byrne, L.A., Hynes, M.J., Connolly, C.D., Murphy, R.A. (2011). Analytical determination of apparent stability constants using a copper ion selective electrode. *J. Inorg. Biochem., 105*, 1656–1661.
17. FSCC (Forest Soil Co-Ordinating Centre) (2006). Manual IIIa: Sampling and Analysis of Soil. In ICP Forests: Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests. http://icp-forests.net/page/icp-forests-manual.
18. Electrochemistry Dictionary and Encyclopedia. (2012). http://electrochem.cwru.edu/ed/dict.htm.
19. Eglīte, L. (2007). Humic substances, their interaction with soil components and immobilisation of humic substances. Doctoral thesis, Riga, University of Latvia, 159 p.
20. Bresnahan, W.T., Grant, C.L., Weber, J.H. (1978). Stability constants for the complexation of copper(II) ions with water and soil fulvic acids measured by an ion selective electrode. *Anal. Chem., 50* (12), 1675–1679.

SMAGO METĀLU PIESĀRŅOJUMA ATTĪRĪŠANA, IZMANTOJOT CEOLĪTU UN HUMĪNSKĀBJU PIEDEVAS

J. Burlakovs, M. Kļaviņš, A. Kārkliņa

K O P S A V I L K U M S

Laboratorijā tika veikti smago metālu piesārņojuma imobilizācijas eksperimenti, izmantojot ceolītus un humīnskābes, kas dažādās kombinācijās tika pievienotas ar varu piesārņotai augsnei. Eksperimentos iegūti viegli interpretējami rezultāti attiecībā uz vara kompleksu stabilitātes konstantes izmaiņām atkarībā no pievienotajām augsnes piedevām.