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An experimental study on the use of natural zeolite for Cu, Pb and Zn immobilization in soil

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An experiment of the immobilization of heavy metals Cu, Pb and Zn in soil by means of natural zeolite was performed in the laboratory. The natural zeolite employed was from a deposit near the village of Sokyrnytsia in the Ukrainian Transcarpathian region. Sandy soil was contaminated by Cu^{2+}, Pb^{2+} and Zn^{2+} nitrates at three contamination levels, 50, 100 and 500 mg/kg of each metal. Sandy soil samples contaminated with three different concentrations of three metal solutions were mixed with 5%, 10% and 20% of zeolite. 200 ml of distilled water was added to each plastic container with soil and zeolite mixtures and left for 1 month. After one month sandy soil samples of 0.5 g from each plastic container were analysed by ICP-OES. Zeolite immobilised metals in the order: $Pb^{2+} > Zn^{2+} > Cu^{2+}$.

Key words: natural zeolite, soil remediation, heavy metals

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INTRODUCTION

A huge problem is soil pollution near highways (Baltrenas, Kliaugiene, 2003). There is a lot of different soil remediation methods currently used for solving this problem (Singh, Oste, 2001). It is difficult to remove contaminated soil from the roadsides and replace it with clean soil. The main requirements for soil remediation are easy application, efficiency and low costs. The aim of soil remediation is to stop migration of pollutants into deeper soil horizons and groundwater. Metal immobilization in soil is one of the *in situ* methods to solve this problem. *In situ* immobilization of metals using inexpensive amendments such as natural zeolites is a promising alternative to current remediation methods (Mench et al., 1998).

The natural zeolite clinoptilolite, which was used in our study, is quarried from a deposit near the village of Sokyrnytsia in the Ukrainian Transcarpathian region. Natural zeolites are hydrated aluminosilicate minerals with a porous structure, exhibiting valuable physicochemical properties such as cation exchange, molecular sieving, catalysis, and sorption. An important property of zeolite is its high ability to exchange cations. Ion exchange is a process by which an ion in solution is exchanged with another type of ion from a molecule. Zeolite is an ion exchanger with electrically charged active sites.

METHODS

Soil samples and additive. Sandy soil was collected near the main highway which connects the biggest cities of Lithuania. Soil was oven-dried at 103 °C for 6 h and thoroughly mixed. Four soil samples were separately contaminated with mixtures of Cu(II) nitrate, Pb(II) nitrate and Zn(II) nitrate at three contamination levels (50 mg/kg, 100 mg/kg and 500 mg/kg of each metal). Four 0.5 kg dried soil samples were separately mixed with three solutions in plastic containers. The four contaminated soil samples were thoroughly mixed and oven-dried at 103 °C for 6 h. Sandy soil samples contaminated with three different concentrations of three metal solutions were mixed with 5%, 10% and 20% of zeolites. 200 ml of distilled water was added to each plastic container with soil and zeolite mixtures and left for 1 month (Table 1).

The zeolite samples were sieved and the 1–3 mm grain size fraction was washed with distilled water and

Table 1. **Soil sample experimental design**
1 lentelė. **Dirvožemio ėminių eksperimentinis modelis**

C = 500 mg/kg (without zeolite)	C = 500 mg/kg + 5% zeo	C = 500 mg/kg + 10% zeo	C = 500 mg/kg+ 20% zeo
C = 100 mg/kg (without zeolite)	C = 100 mg/kg + 5% zeo	C = 100 mg/kg + 10% zeo	C = 100 mg/kg+ 20% zeo
C = 50 mg/kg (without zeolite)	C = 50 mg/kg + 5% zeo	C = 50 mg/kg + 10% zeo	C = 50 mg/kg+ 20% zeo
C = 0 mg/kg (without zeolite)	C = 0 mg/kg + 5% zeo	C = 0 mg/kg + 10% zeo	C = 0 mg/kg + 20% zeo

C – concentration of metal, mg/kg, and amount of zeolite, %; RS – reference soil (not contaminated, without zeolite).

dried at 103 °C temperature for 6 h.

Sample analysis. After one month, sandy soil samples of 0.5 g from each container were leached by 20 ml of concentrated nitrogen acid (HNO_3) and element concentrations were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) at the laboratory of Lulea University of Technology in Sweden. Soil sample analysis was carried out according to the standard procedure for ICP-OES analysis and was accomplished through acid (HNO_3) digestion.

The pH was measured in the substrate–water suspension at a liquid-to-solid ratio = 2 according to the standard method (LST ISO 10390:2005). A sample of ten grams was mixed with 20 ml of distilled water, and this mixture was placed on a shaking table for 15 min.

RESULTS AND DISCUSSION

First of all the pH values of all samples were measured (Fig. 1). The results showed that addition of 5% of natural zeolite to the sandy soil increased the pH value from 5.75 to 6.35. Addition of 10 and 20% of natural zeolite increased the pH value up to 5.89 and 5.83 respectively. In sandy soil samples contaminated with 50 mg/kg of Pb, Zn and Cu, the pH value decreased from 6.89 to 6.65 (in the sample containing 5% of zeolite), to 6.25 (in the sample containing 10% of zeolite) and to 6.14 (in the sample with 20% of zeolite).

In sandy soil samples contaminated with 100 mg/kg of heavy metals, the pH value decreased from 6.76 to 6.40, 6.23 and 5.82 depending on the percentage of zeolite in the samples. The initial pH value in sandy soil samples contaminated with 500 mg/kg was 6.48 and after a month of contact with natural zeolite decreased to 6.05, 6.11 and 6.06 respectively.

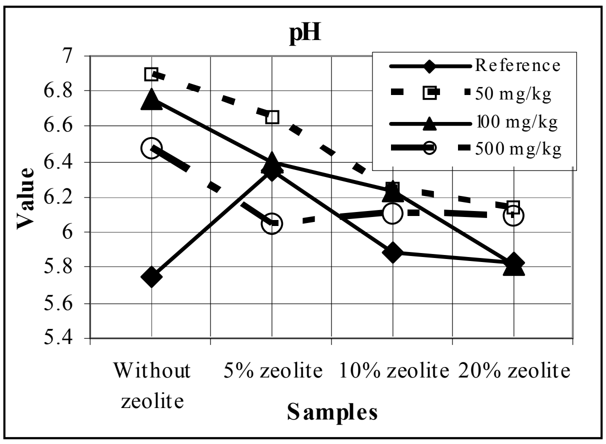

Fig. 1. pH values of sandy soil samples
1 pav. pH reikšmės smėlio dirvožemio mėginiuose

When sandy soil was contaminated with 50 mg/kg of each heavy metal and 5% of natural zeolite was added, the concentration of Pb reduced to 40.7, Zn to 45.9 and Cu to 49.0 mg/kg (Fig. 2). Only 25.2, 37.7 and 42.8 mg/kg of Pb, Zn and Cu respectively remained in the samples with 10% of zeolite. Even lower concentrations of Pb, Zn and Cu remained in the samples with 20% of natural zeolite.

After a month, 83.9 mg/kg of Pb, 91 mg/kg of Zn and 97.4 mg/kg of Cu remained in the soil sample with 100 mg/kg of heavy metals and 5% of zeolite (Fig. 3). The higher the percentages of natural zeolite, the less heavy metal remained in sandy soil samples. Lead was reduced to 50.4 mg/kg, Zn to 66.1 and Cu to 66.2 mg/kg in sandy soil samples with 10% of natural zeolite. At the highest percentage of zeolite (20%), the highest concentration of Cu (70.9 mg/kg) remained in the sandy soil sample; less of Zn (46 mg/kg) and even less of Pb (43.9 mg/kg) was left in the samples after a month's contact with natural zeolite.

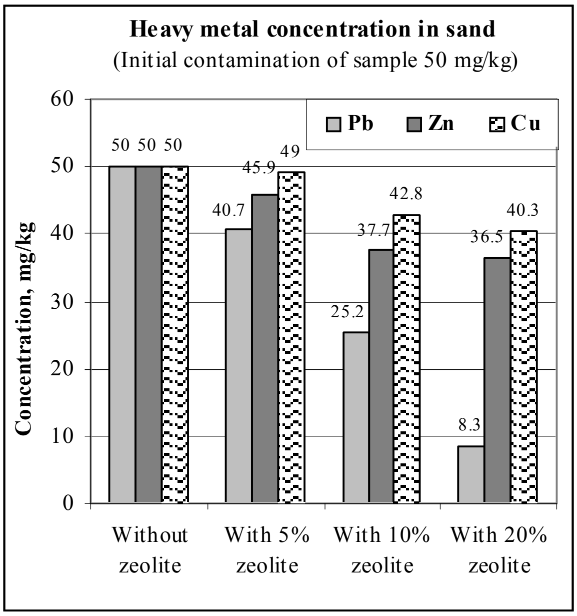

Fig. 2. Residual content of heavy metals in sand depending on the percentage of zeolite in samples at the initial concentration of heavy metals in sand 50 mg/kg
2 pav. Priklausomai nuo procentinio ceolito kiekio ėminiuose likęs sunkiųjų metalų kiekis smėlyje, kai pirminė sunkiųjų metalų koncentracija smėlyje buvo 50 mg/kg

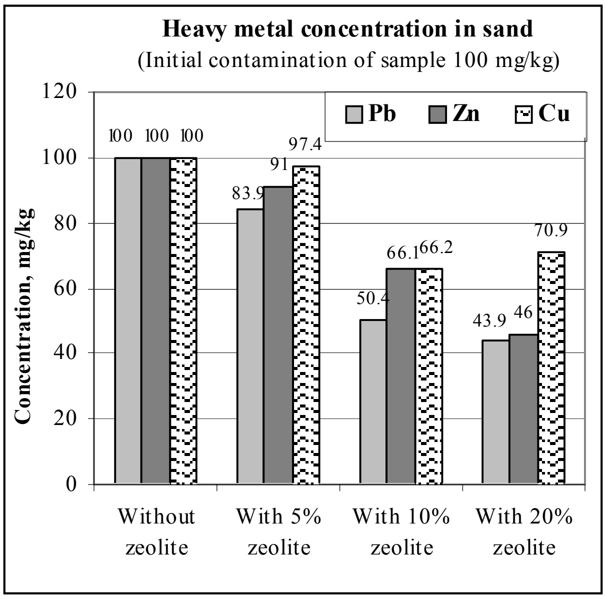

Fig. 3. Residual content of heavy metals in sand depending on the percentage of zeolite in samples at the initial concentration of heavy metals in sand 100 mg/kg

3 pav. Priklausomai nuo procentinio ceolito kiekio ėminiuose likęs sunkiųjų metalų kiekis smėlyje, kai pirminė sunkiųjų metalų koncentracija smėlyje buvo 100 mg/kg

5% of natural zeolite was not enough to reduce the concentration of Cu from 500 mg/kg to the maximum permissible concentration (MPC) of 100 mg/kg in soil, because 396 mg/kg of Cu remained in the soil sample (Fig. 4). For the other two heavy metals, Pb and Zn, 5% of natural zeolite added to a sample was enough to meet the MPC requirements, which are 100 mg/kg and 300 mg/kg respectively. Lead was reduced to 55 mg/kg and Zn to 253 mg/kg.

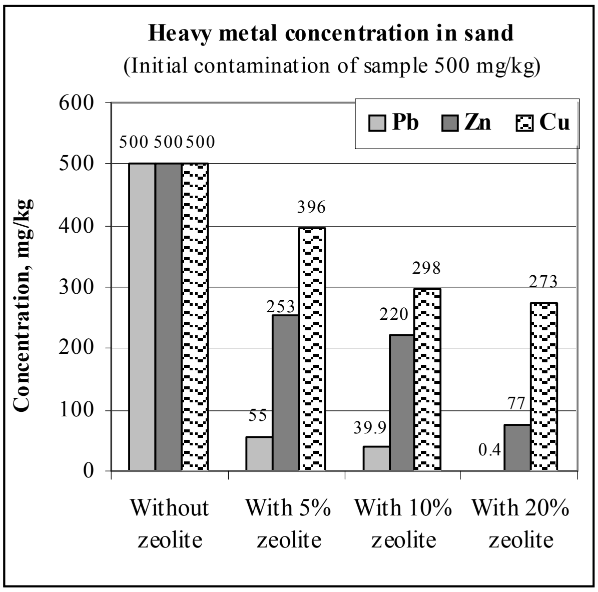

Fig. 4. Residual content of heavy metals in sand depending on the percentage of zeolite in samples at the initial concentration of heavy metals in sand 500 mg/kg

4 pav. Priklausomai nuo procentinio ceolito kiekio ėminiuose likęs sunkiųjų metalų kiekis smėlyje, kai pirminė sunkiųjų metalų koncentracija smėlyje buvo 500 mg/kg

The efficiency of heavy metal immobilization in sandy soil by natural zeolite was calculated, and results are presented in Table 2. The lowest efficiency (16.1%) for Pb sorption from sandy soil was shown by 5% of natural zeolite at a 100 mg/kg concentration level. The highest efficiency (99.9%) of Pb sorption was at the highest contamination level (500 mg/kg) and 20% of natural zeolite in sandy soil. Zinc was adsorbed better (84.6%) at the highest contamination level and 20% of natural zeolite. The lowest efficiency of Zn immobilization in sandy soil was observed at the lowest contamination level and lowest percentage of natural zeolite in sandy soil samples. Only 2% of Cu was adsorbed by 5% of natural zeolite at the lowest contamination level (50 mg/kg) of sandy soil samples.

Table 2. **Efficiency of heavy metal immobilization in sandy soil by natural zeolite**

2 lentelė. **Sunkiųjų metalų sulaikymo gamtiniu ceolitu smėlio dirvožemyje efektyvumas**

Heavy metal	Primary concentration mg/kg	Efficiency, %		
		5% zeolite	10% zeolite	20% zeolite
Cu	50	2.0	14.4	19.4
Pb	50	18.6	49.6	83.4
Zn	50	8.2	24.6	27.0
Cu	100	2.6	33.8	29.1
Pb	100	16.1	49.6	56.1
Zn	100	9.0	33.9	54.0
Cu	500	20.8	40.4	45.4
Pb	500	89.0	92.0	99.9
Zn	500	49.4	56.0	84.6

Copper was immobilized better (45.4%) at the highest contamination level and at the highest percentage of natural zeolite in the sample.

Summarizing the results of heavy metal immobilization in soil by natural zeolite, it could be concluded that Pb was immobilized better than Zn and Cu. At the initial concentration of 500 mg/kg of heavy metals in sandy soil, 10% of natural zeolite was enough to immobilize Pb and Zn. The highest efficiency of Pb, Zn and Cu immobilization in sandy soil by natural zeolite was 99.9, 84.6 and 45.4% respectively.

Such immobilization sequence of heavy metals (Pb > Zn > Cu) in soil by natural zeolite could be explained by the different size of the ionic radius of Pb, Zn and Cu. The natural zeolite clinoptilolite has a lot of various channels of different size. The type of channels varies from 3.0 to 7.6 Å, B type – 3.3–4.6 Å and C type – 2.6–4.7 Å (Meier and Olson, 1992). Because of the different size of their ionic radius, heavy metals are adsorbed differently during the ion exchange process.

The results of the experiment could be applied on the roadsides where runoff is collected in the drainage system. 10% of natural zeolite could be mixed with soil and placed in the drainage system in which the runoff from the road surface is collected. Runoff treatment could be performed by polluted runoff filtration over a soil and zeolite mixture.

CONCLUSIONS

Summarizing the results of Pb, Zn and Cu immobilisation in sandy soil by adding 5%, 10% and 20% of natural zeolite, the following conclusions could be made:

1. Zeolite immobilised metals in the following order: $Pb^{2+} > Zn^{2+} > Cu^{2+}$.
2. Calculating the efficiency of metal reduction and the costs of additive, the content of zeolite in soil should be 10% if the contamination level of soil does not exceed 500 mg/kg.
3. The content of natural zeolite in soil should be higher than 10% if the contamination of sandy soil is higher than 500 mg/kg and in case the traffic increases and thus soil contamination increases as well.
4. This experiment showed that natural zeolite didn't sorb Cu at the desirable range.

Further research should be carried out in natural conditions with naturally contaminated soil (not artificially in the laboratory).

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GAMTINIO CEOLITO PANAUDOJIMO Cu, Pb IR Zn SULAIKYTI DIRVOŽEMYJE EKSPERIMENTINIAI TYRIMAI

S a n t r a u k a

Šiuo metu egzistuoja gausybė skirtingų dirvožemio valymo metodų, naudojamų sprendžiant dirvožemio prie greitkelių užterštumo problemą. Daugelis sunkiųjų metalų šalinimo metodų yra brangūs ir neefektyvūs arba sunkiai pritaikomi. Gana sunku pašalinti arba pakeisti užterštą dirvožemį kelio aplinkoje švariu. Būtina sukurti paprastą, efektyvų, aplinkai palankų bei pigų dirvožemio valymo metodą. Dirvožemio valymo tikslas yra sustabdyti teršalų migraciją į gilesnius dirvožemio sluoksnius bei gruntinį vandenį. Taigi metalų sulaikymas yra vienas iš *in situ* metodų, naudotinų sprendžiant šią problemą. *In situ* metalų sulaikymas nebrangiais sorbentais, tokiais kaip mineralai ceolitai, – daug žadantis alternatyvus dirvožemio valymo metodas.

Eksperimento metu naudotas gamtinis ceolitas iš Sokirnicos telkinio Ukrainoje. Smėlio tipo dirvožemis buvo užterštas Cu^{2+}, Pb^{2+} ir Zn^{2+} nitratais trimis užterštumo lygiais – 50, 100 ir 500 mg/kg kiekvieno metalo. Vėliau mėginiai buvo sumaišyti su 5%, 10% ir 20% ceolito. Po mėnesio buvo atlikta 0,5 g smėlio tipo ėminių iš kiekvienos plastikinės dėžutės ICP-OES analizė. Metalus ceolitas sorbavo šia seka: $Pb^{2+} > Zn^{2+} > Cu^{2+}$.

Эвелина Браннвалл

ЭКСПЕРИМЕНТАЛЬНОЕ ИССЛЕДОВАНИЕ ИСПОЛЬЗОВАНИЯ НАТУРАЛЬНОГО ЦЕОЛИТА ДЛЯ ИММОБИЛИЗАЦИИ Cu, Pb И Zn В ПОЧВЕ

Р е з ю м е

В настоящее время в целях решения существенной проблемы загрязненной почвы возле шоссе применяются разнообразные методы очистки почвы. Многие методы удаления из почвы тяжелых металлов не слишком рентабельны или же их применение трудно осуществимо. Удаление с обочин загрязненной почвы и замена ее на чистую представляет собой сложную задачу. Необходима простая, эффективная, экологичная и дешевая стратегия обработки почв. Цель очистки почвы – остановить перемещение загрязнителей в более глубокие горизонты почвы и грунтовой воды. Таким образом, очистка почвы от металлов является методом *in situ.* Этот метод при использовании недорогих сорбентов из полезных ископаемых, таких как цеолиты, – перспективная альтернатива другим методам, применяемым в настоящее время. Использовался цеолит из деревни Сокирница Украинского Закарпатья. Почва была загрязнена Cu^{2+}, Pb^{2+} и Zn^{2+} нитратами на 3 уровнях, по 50, 100 и 500 мг/кг соответственно. Загрязненные образцы почвы были смешаны с 5, 10 и 20% цеолита. Через 1 месяц песчаные образцы почвы по 0,5 г из каждого пластмассового контейнера были исследованы ICP-OES. Цеолит сорбировал металлы следующим образом: $Pb^{2+} > Zn^{2+} > Cu^{2+}$.