

Laboratory study on the use of natural zeolite from Gunungkidul, Indonesia for Cu, Pb, Zn and Cd immobilization in soil

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Abstract. An experiment of the immobilization of heavy metals Pb, Cu, Zn, and Cd in contaminated soil by using the natural zeolite was performed in the laboratory. The natural zeolite was obtained from Gunungkidul, Yogyakarta, Indonesia. Artificially contaminated levels on 100, 300 and 500 mg/kg were prepared and then mixed with three different dosages of 5%, 10% and 20% of the natural zeolite. The result revealed that the addition of natural zeolite effect on reducing the heavy metal in the contaminated soil. The addition 5% dosage of the natural zeolite was sufficient to reduce the concentration of Pb, Cu and Zn from 500 mg/kg to the maximum permissible of concentration level. Finally, the natural zeolite immobilized the heavy metals in the contaminated soil by following in order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$.

1 Introduction

Soil heavy metal pollution has been becoming a severe problem in the world [1]. Their sources in the environment can be geogenic such as weathering of alteration rocks rich in metals, and human-made sources such as emission from industrial activity, mining site, smelting, and from agricultural fertilizer [1]. Heavy metals are dangerous in the environment, and cause pollutes the food chains, and human health problems [2]. The soil containing heavy metals will be a source of contaminants and are enter the human body by distributed and entering the bloodstream. Another way occur by human consumption through the plants [3,4]. One of the natural material used to immobilize heavy metal was natural zeolite [5,6,7]. This research aims to carry out a laboratory experiment on the heavy metal immobilization in the contaminated soil with natural zeolites obtained from Gunungkidul, Indonesia. There was a previous study on the use of natural zeolite in this study area. However, the information was limited to obtain a comprehensive understanding of the utilization of this material for contaminated heavy metals in soil [8, 9, 10].

2 Material and methods

2.1 Natural zeolite and soil sample

The natural zeolite sample was sampled in Gunungkidul area, Indonesia. The X-ray diffraction (XRD) analysis was used to analyze the mineralogical composition of the natural zeolite sample. The uncontaminated volcanic sandy soils were collected in Kaliurang village, the upper slope of Merapi Volcano in 5 cm depth from surface. This soil samples was obtained from this location because

assuming that have no heavy metal contamination caused by human activity. Cation exchange capacity value was measured by using $BaCl_2$ method. Organic content was analyzed by TOC analyzer. Heavy metals content in uncontaminated soil was analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Particle size was analyzed by using sieving and hydrometer method. The uncontaminated soil was put in the oven and dried at 103 °C for six h and mixed. Uncontaminated soil samples were contaminated with mixtures of Cu(II) nitrate, Pb(II) nitrate, Zn(II) nitrate and Cd(II) nitrate at three contamination levels in order to achieve to approximately for 100 mg/kg, 300 mg/kg and 500 mg/kg of each metal.

2.2 Laboratory experimental procedure

The natural zeolite samples used in this experiment were crushed, sieved and the 1–3 mm grain size fraction obtained was washed with distilled water and put in the oven and then dried at 103° C temperature for 12 h. Three different concentrations of artificially contaminated soil samples containing four metal solutions obtained from the previous step were mixed with 10%, 15% and 20% of natural zeolites by weight. And then 200 ml of pure water was added to the container for each heavy metal with soil and zeolite mixtures and left for one month. The pH was maintained at 6. After one month, 10 gram of soil sample in each container was taken and mixed with 20 ml of pure water, and this mixture was shaken for 20 minutes, and the pH was maintained at 6. The solution obtained was then filtered with a 0.45 um filter, and the filtrate then was measured for Pb, Cu, Zn and Cd. All metals concentration

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in the solution was analyzed by the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

3 Result and discussion

3.1 Natural zeolite sample

The result of mineralogical analysis shows that the natural zeolite composed of zeolite mineral of clinoptilolite in dominant and mordenite. Other minerals also present such as quartz, plagioclase, illite, and smectite. Theoretically, in the natural condition, natural zeolite was found together with other impurities mineral [11]. The natural zeolite properties of the sample can be seen in Table 1.

Table 1. The properties of natural zeolite sample

Component	(%)
Clinoptilolite	26
Mordenite	8
Quartz	9
Smectite	12
Illite	13
Specific surface area (m ²)	27
CEC (meq/100 gram)	98,7

3.2 Soil sample

Characteristic of the physical and chemical of the uncontaminated soil sample is shown in Table 2. The concentration of heavy metals revealed that the soil sample in the range of natural condition [12]. In general, the soil sample was sandy soil and containing minor silt and clay content.

Table 2. Physical and chemical characteristics of uncontaminated soil sample

Soil Sample	Particle size fraction %			pH	CEC ¹⁾ (meq/100 gr)
	sand	silt	clay		
	86.3	7.3	6.4	5.9	24
	Organic ²⁾ (%)	Heavy metal (mg/kg)			
1.2	Pb	Cu	Zn	Cd	
	6	3	11	n.d	

¹⁾ analyzed by BaCl₂ method

²⁾ analyzed by TOC analyzer

n.d: not detected

3.3 Laboratory experimental result

The result shows that artificially contaminated soil sample with a concentration of 100 mg/kg heavy metals and after 10% of natural zeolite was added, the concentration reduced up to 65, 73, 86, and 91 mg/kg for Pb, Cu, Zn, and Cd respectively. The addition of the zeolite dosage up to 20% will decrease up to 31, 35, 43, and 52 mg/kg for Pb, Cu, Zn, and Cd respectively remained in the samples (Figure 1). After 10% of natural zeolite was added, soil sample with 300 mg/kg heavy metals contamination, it shows that the concentration reduced up to 180, 210, 240 and 260 mg/kg for Pb, Cu, Zn, and Cd respectively. The addition of the zeolite dosage up to 20% will decrease up to 40, 49, 60, and 78 mg/kg for Pb, Cu, Zn, and Cd respectively remained in the samples (Figure 2).

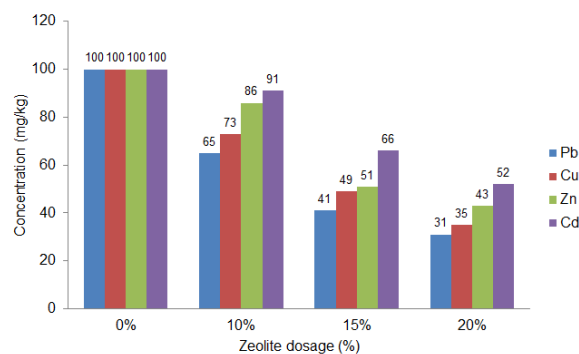


Fig. 1. The effect of zeolite dosage on the concentration of heavy metals in a soil sample with an initial concentration of 100 mg/kg.

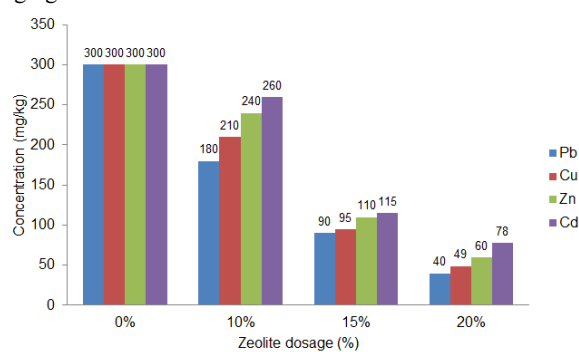


Fig. 2. The effect of zeolite dosage on the concentration of heavy metals in a soil sample with the initial concentration of 300 mg/kg.

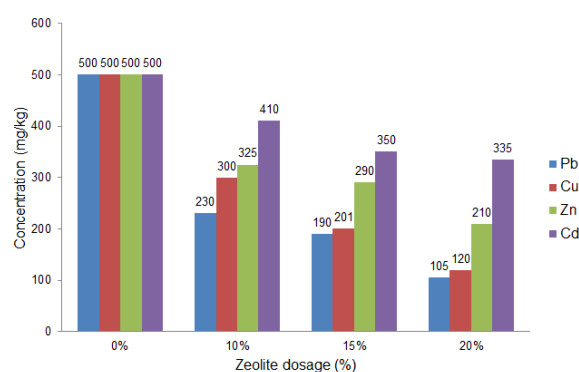


Fig. 3. The effect of zeolite dosage on the concentration of heavy metals in a soil sample with the initial concentration of 300 mg/kg.

Similar result pattern was obtained for soil sample with 500 mg/kg heavy metals contamination. In addition to 10% of natural zeolite, the concentration reduced up to 230, 300, 325, and 410 mg/kg for Pb, Cu, Zn, and Cd respectively. The addition of the zeolite dosage up to 20% will decrease up to 105, 120, 210, and 335 mg/kg for Pb, Cu, Zn, and Cd respectively remained in the samples (Figure 3). These experiments revealed that the higher the dosage of natural zeolite has an implication for reducing reduce heavy metal remained in soil samples. Compared to soil quality standard, the addition 5% dosage of natural zeolite was sufficient to reduce the concentration of Pb, Cu and Zn from 500 mg/kg to the acceptable level of soil quality standard published by Dutch Environmental Agency [13]. However, on Cd concentration, after 20% of natural zeolite was added to a sample, it shows that sufficient to meet the soil quality standard. The

calculation of the efficiency of immobilization of metals in a contaminated soil sample by natural zeolite are shown in Figure 4, 5 and 6. Overall, the lowest efficiency was obtained for Cd, i.e. only up to 33% for 500 mg/kg concentration level by the addition of 20% zeolite. The highest efficiency was obtained for Pb, i.e. achieve up to 86% for 300 mg/kg concentration level by the addition of 20% zeolite. The immobilization sequence of heavy metals obtained in this experiment follow by certain sequence Pb Cu>Zn>Cd. The natural zeolite sample used in this study was dominantly clinoptilolite (see Table 1) and has in the range from 3.0 to 7.6 Å [14]. This different size of their ionic radius may be attributed to the heavy metals which are adsorbed in different ways during the ion exchange process. For immobilization with various heavy metals in contaminated soil, cation selectivity of zeolite is important for selective ion removal. The selectivity of zeolite adsorption to varied cations was the result of the complex phenomenon and factor of the characteristics of zeolite including the diameter of zeolite particles, mineralogical and chemical composition, the internal structure including macropores and micropores and other parameters such as hydrated radius of the ion, tendency to form hydro complexes in the solutions, energy of hydration and also the mobility of ion [15].

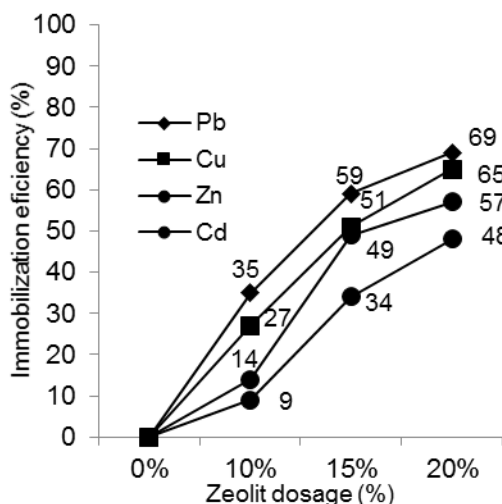


Fig. 4. The heavy metal immobilization efficiency in a soil sample with an initial concentration of 100 mg/kg

The result shows that the immobilization order for the metals ions followed the order $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$. The result revealed that Pb has a higher affinity for ion exchange for soil samples. The one parameter influence the selectivity was related to the hydrated radius of the ion. The hydration radius of the cations for Pb^{2+} (4.01Å), Cu^{2+} (4.19Å), Zn^{2+} (4.30Å) and Cd^{2+} (4.26 Å) respectively. This result is confirmed in the study conducted by Danny *et al.* (2004) [16] and Lee and Moon (2001) [17].

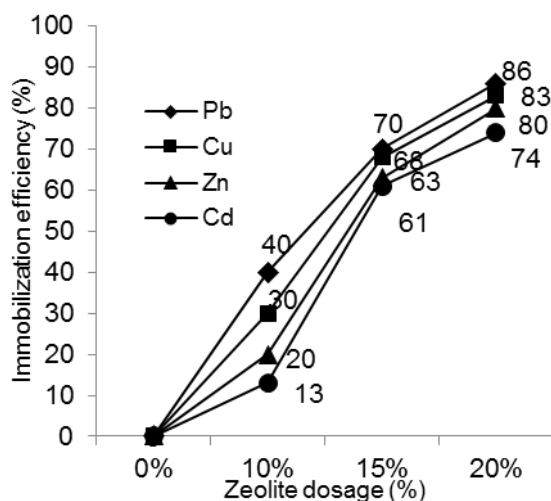


Fig. 5. The heavy metal immobilization efficiency in a soil sample with the initial concentration of 300 mg/kg

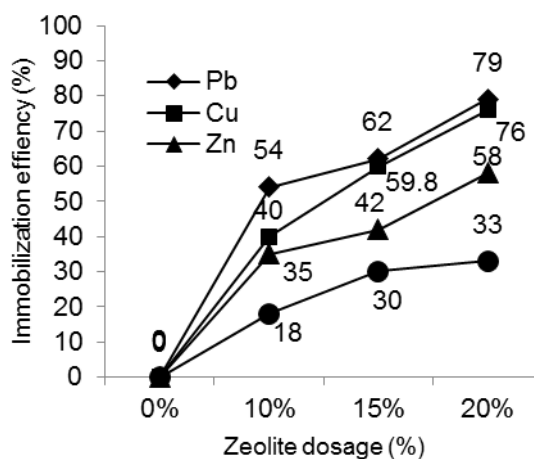


Fig. 6. The heavy metal immobilization efficiency in a soil sample with the initial concentration of 500 mg/kg

The smallest hydration radius should have higher adsorption capacity, and larger quantities of metals can be adsorbed correlated to the higher hydration radius, since the smaller hydration radius through obviously to the micropores and channels of the structure of zeolite [18,19]. The selectivity show that according to the hydration radius, the zeolite select to immobilize Pb rather than Cu, Zn and Cd in multicomponent solutions. Therefore, it shows that Pb concentrations will reduce the ability for zeolite to adsorb the Cu, Zn and Cd ion. It must also be noted that ion-exchange selectivity also depends on the ion concentration and pH solution. Therefore, these factors should be taken into consideration in real contaminated soil immobilization [20].

4 Conclusion

Based on the results of this experiment, the following conclusions could be made:

1. If the contamination of soil is greater than 500 mg/kg, the dosage of natural zeolite must be higher than 10% to obtain the optimum result.
2. Natural zeolite immobilized metals in the following order $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$.

3. The Cd can not be immobilized in this experiment at the acceptance level. The experiment should be conducted for naturally contaminated soil in the future.

Authors also thank Hinode Laboratory, Tokyo Institute of Technology for support of laboratory facility for experiment and analysis.

References

1. C. Li, K. Zhou, W. Qin, C. Tian, M. Qi, X. Yan, & W. Han, (2019). A review on heavy metals contamination in soil: effects, sources, and remediation techniques. *Soil and Sediment Contamination: An International Journal*, 28(4), 380-394.
2. B. J. Alloway, *Heavy Metals in Soils* (1995)
3. D. C. Adriano, *Trace elements in terrestrial environments: Biogeochemistry, bioavailability and risk of metals* (2001)
4. P. W. Abrahams, *Sci. Total Environ.* **29**, 1-32 (2002)
5. H. W. Mielke, P. L. Reagan, *Environ. Health Perspect.* **106**:217–29 (1998)
6. W. Y. Shi, H. B. Shao, H. Li, M. A. Shao, S. Du, *J. Hazard. Mater.* **170**(1), 1-6 (2009)
7. C. F. Lin, S. S. Lo, H. Y. Lin, Y. Lee, *J. Hazard. Mater.* **60**(3), 217-226 (1998)
8. W. Budianta, A. Ardiana, N.D. Andriyani, I.W. Warmada, *Environ. Earth Sci.* **79**, 172 (2020)
9. W. Budianta, A. Ardiana, *IOP Conference Series: Earth and Environmental Science*, **451**(1), 012025 (2020)
10. W. Budianta, A. Ardiana, N. D. Andriyani, F. L. Fahmi, F. L., *IOP Conference Series: Earth and Environmental Science*, **479**(1), 012020 (2020)
11. A. Iijima, *Pure Appl. Chem.* **52**, 2115–2130 (1980)
12. K. H. Wedepohl, *Geochim. Cosmochim. Acta*, **59**(7), 1217-1232 (1995).
13. R. Lacatusu, *European Soil Bureau*, **4**, 93-402 (2000).
14. W. M. Meier, D. H. Olson, C. Baerlocher, *Atlas of zeolite structure types*, (1996)
15. L. Mihaly-Cozmuta, A. Mihaly-Cozmuta, A. Peter, C. Nicula, H. Tutu, D. Silipas, E. Indrea, *J. Environ. Manage.* **137**, 69-80 (2014)
16. C. K. Danny, K. Chun, W. Cheung, K. H. Keith, F. John, G. McKay, *Chemosphere* **54**, 273–281 (2004)
17. D. H. Lee, H. Moon, *Korean J. Chem. Eng.* **18**, 247–256 (2001)
18. E. Erdem, N. Karapinar, R. Donat, *J. Colloid Interf. Sci.* **280**(2), 309-314 (2004)
19. E. R. Nightingale, *J. Phys. Chem. C* **63** (1959)
20. S. Wang, Y. Peng, *Y. Chem. Eng.* **156**(1), 11-24 (2010)