International Journal of GEOMATE, Dec., 2020, Vol.19, Issue 76, pp. 69–75
ISSN: 2186-2982 (P), 2186-2990 (O), Japan, DOI: https://doi.org/10.21660/2020.76.9298
Special Issue on Science, Engineering and Environment

LEAD IMMOBILIZATION IN ARTIFICIAL CONTAMINATED SOIL USING SULFUR-IMPREGNATED CARBONACEOUS BAMBOO

*Takaaki Wajima

Department of Urban Environment Systems, Chiba University, Japan

*Corresponding Author, Received: 11 June 2019, Revised: 18 Sep. 2019, Accepted: 27 July 2020

ABSTRACT: A novel carbonaceous immobilizing agent for heavy metal contaminated soil was prepared from bamboo using sulfur immersion and pyrolysis, and the lead immobilization in artificial contaminated soils using sulfur-impregnated carbonaceous material was estimated. The bamboo was powdered, dried, and then immersed in 0.1 - 1 M K_2S solution for 0 - 24 h to prepare sulfur-immersed materials. The immersed-materials were heated at 400 ^oC for 1 h in nitrogen gas to produce the sulfur-impregnated carbonaceous material by pyrolysis. The abilities of the product to immobilize lead from aqueous solution were examined to obtain the products with high lead immobilization ability. With increasing K_2S concentration, the immobilization ability of the product for lead gradually increases and then above 0.75 M K_2S those are almost constant, while 15 min is sufficient for the immersed time to obtain the product with high lead immobilization ability. The product prepared from material immersed in more than 0.75 M K_2S solution for more than 15 min has a maximum immobilization ability for lead ion of 2.78 mg/g. The lead immobilization using the sulfur-impregnated product is sustainable due to the formation of leadhillite [$Pb_4SO_4(CO_3)_2(OH)_2$] and shannonite [$PbCO_3 \cdot PbO$]. The product can immobilize lead ion in various artificial lead-contaminated soils. By mixing artificial lead-contaminated soil with the sulfur-impregnated product, the eluted solution became neutral, and the eluted concentrations of lead ion dropped below the Japanese elution standard for soil.

Keywords: Sulfur-impregnation, Lead immobilization, Bamboo, Artificial contaminated soil, Pyrolysis

1. INTRODUCTION

Soil contamination with heavy metals is a worldwide problem. Accumulation of heavy metals in soils affect soil ecology, agricultural productivity, quality of agricultural products, water resources, and serious health problems for human and animal [1]. In the United States, for example, approximately 63% of the sites on the National Priority List (NPL) for the treatment of contaminated soils are contaminated by metals, and lead is the most common metal, found at 15% of the sites. In Japan, according to a report by the Ministry of Environment, 43% of the contaminated sites that exceed the environmental quality standards are contaminated by lead compounds. Soil contamination by lead compounds is also prevalent in other developed and developing countries where lead compounds are used extensively in industrial activities without careful contamination management.

Lead is a ubiquitous heavy metal pollutant in soils due to their wide use. The primary sources of Pb contamination include industrial activities such as mining, smelting of metals, and the use of Pb-containing products such as paints, lead-acid batteries, bullets, gasoline and pesticides [2]. It can damage human nervous (especially children) and reproductive systems [3]. The high concentration of Pb in the soil poses risks to human and animal health by the leaching of metals from the soil into water and the consumption of edible plants growth in the contaminated soil. Therefore, proper remediation is necessary to reduce metal availability in soil for protecting human health.

Among available remediation technologies, in situ immobilization of heavy metals using a chemical amendment can be a cost-effective and environmentally sustainable remediation approach for the immobilization of heavy metals by reducing the mobility and availability. This immobilization technique may provide a long-term remediation solution if low solubility minerals and/or stable precipitates are produced in situ [4]. Therefore, the choice of the soil amendments need that the amendments must reduce heavy metals transfers from contaminated soils to the surface water or groundwater and uptake by plants and organism. The most common agents for lead immobilization are phosphate-based compounds [5-7]. Although these studies have successfully demonstrated that phosphates effectively immobilize lead in various contaminated soils, there are several concerns about the use of phosphate as agents for lead immobilization. First, from an environmental protection point of view, excessive supplied phosphate can lead to eutrophication in the natural environment. Second, from a resource conservation point of view, phosphate is becoming a precious element, especially in countries such as Japan that import a major portion of their phosphate requirements. For these reasons, research on other types of lead immobilization agents is needed. Soil amendments, lime [8], calcium carbonate [9], red-mud [10], fly ash [11] and so on, may decrease leachable concentrations of contaminants and thus reduce the detrimental effects of heavy metals on environmental receptors, such as microorganisms, plants, animals, water and humans [12].

In previous studies, sulfur-impregnated adsorbents with high removal abilities for heavy metals were prepared from paper sludge, cedar bark and rice husk using K_2S solution [13-15]. According to the Pearson theory, sulfur, as a soft base, should interact with heavy metals such as Zn^{2+}, Pb^{2+}, Cd^{2+} and Ni^{2+} (soft acids) rather than with oxygen (a hard base) in the activated carbon. From these results, it would be possible to produce a low-cost agent to immobilize the metal ions in contaminated soils from agricultural waste.

Bamboo is a renewable bioresource and abundantly found in different geographic areas of the world. Bamboos, fast-growing plants, are natural composite materials useful in construction, textile industry and so on. Large quantities of bamboo waste are generated every year, which could be a biomass feedstock for char production due to its high fraction of lignocelluloses [16]. Bamboo charcoal is one of the promising adsorbents enriched with microporous structure and higher surface area. The surface area of bamboo charcoal is generally 3-10 times higher than compared to the world charcoal. The surface porous structure and heterogeneity of charcoal materials can be improved by modification process which has significant effects on adsorption performance. The physical and chemical modification of bamboo charcoal can enhance its affinity to adsorbate ions which is evidenced by earlier studies [17]. Recently, very few studies have been conducted for adsorption of heavy metals using bamboo charcoal [18,19].

From these background, in this study, we attempted to prepare the lead immobilization agent from bamboo using sulfur-impregnation, and lead immobilization ability of the sulfur-impregnated product was estimated using artificial lead-contaminated soils.

2. MATERIALS AND METHODS

2.1 Raw Sample

Bamboo, which was collected from a forest area in Chiba prefecture, Japan, first pulverize under 3 mm length, then washed with distilled water, and dried and stored for use. Properties of bamboo sample are shown in Table 1, which was analyzed using JIS M8812, and mineralogical composition of bamboo is shown in Fig. 1, which indicates that bamboo mainly composed of cellulose. All reagents were purchased from Wako Chemical Co., Japan at analytical grade.

Table 1 Properties of bamboo sample

Moisture	Ash	Fixed carbon and Volatile matter		
		C	H	N
11%	2%	44.9%	5.4%	0.2%

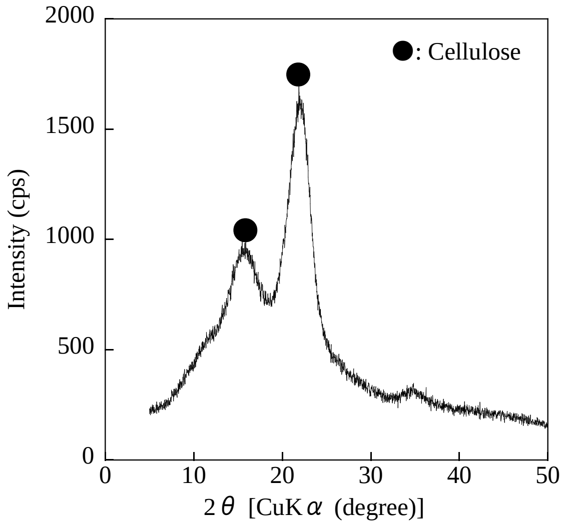


Fig.1 XRD patterns of bamboo

2.2 Sulfur Impregnation

20 g of sample was immersed in 200 mL of 0.1 - 1 M K_2S solution for 0 - 24 h, then filtered and dried in a drying oven overnight to obtain sulfur-immersed samples. These samples were pyrolyzed using a horizontal reactor. Sulfur-immersed samples were put in a ceramic board, and installed in a transparent quartz tube of 0.45 mm inside diameter and 1 m in length. Before pyrolysis, N_2 gas was injected into the tube for 30 min at a rate of 1.0 L/min to replace the air in the tube. The board was heated in an electric furnace at 400 ºC for 1 h, with a continuous flow of N_2 gas at a rate of 1.0 L/min. After heating, the solid was cooled to room temperature with a steady N_2 gas flow (1.0 L/min) in the tube, then washed with distilled water and dried in drying oven overnight to obtain the sulfur-impregnated material.

The abilities of the material for immobilization of lead ion from aqueous solution were examined as follows. 0.1 g of the sample was added to 10 mL of $Pb(NO_3)_2$ solution with 10 mM in 50 mL centrifuged tube and was shaken in a reciprocal shaker for 24 h. After shaking, the slurry was centrifuged, and the pH of the supernatant and the concentration of Pb^{2+} in the supernatant were measured by pH meter (D-53, Horiba) and atomic absorption spectrophotometer (AAS) (AAnalyst200, PerkinElmer), respectively. The immobilization ratios of Pb^{2+} were calculated using the following equation:

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

Here, R = Immobilization ratio of Pb^{2+} (%), C_0 = Initial concentration of Pb^{2+} in the solution (mg/L), and C_e = Measure concentration of Pb^{2+} in the solution (mg/L).

After lead immobilization, each sample (1.0 g) was added into 10 mL of distilled water in 50 mL of centrifuged tube, and tube was shaken for 6 h. After shaking, the slurry was centrifuged, and the concentration of Pb^{2+} in the supernatant was measured by AAS to calculate the elution of lead

The samples were analyzed by powder X-ray Diffraction (XRD) with monochrome CuKα radiation (Ultima IV, Rigaku).

2.3 Lead Immobilization

Four soil samples, Akadama soil (Emata), Kanuma soil (Emata), black soil (Emata), and river sand (Heiwa), were used to prepare artificially lead-contaminated soils. Lead-contaminated soil was artificially prepared by mixing 30 g of soil sample and 300 mL of 1000 mg-Pb/L aqueous solution (provided by $Pb(NO_3)_2$) using a rotary stirrer for 6 h. After mixing, the mixture stands at room temperature for 7 days, and then filtrate. The concentration of Pb^{2+} in the filtrate was measured by AAS to calculate the content of lead in artificially contaminated soils. The solid was dried in air for 7 days to obtain artificially contaminated soil.

1 g of artificially contaminated soil without or with 0.01 – 0.1 g of sulfur-impregnated product was added into 50 mL of a conical flask, and 10 mL of distilled water was then poured. The flask was shaken with shaking incubator at 50 °C for 6 h, and then filtrate. The pH of the filtrate was measured by pH meter, and the eluted concentration of Pb^{2+} in the filtrate is measured by AAS.

3. RESULTS AND DISCUSSION

3.1 Lead Immobilization of Sulfur-Impregnated Product

Figure 2 shows the lead immobilization of the product from bamboo via pyrolysis of the bamboo immersed in 0.5 mol/L K_2S solution for various times, and pH of the solution after lead immobilization. With increasing immersion time, lead immobilization of the product rapidly increases, and then be almost constant (about 55%) after 15 min. It is noted that pH of the solution is almost 5.2 after addition of the product.

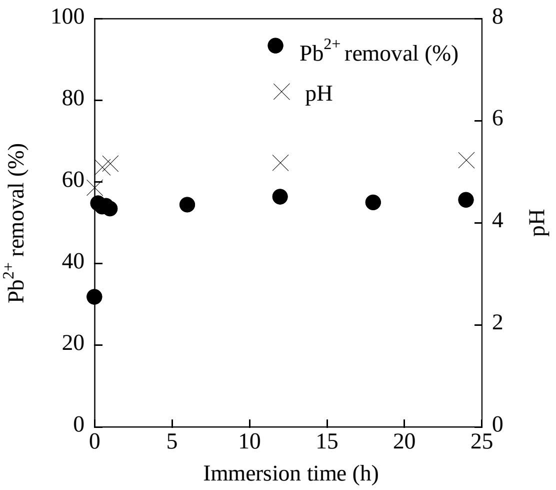


Fig.2 Lead immobilization of the product from bamboo via pyrolysis of the bamboo immersed in 0.5 mol/L K_2S solution for various times, and pH of the solution after lead immobilization

Figure 3 shows the lead immobilization of the product from bamboo via pyrolysis of the bamboo immersed in K_2S solution with various concentrations, and pH of the solution after lead immobilization. With increasing K_2S concertation to 0.75 mol/L, lead immobilization of the product increases, and be almost constant (approximately 80%) above 0.75 mol/L K_2S solution, which is more than 2 times higher than the product without sulfur-impregnation. It is noted that pH of the solution after lead immobilization of the product with sulfur-impregnation is 5.0 - 5.5, which is higher than that without sulfur-impregnation (4.8).

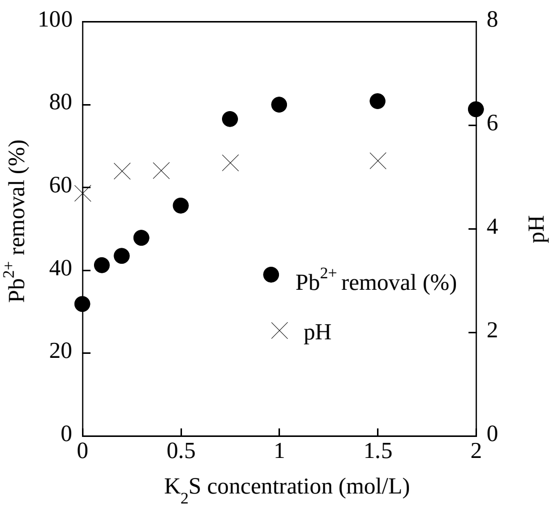


Fig.3 Lead immobilization of the product from bamboo via pyrolysis of the bamboo immersed in K_2S solution with various concentrations, and pH of the solution after lead immobilization

Figure 4 shows the XRD patterns of (a) immersed bamboo and (b) the products from bamboo via pyrolysis of the bamboo immersed in 0.5 mol/L K_2S solution for various times, and Figure 5 shows the XRD patterns of (a) immersed bamboo and (b) the products from bamboo via pyrolysis of the bamboo immersed in K_2S solution with various concentrations. Regardless of the immersed conditions, the bamboo after K_2S immersion have cellulose peaks, which is almost same as raw bamboo (Fig. 4 (a), Fig. 5 (a)). After pyrolysis, the pyrolyzed bamboo products have amorphous structure (Fig. 4 (b), Fig. 5 (b)).

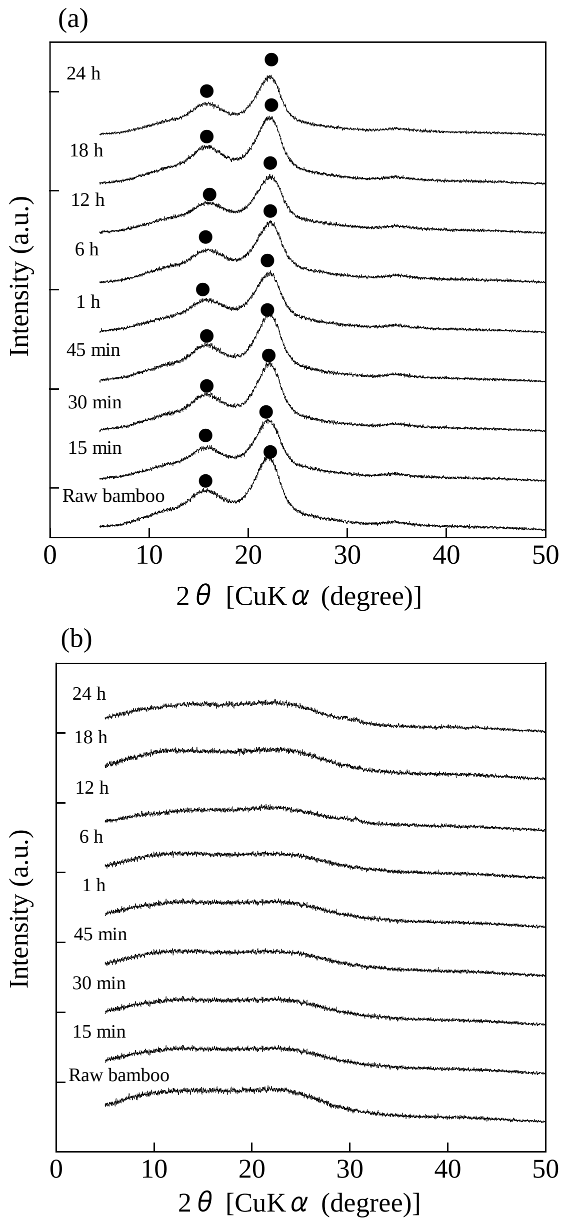


Fig. 4 XRD patterns of (a) immersed bamboo and (b) the products from bamboo via pyrolysis of the bamboo immersed in 0.5 mol/L K_2S solution for various times

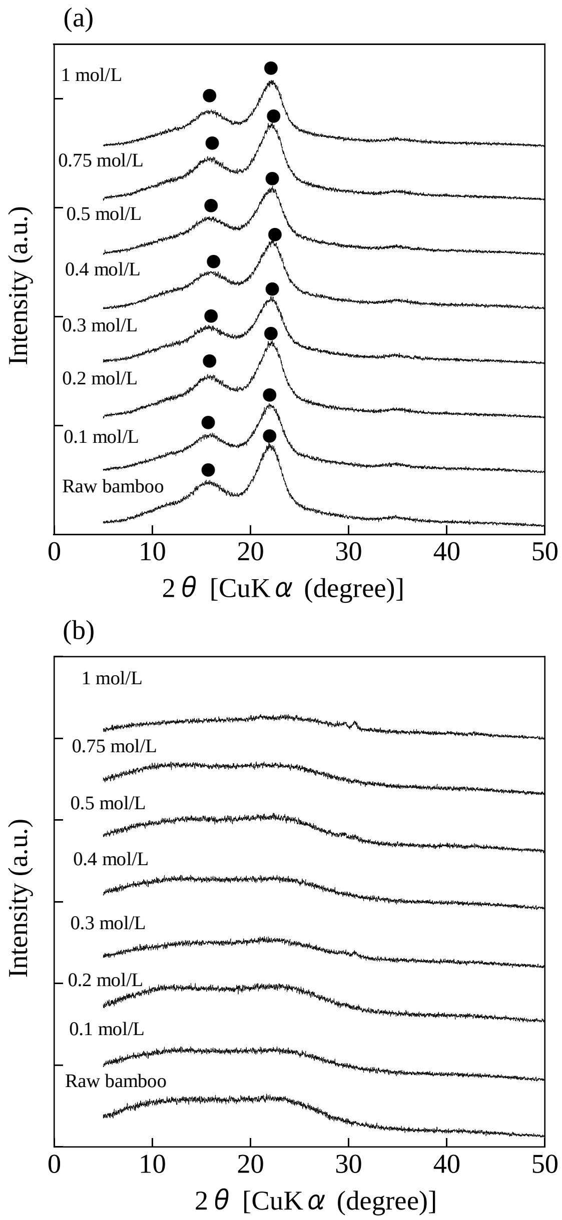
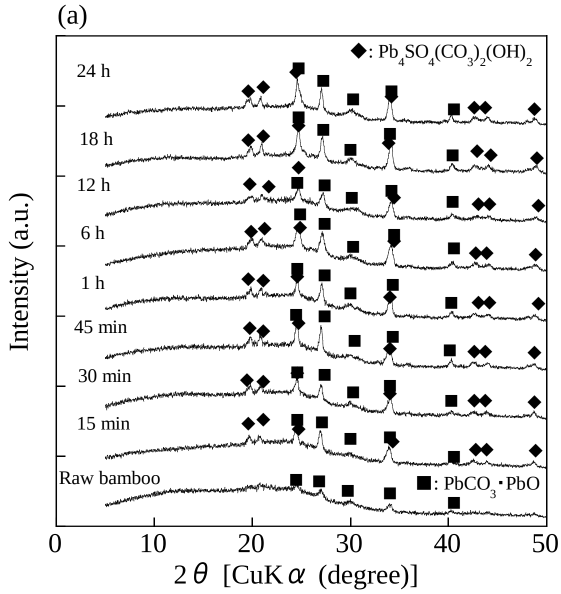


Fig. 5 XRD patterns of (a) immersed bamboo and (b) the products from bamboo via pyrolysis of the bamboo immersed in K_2S solution with various concentrations

Figure 6 shows the XRD patterns of the products after lead immobilization test using (a) the products from bamboo via pyrolysis of the bamboo immersed in 0.5 mol/L K_2S solution for various times and (b) the products from bamboo via pyrolysis of the bamboo immersed in K_2S solution with various concentrations. After lead immobilization test, while shannonite [$PbCO_3 \cdot PbO$] appears in the product without sulfur-impregnation, shannonite and leadhillite [$Pb_4SO_4(CO_3)_2(OH)_2$] appear in the product with sulfur-impregnation, which means that sulfur-impregnated product has higher lead removal ability than the product without sulfur-impregnation, due to the formation of leadhillite by sulfur content in the product.



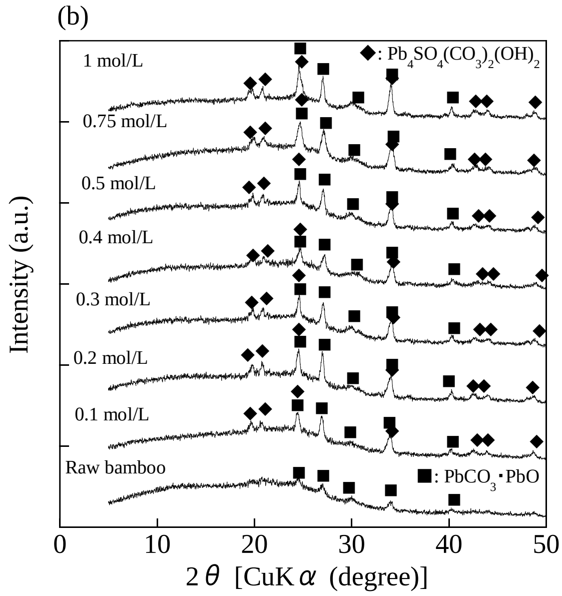


Fig. 6 XRD patterns of the products after lead immobilization test using (a) the products from bamboo via pyrolysis of the bamboo immersed in 0.5 mol/L K_2S solution for various times and (b) the products from bamboo via pyrolysis of the bamboo immersed in K_2S solution with various concentrations

From these results, lead immobilization agent can be prepared from bamboo via pyrolysis of the bamboo immersed in higher than 0.75 mol/L K_2S solution for more than 15 min, indicating a maximum immobilization ability for lead ion of 2.78 mg/g.

Figure 7 shows the lead elution from the products from bamboo via pyrolysis of the bamboo immersed in K_2S solution with various concentrations. Lead elution from the product without sulfur impregnation is 35%, while that of the product with sulfur-impregnation is zero, which means that the sulfur-impregnated product can strongly immobilize lead in the product.

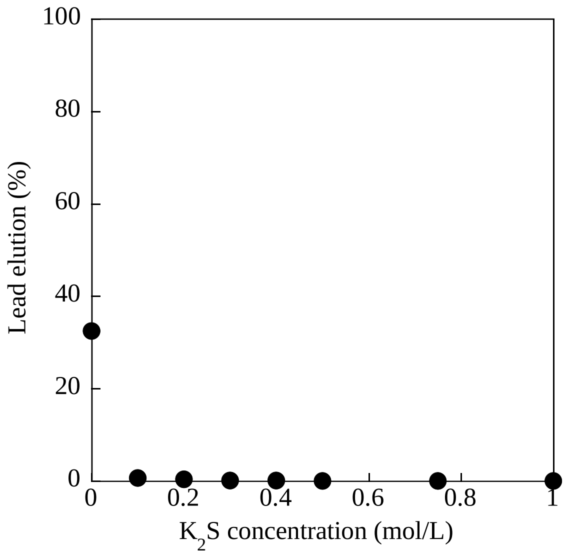


Fig. 7 Lead elution from the products from bamboo via pyrolysis of the bamboo immersed in K_2S solution with various concentrations

3.2 Lead Immobilization

The lead immobilization of the obtained product was examined using artificial contaminated soils. It is noted that the lead content of artificial contaminated soils used in this experiment is black soil (9799 mg/kg) > akadama soil (8347 mg/kg) > kanuma soil (6969 mg/kg) > river sand (4185 mg/kg).

Figure 8 shows the pH of the solution and the eluted lead concentrations after elution test using artificial contaminated soils with addition of sulfur-impregnated product. Without addition of the product, pH of the solution is weak acidic (pH 4-6), and with increasing addition of the product, pH of the solution increased. With addition of 0.1 g product, pHs of the solution using akadama soil, kanuma soil, and black soil are neutral, while that using river sand is weak alkaline. It is considered that the product is alkaline material and three soils have pH buffering ability.

Without addition of the product, high concentrations of lead were eluted from kanuma soil (85.5 mg/L) and akadama soil (63.5 mg/L), while elution from black soil (1.0 mg/L) and river sand (1.1 mg/L) are low. With increasing addition of the product, the lead elution decreases, and with addition of 0.1 g product, the lead elution from all samples are not detected using AAS. It is noted that Japanese standard of soil elution is less than 0.01 mg/L. It would be considered that the product can immobilized lead ion in various soil.

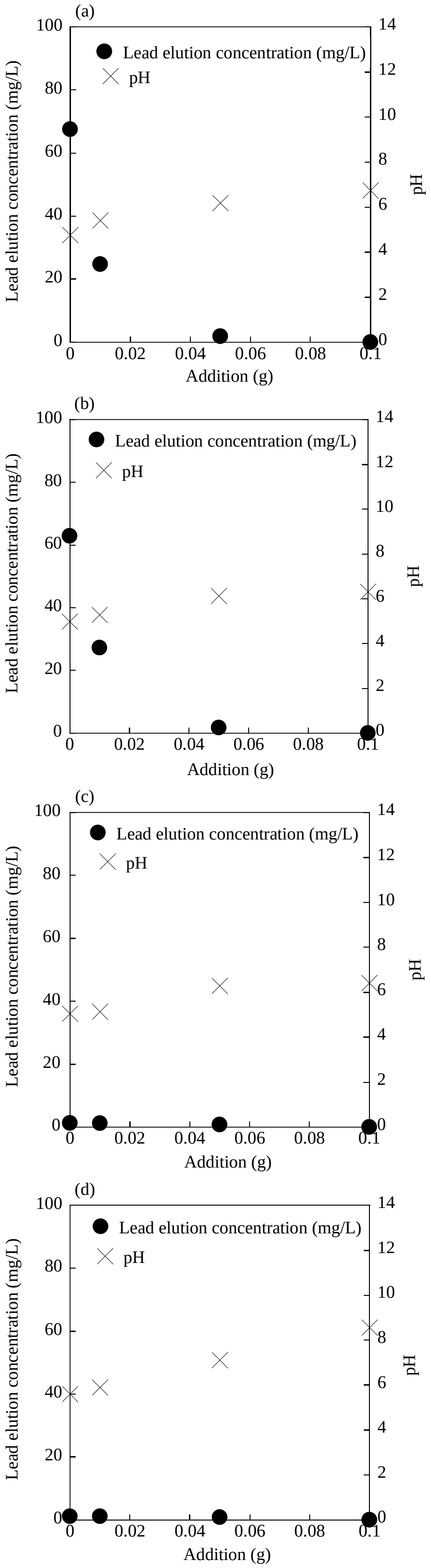


Fig. 8 The pH of the solution and the eluted lead concentrations after elution test using artificial contaminated soils with addition of sulfur-impregnated product: (a) Akadama soil, (b) Kanuma soil, (c) Black soil, and (d) River sand

From these results, it would be possible that, by mixing lead-contaminated soil with sulfur-impregnated product, the eluted solution becomes neutral and the concentration of lead drops below the Japanese eluted standard for soil.

4. CONCLUSION

A novel carbonaceous immobilizing agent for heavy metal contaminated soil can be prepared from rice straw using sulfur immersion and pyrolysis, and can immobilize lead ion in various artificial lead-contaminated soils. Lead immobilization agent with a maximum immobilization ability for lead ion of 2.78 mg/g can be prepared from bamboo via pyrolysis of the bamboo immersed in higher than 0.75 mol/L K_2S solution for more than 15 min, due to the formation of leadhillite by sulfur content in the product. By mixing four types artifical lead-contaminated soil with sulfur-impregnated product, the eluted solution becomes neutral and the lead elution drops below the Japanese eluted standard for soil.

5. ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grant Number 16K00609.

6. REFERENCES

[1] Raicevic S., Kaludjerovic-Radoicic T. and Zouboulis A.I., In situ Stabilization of Toxic Metals in Polluted Soils using Phosphates: Theoretical Prediction and Experiment Verification, J. Hazard. Mater., Vol. B117, 2005, pp.41-53.

[2] Cao X.D., Wahbi A., Ma L.N., Li B. and Yang Y.L., Immobilization of Zn, Cu, and Pb in Contaminated Soils using Phosphate Rock and Phosphoric Acid, J. Hazard. Mater., Vol. 164, 2009, pp.555-564.

[3] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile for Lead, Atlanta, 2007.

[4] Vangronsveld J. and Cunningham S.D., Introduction to the concepts. In Metal Contaminated Soils: in situ Inactivation and Phytorestoration, New York: Springer, 1998. pp.1–15.

[5] Cui Y.S., Du X., Weng L.P. and Riemsdijk W.H., Assessment of in situ Immobilization of Lead (Pb) and Arsenic (As) in Contaminated Soils with Phosphate and Iron: Solubility and Bioaccessibility, Water Air Soil Pollut., Vol. 213, 2010, pp.1-4.

[6] Munksgaard N., Lottermoser B.G. and Blake K., Prolonged Testing of Metal Mobility in Mining-Impacted Soils Amended with Phosphate Fertilisers, Water Air Soil Pollut., Vol. 223, 2011,

pp.2237-2255.
[7] Mignardi S., Corami A. and Ferrini V., Evaluation of the Effectiveness of Phosphate Treatment for the Remediation of Mine Waste Soils Contaminated with Cd, Cu, Pb, and Zn, Chemosphere, Vol. 86, 2012, pp.354-360.
[8] Gray C.W., Dunham S.J., Dennis P.G., Zhao F.J. and McGrath S.P., Field Evaluation of in situ Remediation of a Heavy Metal Contaminated Soil using Lime and Red-mud, J. Environ. Pollut., Vol. 142, 2006, pp.530–539.
[9] Wang Y.M., Chen T.C., Yeh K.J. and Shue M.F., Stabilization of an Elevated Heavy Metal Contaminated Site, J. Hazard. Mater., Vol. 88, 2001, pp.63-74.
[10] Lee S.H., Lee J.S., Choi Y.J. and Kim J.G., In situ Stabilization of Cadmium-, Lead-, and Zinc-Contaminated Soil using Various Amendments, Chemosphere, Vol. 77, 2009, pp.1069-1075.
[11] David H., Jonathan P. and Philippe S., Heavy Metal Immobilization by Cost-Effective Amendments in a Contaminated Soil: Effects on Metal Leaching and Phytoavailability, J. Geochem. Explor., Vol. 123, 2012, pp.87–94.
[12] Lombi E., Zhao F.J., Zhang G., Sun B., Fitz W., Zhang H. and McGrath S.P., In situ Fixation of Metals in Soils using Bauxite Residue: Chemical Assessment, J. Environ. Pollut., Vol. 118, 2002, pp.435-443.
[13] Wajima T., Preparation of Carbonaceous Heavy Metal Adsorbent from Cedar Bark using Sulfur-Impregnation, Int. J. Chem. Eng. Appl., Vol. 18, 2017, pp.272-276.
[14] Wajima T., A New Carbonaceous Adsorbent for Heavy Metal Removal from Aqueous Solution prepared from Paper Sludge by Sulfur-Impregnation and Pyrolysis, Process Saf. Environ. Prot., Vol. 112, 2017, pp.342-352.
[15] Wajima T., Preparation of Sulfur-Impregnated Carbonaceous Adsorbent from Rice Husk for Heavy Metal Removal from Aqueous Solution, Int. J. Environ. Sci. Dev., Vol. 9, 2018, pp.38-42.
[16] Shen S., Nges I.A., Yun J. and Liu J., Pre-treatments for Enhanced Biochemical Methane Potential of Bamboo Waste, Chem. Eng. J., Vol. 240, 2014, pp.253-259.
[17] Fan Y., Wang B., Yuan S., Wu X., Chen J. and Wang L., Adsorptive Removal of Chloramphenicol from Wastewater by NaOH Modified Bamboo Charcoal, Bioresour. Technol., Vol. 101, 2010, pp.7661-7664.
[18] Wang F.Y., Wang H. and Ma J.W., Adsorption of Cadmium (II) Ions from Aqueous Solution by a New Low-Cost Adsorbent Bamboo Charcoal, J. Hazard. Mater., Vol. 177, 2010, pp.300-306.
[19] Tan Z., Niu G. and Chen X., Removal of Elemental Mercury by Modified Bamboo Carbon, Chin. J. Chem. Eng., Vol. 23, 2015, pp.1875-1880.