Research Article

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Study of the remediation effects of passivation materials on Pb-contaminated soil

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Abstract: The passivation effects of blast furnace slag, fly ash, corncob biochar, and phosphate fertilizer in Pb-contaminated soil was evaluated against the soil pH, available Pb content, Pb fractions, and bioactivity coefficient. Blast furnace slag and fly ash could increase soil pH, while corncob biochar and phosphate fertilizers lowered soil pH. The available Pb content in the blast furnace slag and phosphate fertilizer treatment groups was significantly lower than in other treatments. Also, blast furnace slag and phosphate fertilizer could significantly convert nonresidual Pb into residual Pb. Combined with the environmental impact after application and cost of the material, it is recommended that blast furnace slag can be used as a passivation agent for low-concentration Pb-contaminated soil.

Keywords: Pb-contaminated soil, blast furnace slag, phosphate fertilizer, passivation rate, biological activity coefficient

1 Introduction

The passivation of trace element-contaminated soils is becoming a commonly used soil remediation technique used to reduce element mobility in soils by adding immobilizing agents (amendments). Currently, there are

many passivation materials used for the chemical remediation of Pb-contaminated soil. The passivation mechanisms mainly include precipitation, adsorption, ion exchange, and surface complexation [1,2]. A passivation material should be able to effectively remedy contaminated soil and, at the same time, be low cost and high accessible for it to be used for the massive remediation of contaminated soil [3,4]. Both blast furnace slag and fly ash are industrial by-products, which are large in output and low in the utilization rate in China. Blast furnace slag, the by-product of iron smelting, has good activity and adsorption due to its structural features [5].

It has been proven that blast furnace slag performs excellently at adsorbing in wastewater [6]. Also, blast furnace slag can significantly reduce the leachabilities of Ni and Mn when used to remediate heavy metal-contaminated soil [5]. However, little research has been conducted on the application of blast furnace slag for the remediation of agricultural soil contaminated by Pb.

Fly ash mainly comes from coal-fired power plants. There are many studies carried out on the ability of fly ash to adsorb metallic ions on liquid and solid surfaces [7]. Fly ash is regarded as a potentially effective soil remediation additive [8,9]. Biochar is another low-cost soil amendment having good passivation capabilities for heavy metal due to its environmental stability and porous structure. Biochar, composed of various waste biomass, is not only economical but also adsorbs heavy metals and organic pollutants well [10,11].

In addition to the aforementioned industrial waste or bio-products, phosphorus has also been increasingly used for the *in situ* remediation of Pb-contaminated soil because of its low cost and special effect on Pb contamination. Juhasz et al. proved that phosphate could reduce the bioavailability of Pb in soil in *in vitro* experiment [12]. Murtaza et al. used five kinds of phosphate fertilizers to remedy sewage-irrigated soil and found that the bioavailability of heavy metal in soil was effectively reduced by different amounts of phosphate fertilizer [13].

There are many methods to evaluate the remediation effects of passivation materials on heavy metal-contaminated soil. The effectiveness and the cost of remediation are the most important two indicators for assessing these

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methods. This study analyzed the available Pb content in soil and the transformation of Pb fractions using diethylene triamine pentaacetic acid (DTPA) extraction or Community Bureau of Reference (BCR) sequential extraction, followed by evaluation of the remediation effect according to the passivation rate and biological activity coefficient. The passivation rate can show the passivation capacity of the passivation material. The biological activity of heavy metal, which has the closest correlation with human beings and other living creatures, can be described with the biological activity coefficient.

There have been few reports on the application of blast furnace slag, fly ash, corncob biochar, or phosphate fertilizer for the remediation of Pb-contaminated soil. The objectives of this study are to demonstrate the feasibility of the aforementioned amendments and to select the most economical and effective passivation material. Thus, through soil culture experiments, this article compared the performances of blast furnace slag, fly ash, corncob biochar, and phosphate fertilizer in remedying Pb-contaminated soil by determination of pH of soil, the DTPA-extracted Pb content, and the change of Pb fractions. The remediation effects of the four passivation materials were compared based on their passivation rates and biological activity coefficients of Pb. The practical way and passivation material for low concentration Pb-contaminated soil remediation were proposed. The results of this article can provide practical methods and scientific basis for the remediation of Pb-contaminated soil.

2 Materials and methods

2.1 Experimental materials

The test soil was obtained from the surface (0–20 cm) of farmland in the suburb of Baoding City, Hebei Province. The basic properties of the test soil are listed in Table 1.

The corncobs were collected from the cafeteria of Hebei University; the phosphate fertilizer (Sinochem,

Table 2: The contents of heavy metals in passivation materials

Contents (mg/kg)	Cd	As	Pb	Cr	Ni
Blast furnace slag	0.18	1.42	1.84	15.61	21.77
Fly ash	0.19	14.59	8.45	14.52	30.64

China) whose main ingredient is superphosphate ($P_2O_5 \geq 12\%$) was purchased in the market. The blast furnace slag and fly ash for the test were provided by Yanxing Mineral Products Trading Co. Ltd. The contents of heavy metals in blast furnace slag and fly ash are presented in Table 2.

The blast furnace slag was washed with deionized water and then dried to constant weight at 105°C and then ground to 150 µm by a pulverizer.

The corncobs were washed with deionized water and then dried for 2 h at 30°C. The dried corncobs were cut into pieces with ceramic scissors and fired at 600°C for 2 h in a muffle furnace. After cooling, they were ground to 150 µm and then made into corncob biochar.

2.2 Experimental apparatus

Pb in soil was determined using A Model TAS 990super flame atomic absorption spectrometer (Beijing Puxi General Instrument Co., Ltd). A benchtop digital pH meter (Mettler Toledo Co., Ltd) was used throughout the analysis.

2.3 Experimental methods

$Pb(NO_3)_2$ (400 mg/kg (Pb in soil)) was added to the soil to simulate Pb contamination. The four passivation materials, namely, blast furnace slag, fly ash, corncob biochar, and phosphate fertilizer, were mixed (5%) with 1 kg Pb-contaminated soil in flowerpots. A control soil to which no passivation material was added was also prepared. Each treatment group had three replicates. The flowerpots were placed in a greenhouse at 25°C, and the

Table 1: Physical and chemical properties of the original soil

pH	Organic matter (g/kg)	Total nitrogen (g/kg)	Total phosphorus (g/kg)	Cation exchange capacity (cmol/kg)	Total Pb (mg/kg)
8.53	15.32	8.43	2.62	132.34	29.67

soil moisture was maintained at 60%. Soil samples were collected on the 10th, 20th, 30th, 45th, and 60th day.

2.4 Determination methods and statistical analysis

The pH of the soil was determined by using a pH meter with a water–soil ratio of 2.5:1. The Pb content of the soil was determined by the DTPA extraction method [14]. The fractions of Pb in the soil were determined through BCR sequential extraction, a method proposed by the Institute for Reference Materials and Measurements [15].

The passivation rate of material was calculated using the following equation:

$$\eta = \frac{C_0 - C_i}{C_0} \times 100 \quad (1)$$

where η is the passivation rate of passivation material (%), C_0 is the soil DTPA-extracted Pb content before passivation (mg/kg), and C_i is the soil DTPA-extracted Pb content after passivation (mg/kg).

The biological activity coefficient of soil Pb was calculated by the following equation [16]:

$$K = \frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4} \quad (2)$$

where K denotes the biological activity coefficient of soil Pb. F_1 , F_2 , F_3 , and F_4 are the contents of acid soluble, reducible, oxidizable, and residual Pb in soil (mg/kg), respectively.

The statistical software SPSS 19.0 was used to analyze the test data. LSD was used to determine whether there were significant differences among the treatment groups ($p < 0.05$). Origin 9.1 was used for plotting.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Impact of passivation materials on soil pH

The impacts of blast furnace slag, fly ash, corn cob biochar, and phosphate fertilizer on the soil pH are shown in Figure 1. The soil pH varied according to the

Figure 1: Variation of soil pH after addition of different passivation materials.

passivation materials. The pH significantly increased after adding blast furnace slag and fly ash ($p < 0.05$), which were 0.31–0.52 and 0.22–0.45 higher than the control group, respectively. The pH of soil decreased significantly after adding corn cob biochar and phosphate fertilizer ($p < 0.05$), which were 0.14–0.38 and 1.17–1.44 lower than the control, respectively.

The pH of blast furnace slag and fly ash is 10.21 and 9.04, respectively. Their high alkalinity is the main reason for the increase in soil pH. The soil pH decreased after the addition of corn cob biochar even though the corn cob biochar is alkaline. The reason for this is that the biochar gradually releases ions like K^+ and Mg^{2+} while adsorbing H^+ in soil onto its surface, thereby leading to the decline of soil pH. The study by Huang et al., which is in agreement with our findings, showed that the pH of soil would decrease with the addition of superphosphate [17].

3.2 Impact of passivation materials on available Pb content

Figure 2 depicts the impact of blast furnace slag, fly ash, corn cob biochar, and phosphate fertilizer on the Pb content in soil. Compared with the control, the Pb content significantly decreased after addition of all four passivation materials to the Pb-contaminated soil. After 60 days, compared with the control, the Pb content of the soils treated with blast furnace slag, fly ash, corn cob biochar, and phosphate fertilizer decreased ($p < 0.05$) by 19.94%, 6.75%, 5.63%, and 54.93%, respectively. It indicates that the four passivation materials are able to reduce the Pb content in soil significantly although the available Pb contents in blast furnace slag and

Figure 2: Variation of available Pb contents in soil after addition of different passivation materials.

phosphate fertilizer treatments are much lower than those in fly ash and corncob biochar treatments.

The negative charges on the surface of blast furnace slag can adsorb positive ions through electrostatic attraction, and the slag also has pores on its surface, which are conducive to the adsorption of Pb. By this mechanism, the Pb content is reduced by blast furnace slag. It has been proven that fly ash can adsorb Pb ions better than Zn^{2+} , Cu^{2+} , and Cd^{2+} [18].

Alkaline fly ash leads to an increase in soil pH, which helps Pb ions to form precipitates. Fly ash causes pozzolanic reaction and forms precipitate (Pb_2SiO_4) with the Pb ions in soil, thereby effectively reducing the bioavailability of soil Pb. Furthermore, fly ash reduces the content of soil Pb due to its adsorption of Pb [19,20].

Biochar reduces the availability of Pb mainly through ion exchange, electrostatic adsorption, and precipitation, resulting in the remediation of heavy metal-contaminated soil [21]. Phosphate fertilizer reduces the biotoxicity of soil Pb by forming stable pyromorphite with Pb, and hence, the passivation of Pb is realized [22]. After adding different kinds of phosphate fertilizers into the soil contaminated by Pb and Cd, Kede et al. found that both the DTPA- and Toxicity Characteristic Leaching Procedure (TCLP)-extracted Pb contents of treatment groups were significantly lower than those of control [23].

3.3 Impact of passivation materials on distribution of Pb fractions

Figure 3 depicts the impact of blast furnace slag, fly ash, corncob biochar, and phosphate fertilizer on the Pb fractions. Pb-contaminated soil samples treated with the

four passivation materials all resulted in low Pb bioavailability over time. After 60 days, compared with the control, the acid-soluble Pb content of blast furnace slag, fly ash, corncob biochar, and phosphate fertilizer treatment groups was significantly reduced ($p < 0.05$) by 90.31%, 48.97%, 44.01%, and 80.73%, respectively. The reducible Pb content was significantly reduced ($p < 0.05$) by 98.56%, 16.88%, 12.2%, and 40.08%, respectively. The oxidizable Pb content of the blast furnace slag and corncob biochar treatment groups increased significantly ($p < 0.05$) by 43.35% and 43.33%, respectively, while the oxidizable Pb content of the fly ash treatment group decreased significantly ($p < 0.05$) by 52.23%. The oxidizable Pb content of the phosphate fertilizer treatment group decreased by 1.12%. The residual Pb content of the blast furnace slag and phosphate fertilizer treatment groups increased significantly ($p < 0.05$) by 11.18% and 26.17%, respectively, while the residual Pb content of fly ash and corncob biochar treatment groups decreased significantly ($p < 0.05$) by 9.65% and 26.59%, respectively.

The result showed that blast furnace slag, fly ash, corncob biochar, and phosphate fertilizer were able to reduce the bioavailability of soil Pb significantly. Of these passivation materials, blast furnace slag and phosphate fertilizer had better remediation effects than fly ash and corncob biochar. The soil Pb transformed from acid-soluble and reducible fractions into oxidizable and residual fractions after adding blast furnace slag, while after the addition of phosphate fertilizer, the soil Pb transformed from acid-soluble, reducible, and oxidizable to a residual fraction. The increase in soil pH after treatment with blast furnace slag and fly ash was conducive to the decrease in Pb bioavailability.

Blast furnace slag has a great ability to adsorb Pb due to its porous structure and silicate composition. Moreover, the calcium ions released during dissolution will allow other metal ions to adsorb on its surface. Furthermore, the alkaline environment results in the formation of precipitates, effectively removing metal ions from solution [24]. The formation of low-solubility Pb-phosphate precipitates leads to the transformation of Pb from nonresidual to residual, and accordingly, the residual Pb content in soil is increased [25].

3.4 Effectiveness evaluation of passivation materials

The passivation rates of the four test materials and their effects on the biological activity coefficients of Pb are

Figure 3: Comparison of the changes of Pb fractions in soil with different treatments. F_1 , F_2 , F_3 , and F_4 , respectively, indicates acid-soluble, reducible, oxidizable, and residual Pb in soil.

presented in Table 3. All four passivation materials had remediation effects on Pb-contaminated soil. The passivation rates of the four materials differed under the same conditions of pollution. The passivation rates of the materials used in the experiment decreased in the following order: phosphate fertilizer, blast furnace slag, fly ash, and corncob biochar. Evaluation of Pb biological activity after treatment with the passivation materials provided the following order from highest to lowest activity: blast furnace slag > phosphate fertilizer > fly ash > corncob biochar. Of the four test passivation materials, phosphate fertilizer was the most effective,

while blast furnace slag was most effective in inhibiting the biological activity of Pb.

Blast furnace slag is an industrial by-product, which is available in large amounts in China and is easy to obtain at low cost. The use of phosphate fertilizer may cause the migration of phosphorus, resulting in secondary pollution. Thus, blast furnace slag is the best passivation material for Pb-contaminated soil. Blast furnace slag is economical, effective, and environmental friendly. The use of blast furnace slag will help in reusing industrial waste and also reducing the harm it does to the environment.

Table 3: Passivation rates and biological activity coefficients during passivation process

Passivation materials	Passivation rates (%)					Biological activity coefficients				
	10 days	20 days	30 days	45 days	60 days	10 days	20 days	30 days	45 days	60 days
Blast furnace slag	6.45	4.28	7.68	15.62	19.94	0.22	0.18	0.15	0.06	0.04
Fly ash	3.89	1.62	4.46	5.17	6.75	0.60	0.63	0.56	0.63	0.50
Corn cob biochar	0.72	−2.47	6.01	5.29	5.63	0.63	0.60	0.56	0.56	0.53
Phosphate fertilizer	43.3	44.25	42.09	50.59	54.93	0.54	0.38	0.39	0.44	0.31

4 Conclusions

Blast furnace slag was the best passivation material under the experimental conditions of this study. The soil pH increased after blast furnace slag or fly ash was added to the Pb-contaminated soil precipitates. Although the soil pH decreased after adding corn cob biochar or phosphate fertilizer, the remediation effects of the two materials were not reduced. Blast furnace slag, fly ash, corn cob biochar, and phosphate fertilizer could all reduce the available Pb content in soil significantly. The blast furnace slag and phosphate fertilizer treatment groups had much better remediation performances than the fly ash and corn cob biochar treatment groups. Blast furnace slag and phosphate fertilizer could effectively promote Pb to transform from nonresidual fraction to residual one, thereby reducing the bioavailability of Pb resulting in the passivation of soil Pb. The passivation rates of the four materials in a descending order were phosphate fertilizer, blast furnace slag, fly ash, and corn cob biochar; and the abilities of the four materials in inhibiting the biological activity of Pb in an ascending order were blast furnace slag, phosphate fertilizer, fly ash, and corn cob biochar. We recommend that blast furnace slag can be used as a passivation material in the remediation of soil with low Pb concentrations as this will help the environment and can be performed at low cost.

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Conflict of interest: The authors declare no conflict of interest.

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