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Research Article

Immobilization of Lead from Pb-Contaminated Soil Amended with Peat Moss

Seul-Ji Lee,[1,2] Myoung-Eun Lee,[1,2] Jae Woo Chung,[1,2] Jin Hee Park,[3] Keun Young Huh,[2,4] and Gee-Ill Jun[1,2]

[1] *Department of Environmental Engineering, Gyeongnam National University of Science and Technology (GNTECH), Jinju 660-758, Republic of Korea*
[2] *Green Technology Institute, GNTECH, Jinju 660-758, Republic of Korea*
[3] *Centre for Mined Land Rehabilitation, The University of Queensland, St. Lucia, QLD 4072, Australia*
[4] *Department of Landscape Architecture, GNTECH, Jinju 660-758, Republic of Korea*

Correspondence should be addressed to Jae Woo Chung; jwchung@gntech.ac.kr

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Immobilization of lead (Pb) using soil amendments can reduce Pb toxicity and bioavailability in soil. This study evaluated Pb immobilization in a Pb-contaminated soil by using peat moss through various tests. The Pb-contaminated soil (2000 mg Pb·kg^{-1}) was amended with 1%, 5%, and 10% of peat moss to immobilize Pb in the soil. The immobilization properties of Pb in the contaminated soil were evaluated by a column leaching experiment, a microcosm test, and a batch incubation test. Peat moss significantly reduced the Pb leaching in all of the experiments and more effectively reduced mobility and toxicity of Pb in the column leaching and microcosm tests than bioavailability in the batch incubation test. The immobilized lead from the soils amended with 1%, 5%, and 10% of peat moss was 37.9%, 87.1%, and 95.4% from the column leaching test, 18.5%, 90.9%, and 96.4% from the microcosm test, and 2.0%, 36.9%, and 57.9% from the NH_4NO_3 extraction method, respectively, indicating that peat moss can be effectively used for the remediation of Pb-contaminated soil.

1. Introduction

Health authorities in many parts of the world have become increasingly concerned about the effects of heavy metals on the environment and human health and their potential implications to the international trade [1]. It is a global urgency to ensure that the heavy metal concentration of foodstuffs produced complies with the regulatory standards of other countries. Heavy metals released into the ecosystem accumulate in plants and animals and may finally result in potential health risk to humans [2, 3]. A major source of heavy metals in the human food chain is plants grown in contaminated soil. With greater public awareness of the effects of contaminated soil on the ecosystem and human health, the scientific community and regulatory agencies have shown increasing interest in the development of effective technologies to remediate contaminated sites.

Activities such as mining, smelting, and disposal of industrial wastes have contaminated soil and water resources with heavy metals such as Pb, Cd, and Zn in many parts of the world [4, 5]. The Pb-contaminated soil can give rise to serious problems. In humans, Pb exposure can lead to an acute and chronic toxicity depending on the level and duration of exposure, even though acute toxicity is actually a rare condition [6]. High levels of Pb exposure may cause problems in the synthesis of hemoglobin, compromise the kidneys, gastrointestinal tract, joints, and the reproductive system, and result in an acute or chronic damage to the nervous system [7, 8].

Various remediation technologies such as soil washing, soil flushing, electrokinetic process, phytoremediation, and stabilization/solidification have been used to reduce the adverse effects of heavy metal-contaminated soils [9]. Among these remediation technologies, physicochemical technologies, including separation and removal methods, often take a long time and consume a great deal of energy when trying to meet the cleanup goals. An economical and effective alternative is *in situ* immobilization by use of organic adsorbents, which can reduce human exposure to heavy metals. Organic soil amendment can improve the soil properties for plant growth by providing nutrients as well as immobilizing heavy metals [10]. Heavy metals can be immobilized by sorption and precipitation with soil amendments [11, 12]. It has been reported that bark, chitosan, zeolite, clay, fly ash, rice bran, and peat moss are some examples of low-cost adsorbents for heavy metal immobilization [13, 14]. Although organic adsorbents do not remove heavy metals from the soil, they can reduce the mobility and dispersion of heavy metals [15].

Peat moss is the partly carbonized remains of various mosses of the genus *Sphagnum*, yellowish-brown to brown and composed of more than 90% of organic matter. Peat moss helps the soil by providing organics and nutrients, preventing the soil from hardening, and improving the water holding capacity of the soil. In addition, it helps to mitigate excess salt accumulation and buffer pH, thereby providing effective reclamation of the soil [16, 17]. Peat mainly contains lignin and cellulose, which have polar functional groups, such as alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers. These functional groups can participate in chemical bonding, and therefore peat moss is regarded as an effective adsorbent for the removal of heavy metals [14].

This study evaluated Pb immobilization in a Pb-contaminated soil by using peat moss. Although there have been a number of studies about the application of peat moss for the removal of heavy metals in wastewater, only a limited number of studies on heavy metal immobilization in contaminated soils using peat moss have been presented [18, 19]. In this study, the effects of peat moss on the immobilization of Pb in the Pb-contaminated soil were investigated through various tests. A column leaching experiment was carried out to determine the leaching potential of Pb in a peat moss-amended Pb-contaminated soil; a microcosm test was conducted to evaluate heavy metal toxicity to plants and soil organisms; a batch incubation test was carried out to investigate the amount of bioavailable Pb after the Pb immobilization.

2. Materials and Methods

2.1. Soils Characterization and Preparation of Pb-Spiked Soil. A Pb-spiked soil was used in this study. The soil used for spiking was collected from an uncontaminated site. The soil texture was measured by particle size analysis (PSA) and classified according to the U.S. Department of Agriculture (USDA) criteria. The collected soil was air-dried, sieved to smaller than 2 mm using a 10-mesh sieve, and then stored in plastic bags. The soil sample was analyzed for physicochemical properties such as pH, electrical conductivity (EC), water holding capacity (WHC), organic matter (OM) content, cation exchange capacity (CEC), and total and NH_4NO_3-extractable Pb concentrations. Soil pH and EC were determined in a soil : water = 1 : 5 (w/v) suspension by using a pH-EC meter (P25, Istek, Korea). The soil maximum WHC was measured using the Grant method [20]. Soil OM content was determined by the loss-on-ignition method [21]. The CEC of the soil was determined by the 1 M NH_4OAc extraction method (soil : water = 1 : 10, pH = 7). For the total heavy metal content, 1.5 g of air-dried soil was weighed into a Teflon-coated graphite block digestion system (OD-98-002, Korea), and 7 mL of HNO_3 and 21 mL of HCl were added, and then, the mixture was shaken at 105°C for 2 hours. To measure the extractable Pb concentration, 5 g of the soil sample was extracted for 2 hours using 12.5 mL of 1 M NH_4NO_3 solution in a shaking incubator (KSI-200FL, KOENCON, Korea) [4].

Figure 1: Experimental apparatus of column leaching test.

The soil was spiked with Pb to a Pb concentration of 2000 $mg \cdot kg^{-1}$ using a $Pb(NO_3)_2$ solution. One kg of the soil was mixed with 1 L of 2000 $mg \cdot L^{-1}$ $Pb(NO_3)_2$ solution in a plastic bag. And then a drying and watering procedure with manual mixing was repeated three times. The Pb-spiked soil was amended with 1%, 5%, and 10% of peat moss and incubated for 14 days at 37°C. The soils were kept moist at 60% of WHC. The peat moss was purchased from Demetra (Russia), dried, and used without having been activated. The OM content of the peat moss was 93%, and the elements composition measured by an element analyzer (Flash 2000 series, Perkin Elmer, USA) consisted of 70% carbon, 6% hydrogen, 0.7% nitrogen, and 0.5% sulfur.

2.2. Leaching Experiments. Three types of leaching experiments such as column leaching test, microcosm test, and batch incubation test were conducted. The column leaching test was conducted using 50 mL polyethylene columns (3 cm in diameter and 7.5 cm in height). The columns were filled with 30 g of Pb-spiked soils amended with 1%, 5%, and 10% of peat moss, respectively. The columns were leached with 1 mM of $CaCl_2$ solution adjusted to pH 5.4 at a flow rate of 20 $mL \cdot h^{-1}$ using peristaltic pumps. The pH of the solution was adjusted to mimic the pH of acid rain. $CaCl_2$ concentration was set to 1 mM to prevent the blocking of soil pores by the dispersion of soil particles according to the leaching method of Schwab et al. [22]. Flow rate was determined from the properties of the soil placed in the column, which was optimized to prevent pending in the column. The columns were leached for 10 pore volumes, and leachate sample was collected per pore volume. Figure 1 shows the experimental apparatus used for the column test to evaluate Pb leaching potential in the peat moss-amended soil.

The microcosm test was conducted by using plastic pots. Plastic pots (600 mL capacity; 10 cm diameter) were filled with 300 g of Pb-spiked soil samples amended with 1%, 5%,

FIGURE 2: Experimental apparatus to collect pore water from microcosm test.

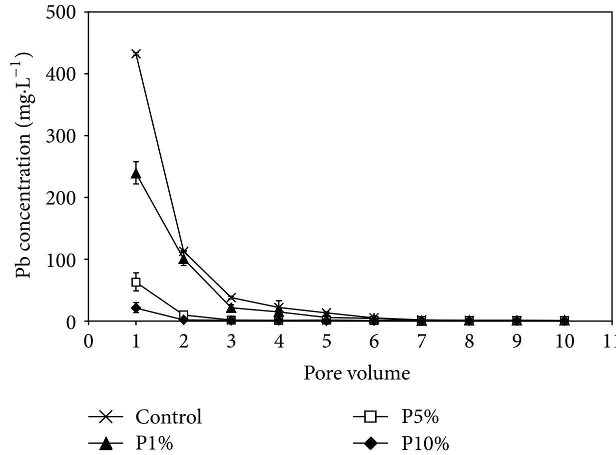

FIGURE 3: Pb concentration in the leachate from Pb-contaminated soils amended with peat moss through the column leaching experiment (control: Pb-contaminated soil without peat moss, P1%: Pb-contaminated soil with 1% peat moss, P5%: Pb-contaminated soil with 5% peat moss, and P10%: Pb-contaminated soil with 10% peat moss).

and 10% of peat moss, respectively. Rhizon samplers (Rhizosphere Research Products, Wageningen, Netherlands) were placed horizontally 2.5 cm from the bottoms of the pots, respectively. The pots were placed on plastic saucers to prevent leachate draining from the soils, and the test was carried out in a temperature-controlled greenhouse (25 ± 3°C; 12 hours light). Figure 2 shows the experimental setup for collecting pore water from the pot test. Soil moisture content was kept at 60% of WHC. The soil was allowed to equilibrate for 7 days, and then additional water was added from the saucer to compensate for the moisture loss due to evaporation. Pore water samples were collected, using the rhizon samplers every 7 days for 35 days after the pot experiment was set up, and used for analyzing Pb concentration.

A batch incubation test was conducted to evaluate the bioavailable Pb using the 1 M NH_4NO_3 extraction method, in which NH_4NO_3 has been used as an indicator of bioavailability and/or phytoavailability of heavy metals [23, 24]. Three grams of air-dried soil samples amended with 1%, 5%, and 10% of peat moss, respectively, were put into 50 mL tubes and extracted with 1 M NH_4NO_3 solution (soil : solution = 1 : 2.5) for 2 hours in a shaking incubator.

2.3. Analytical Methods. All experiments were carried out in triplicates, and the results were compared with those of the control soil, which used Pb-spiked soil without peat moss amendment. All the samples were filtered with a 0.45 μm filter (Advantec, Japan) before the analysis. Concentrations of metal ions were analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, 5300DV, Perkin Elmer, USA). The data in tables and figures are the average of triplicates, and the error bar indicates the standard deviation of the triplicates.

3. Results and Discussion

3.1. Soil Characterization. Various physicochemical properties of the soil were examined. The texture of the soil was loamy sand according to the United States Department of Agriculture (USDA) criteria containing sand more than 85%. The pH and EC of the soil were 4.97 and 0.035 $\mu S \cdot cm^{-1}$, respectively. The maximum WHC and OM content were 34% and 5.58%, respectively. The CEC of the soil was 6.49 $cmol \cdot kg^{-1}$. The concentrations of the total Pb, Cu, and Zn were negligible in the soil. The total and the NH_4NO_3-extractable Pb concentrations were 0.4 $mg \cdot kg^{-1}$ and 0.061 $mg \cdot kg^{-1}$, respectively.

3.2. Column Leaching Test. The Pb concentrations in the leachates eluted from the Pb-spiked soils amended with 1%, 5%, and 10% of peat moss and the control are compared according to the pore volume in Figure 3. The Pb concentration was reduced with increasing amount of amended peat moss. The Pb concentration in the first pore volume of the leachate was 432.3 $mg \cdot L^{-1}$ for the control and 239 $mg \cdot L^{-1}$, 62.5 $mg \cdot L^{-1}$, and 21.2 $mg \cdot L^{-1}$ for the 1%, 5%, and 10% peat moss-amended soils, respectively. The Pb concentration in the sixth pore volume was 5.2 $mg \cdot L^{-1}$ for the control and 4.5 $mg \cdot L^{-1}$, 0.9 $mg \cdot L^{-1}$, and 0.6 $mg \cdot L^{-1}$ for the 1%, 5%, and 10% peat moss-amended soils, respectively. Low Pb concentrations were detected after the seventh pore volume of all the peat moss-amended soils, which may be due to the sorption of Pb on humic fractions. Peat moss contains high contents of humic substances with the functional groups such as carboxyl, phenolic, and alcoholic, which are very effective in heavy metal sorption because they form chelating complexes [25, 26]. The sorption of heavy metal by organic mixtures such as peat moss occurs by surface complexation reaction [27].

Figure 4 shows the cumulative Pb concentrations leached from the column test for 10 pore volumes. The total leached Pb concentration for 10 pore volumes was 314.7 $mg \cdot kg^{-1}$ for the control, and those were 195.3 $mg \cdot kg^{-1}$, 40.7 $mg \cdot kg^{-1}$, and 14.5 $mg \cdot kg^{-1}$ for the 1%, 5%, and 10% peat moss-amended soils, respectively. The total leached Pb concentrations from soils amended with 1%, 5%, and 10% peat moss were 62.1%, 12.9%, and 4.6% of that from the control soil,

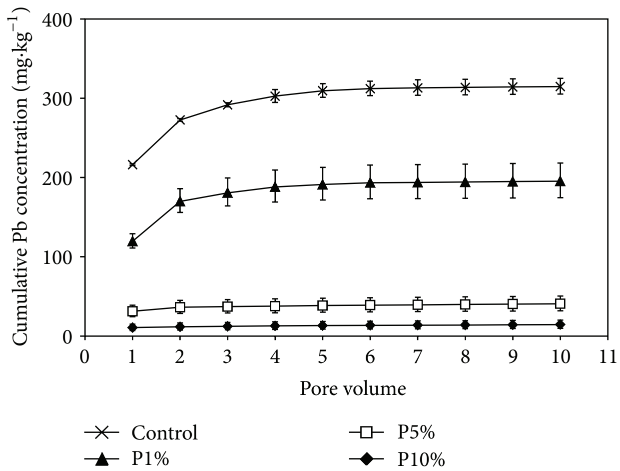

Figure 4: Cumulative curve of Pb concentration in the leachate from Pb-contaminated soils amended with peat moss through the column leaching experiment (control: Pb-contaminated soil without peat moss, P1%: Pb-contaminated soil with 1% peat moss, P5%: Pb-contaminated soil with 5% peat moss, and P10%: Pb-contaminated soil with 10% peat moss).

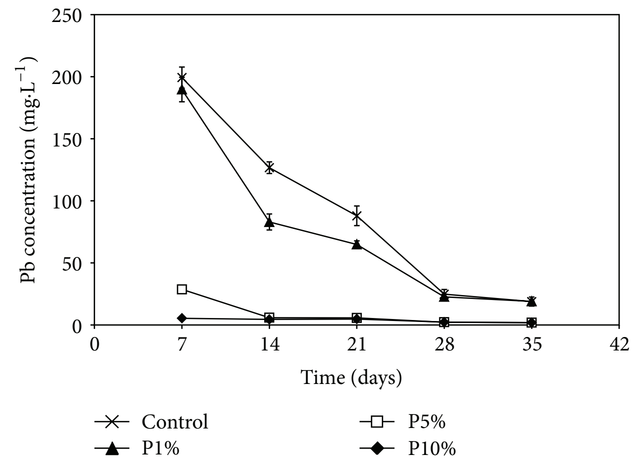

Figure 5: Pb concentration in pore water leached from Pb-contaminated soils amended with peat moss according to time through the microcosm test (control: Pb-contaminated soil without peat moss, P1%: Pb-contaminated soil with 1% peat moss, P5%: Pb-contaminated soil with 5% peat moss, and P10%: Pb-contaminated soil with 10% peat moss).

indicating the effective immobilization of Pb in the soils by the peat moss.

3.3. Microcosm Test. Pb concentration in the pore water obtained during the microcosm test also showed the effectiveness of peat moss in immobilizing Pb in the soil (Figure 5). The heavy metal concentration in the pore water provides information about water-soluble metal contents, which can be exposed to plant roots or soil microorganisms, and can be used to evaluate acute metal toxicity of heavy metals [28, 29]. The Pb concentration in the pore water decreased with increasing amount of peat moss. The Pb concentration of the soil pore water in the control was 199.5 $mg \cdot L^{-1}$ after 7 days of incubation. The peat moss amendment significantly decreased the Pb concentration in the pore water. The Pb concentrations of the pore water samples from the soils amended with 1%, 5%, and 10% peat moss were 190.7 $mg \cdot L^{-1}$, 28.6 $mg \cdot L^{-1}$, and 5.3 $mg \cdot L^{-1}$, respectively. After 35 days of incubation, the Pb concentration in the pore water was reduced to 22.4 $mg \cdot L^{-1}$ in the control, and those were 18.7 $mg \cdot L^{-1}$, 1.8 $mg \cdot L^{-1}$, and 1.7 $mg \cdot L^{-1}$ in the 1%, 5%, and 10% peat moss-amended soils, respectively.

Figure 6 shows the cumulative Pb concentrations of the pore water from the microcosm test of 35 days. After 35 days, the cumulative Pb concentration of the pore water was 30.7 $mg \cdot kg^{-1}$ for the control, and those of the pore waters were 25 $mg \cdot kg^{-1}$, 2.8 $mg \cdot kg^{-1}$, and 1.2 $mg \cdot kg^{-1}$ for the 1%, 5%, and 10% of peat moss-amended soils, respectively. The total leached Pb concentrations from soils amended with 1%, 5%, and 10% peat moss were 81.0%, 9.1%, and 3.9%, respectively, compared with that of the control soil, indicating that peat moss may be effectively used to reduce Pb toxicity to plants and soil organisms.

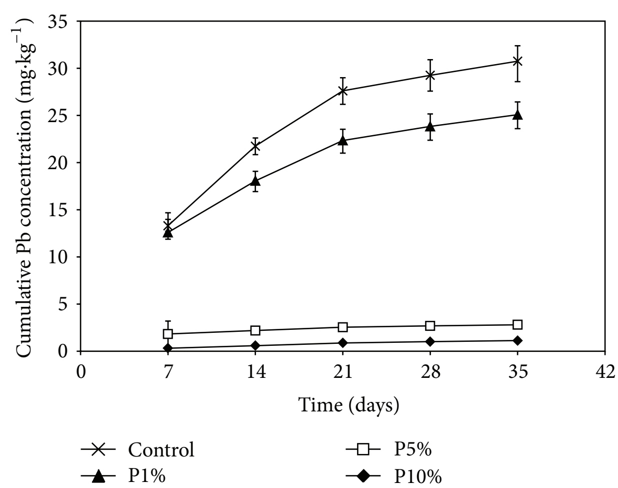

Figure 6: Cumulative Pb concentration in pore water leached from Pb-contaminated soils amended with peat moss according to time through the microcosm test (Control: Pb-contaminated soil without peat moss, P1%: Pb-contaminated soil with 1% peat moss, P5%: Pb-contaminated soil with 5% peat moss, and P10%: Pb-contaminated soil with 10% peat moss).

3.4. Batch Incubation Test. The effect of peat moss on the bioavailability of Pb was examined by measuring the NH_4NO_3-extractable Pb concentration through the batch incubation test (Figure 7). Plants can uptake heavy metal species that are weakly bound to soil constituents. Metal species weakly bound to soil particles are extractable from the soil by using dilute or neutral salt solutions of replaceable cations, such as NH_4NO_3, $MgCl_2$, $CaCl_2$, or NH_4OAc [30]. The NH_4NO_3-extractable Pb concentration was 911.5 $mg \cdot kg^{-1}$ in the control, and those were 893.2 $mg \cdot kg^{-1}$, 574.7 $mg \cdot kg^{-1}$, and 383.5 $mg \cdot kg^{-1}$ in the 1%, 5%, and 10% peat moss-amended

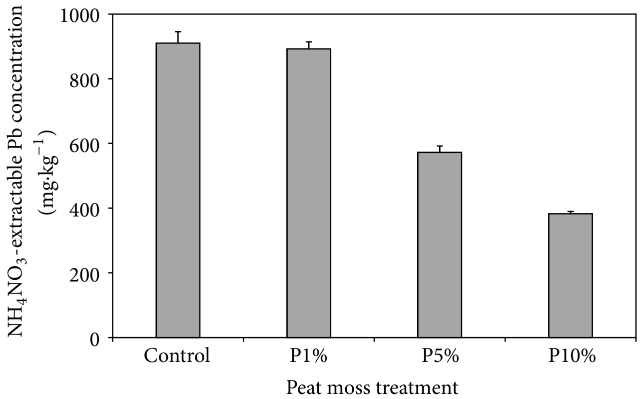

Figure 7: NH_4NO_3-extractable Pb concentration of Pb-contaminated soils amended with peat moss (control: Pb-contaminated soil without peat moss, P1%: Pb-contaminated soil with 1% peat moss, P5%: Pb-contaminated soil with 5% peat moss, and P10%: Pb-contaminated soil with 10% peat moss).

soils, respectively. The NH_4NO_3-extractable Pb concentrations of the soils amended with 1%, 5%, and 10% of peat moss were 98.0%, 63.0%, and 42.1% of that of the control soil, indicating that the peat moss amendment decreased the bioavailable Pb in the soil and, therefore, might be able to reduce the potential of Pb accumulation in humans via the food chain. This result was also attributed to the increase of humic fractions containing functional groups that increased ion-exchange or complexation with Pb in the soil. Kumpiene et al. (2007) also showed that the addition of peat moss significantly reduced the Pb leaching through a batch test [25]. An organic matter such as peat moss plays an important role in metal binding upon soil acidification.

3.5. Comparison of Pb Immobilization according to Experimental Method. Many studies have shown that the uptake of heavy metals by plants correlated with the available Pb more than with the total Pb concentration in the soil [31]. Therefore, it is important to reduce the available Pb concentration to prevent heavy metal dispersion in the ecosystem. Phytoavailable metal contents depend on the soil pH, dissolved organic carbon (DOC), cation exchange capacity of the soil, Fe and Mn oxides content, and so forth [32]. The immobilized Pb, which is defined as the reduced percent in the extracted Pb concentration in the soil amended with peat moss, can be expressed by (1)

$$\text{immobilized Pb}\,(\%) = \frac{\text{Extractable Pb in }\left(\text{control} - \text{sample}\right)}{\text{Extractable Pb in control}} \times 100. \tag{1}$$

Table 1 shows immobilized Pb values calculated from three types of experiments, which are the column leaching experiment for 10 pore volumes, the microcosm test for 35 days, and the batch incubation test. The values show that the immobilized Pb increased as the amount of peat moss increased. The immobilized lead in soils amended with 1%, 5%, and 10% of peat moss was 37.9%, 87.1%, and 95.4% for

Table 1: Comparison of immobilized Pb according to the experimental method (control: Pb-contaminated soil without peat moss, P1%: Pb-contaminated soil with 1% peat moss, P5%: Pb-contaminated soil with 5% peat moss, and P10%: Pb-contaminated soil with 10% peat moss).

Experimental method		Column Experiment	Microcosm test	Batch incubation test
Immobilized Pb (%)	P1%	37.93 ± 4.98	18.47 ± 0.58	2.00 ± 1.40
	P5%	87.06 ± 2.52	90.89 ± 0.15	36.90 ± 0.49
	P10%	95.44 ± 1.49	96.35 ± 0.03	57.90 ± 0.90

the column leaching test, 18.5%, 90.9%, and 96.4% for the microcosm test, and 2.0%, 36.9%, and 57.9% for the batch incubation test, respectively.

The sorption mechanism of metals by the peat moss includes ion-exchange, surface adsorption, chemisorption, complexation, and adsorption-complexation of which ion-exchange is considered the most prevalent mechanism [33]. Ion exchange involves electrostatic interactions between metals and charged particle surfaces. The displacement of an adsorbed metal can be associated with the strength of the adsorption. Complexation forms more stable binding than ion exchange. Thus, the metals adsorbed mainly through electrostatic physical interaction and the ion exchange can be relatively easily displaced from the peat surface. In this study, 1 M NH_4NO_3 solution used for the batch incubation test was the strongest extractant, and some of the weakly bound Pb on the peat moss might be displaced by the solution. Therefore, the experimental results showed that the peat moss reduced the mobility and toxicity of Pb more effectively in the column leaching and microcosm tests than bioavailability in the batch incubation test. The results of this study indicate that peat moss can be used as an effective soil conditioner to remediate Pb-contaminated soil.

4. Conclusions

The effects of peat moss on the immobilization of Pb in Pb-contaminated soil were investigated through three types of leaching experiments, namely, the column leaching test, microcosm test, and batch incubation test. The results of this study demonstrate that peat moss is effective in Pb immobilization in contaminated soil. Peat moss significantly reduced the Pb leaching in all of the three types of experiments. The immobilized lead of the soils amended with 1%, 5%, and 10% of peat moss was 37.9%, 87.1%, and 95.4% for the column leaching test, 18.5%, 90.9%, and 96.4% for the microcosm test, and 2.0%, 36.9%, and 57.9% for the NH_4NO_3 extraction method, respectively.

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