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Original Research

Remediation of Cd-, Pb- and Cu-Contaminated Agricultural Soils by Phosphate Fertilization and Applying Biochar

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Abstract

In this study, biochar (BC), triple superphosphate (TSP), and TSP+BC amendments were utilized for remediation of Cd, Pb, and Cu co-contaminated agricultural soils. The toxicity characteristic leaching procedure (TCLP), the European Community Bureau of Reference (BCR), X-ray diffraction, and scanning electron microscopy-energy dispersive spectrometer techniques were employed to evaluate the effectiveness of the three types of amendments. After soil amendment, pH, heavy metal concentrations in TCLP extracts, and BCR speciation of heavy metals showed significant changes. The application of BC, TSP, and TSP+BC to co-contaminated soils slightly increased soil pH; decreased Pb, and Cu leachability in the TCLP extracts; and lowered the concentrations of the acid-soluble fraction of heavy metals. The application of TSP+BC mixture at the same dose as BC and TSP produced the greatest reduction in available heavy metal concentration. The optimum mass ratio of TSP to BC was 1:3. Overall, the TSP+BC mixture was highly effective in immobilizing Cd, Pb, and Cu in co-contaminated agricultural soils. The experimental results demonstrate that the rational application of the TSP and BC provides benefits of retrenching phosphorus resources, decreasing phosphorus pollution, and lowering the feed costs of debasing soil remediation treatments.

Keywords: biochar; triple superphosphate; soil remediation; contaminated agricultural soil

Introduction

Soil contamination by heavy metals is of great concern at the global scale because of its serious potential hazards to agricultural productivity, water environment, and human health [1-3]. In China, approximately 20 million hectares of arable land, equivalent to nearly 20% of China's total agricultural land area, is subject to heavy metal contamination [2]. The major heavy metal contaminants are cadmium (Cd) followed by lead (Pb), copper (Cu), etc. These heavy metals often coexist in contaminated soils and cannot be naturally degraded [4, 5]. Therefore, for safe food production it is imperative to develop effective methods of remediating soils co-contaminated with heavy metals.

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Among various remediation techniques (excavation, landfilling, and soil washing), chemical passivation immobilization technology is comparatively easy to implement and cost-effective in metal-polluted soils [6]. In the literature, numerous materials have been used to immobilize heavy metals in contaminated soils, such as biochar (BC) [7], phosphates [8], and liming materials [9], and possible immobilization mechanisms include adsorption, binding, co-precipitation, and electrostatic interaction. Notably, BC and phosphorous (P)-based amendments have been widely applied for immobilizing Pb, Cd, and Cu in contaminated soils [10, 11].

BC is the product of biomass pyrolysis under oxygen-limited conditions. Previous studies have demonstrated the effectiveness of BC's potential in immobilizing heavy metals in contaminated soils [12]. For example, Ahmad [13] reported that BC is able to decrease the bioavailability of Pb and Sb in contaminated soils, and Rizwan [14] found that BC could be effective for both Pb and Cu immobilization in co-contaminated soils. BC is more effective for immobilizing heavy metals due to its microporous structure, surface-active functional groups, and high cation exchange capacity and pH [15, 16]. In addition, BC has potential uses in long-term carbon sequestration, increasing soil fertility, and promoting plant growth [17].

P-based amendments have also been investigated as an efficient and cost-effective method of soil remediation [18]. Some studies have shown that the triple superphosphate (TSP) fertilizer and phosphate rock tailing can significantly reduce the phytoavailability of Cd, Pb, and Cu in multi-metal contaminated soils [19, 20]. The P-based amendment immobilization mechanism relies on the formation of metal-phosphate precipitates [21]. Although P-based amendments may be effective at immobilizing and reducing the bioavailability of Cd, Pb, and Cu in contaminated soils, there are several potential drawbacks. Typically, high P doses can result in excess P, which may lead to the destruction of soil structure and water eutrophication, and increase the availability of some contaminants (e.g., antimonate and As) in multi-metal-contaminated soils [22-24]. Thus, it is necessary to control the amount of P-based amendments in soil remediation processes. Simultaneous application of BC and P-based amendments may reduce the P doses due to BC's physical and chemical properties. However, at present, to the best of our knowledge, few studies have sought to understand the direct synergetic effects of BC and P-based amendments for remediation of multi-metal-contaminated soils.

The objectives of this study were to determine: (1) the efficacy of different application rates of TSP fertilizer and coconut shell BC compounds (TSP+BC) in immobilizing Cd, Pb, and Cu in contaminated soils; and (2) BC- and P-induced metal transformation in soils.

Materials and Methods

Materials

All chemicals and reagents employed in this study were of analytical grade. Aqueous solutions were prepared using deionized water (18.3 MΩ.cm, Barnstead UltraPure water). Lead nitrate ($Pb(NO_3)_2$), copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$), sodium nitrate ($NaNO_3$), cadmium nitrate tetrahydrate ($Cd(NO_3)_2.4H_2O$), and TSP were purchased from Chengdu Chemical Co., Ltd. Coconut shell residuals (the biomass feedstock) with particle sizes of 2-4 mm were collected from Hainan Province, China.

Soil and BC Characterization

The original soil for the pot experiment was collected from a paddy field located in a suburb of Mianzhu City, China. Preliminary characterization indicated soil Cd, Pb, and Cu concentrations of 0.84, 32.1, and 59.6 mg kg^{-1}, respectively. This Cd concentration exceeds Level III of the China Environmental Quality Standard for Soil (GB15618-1995). In order to meet the study objectives, highly contaminated soil was artificially prepared using the collected soil samples with the addition of $Cd(NO_3)_2.4H_2O$, Pb $(NO_3)_2$, and $Cu(NO_3)_2$. The concentrations of Cd, Pb, and Cu in the prepared soil were 10.0, 5120.5, and 4157.9 mg kg^{-1}, respectively. The heavy metals in the soil were digested using the HNO_3/H_2O_2 hot block digestion procedure [25].

BC was synthesized from coconut shells by heating at 700ºC for 2 h under nitrogen atmosphere followed by heating at a rate of 10ºC min^{-1}. The BC samples were ground and sieved to yield size fractions of 0.42-0.71 mm. The physical and chemical properties of the BC applied to the soils were determined through a pot experiment as detailed by Li et al. [26]. In this study, the selection of BC was based on the results from our preliminary experiments and previous studies [26].

Incubation Experiment

Each 10 g air-dried sample of prepared soil was placed in a 100 mL polyethylene plastic container. Amendment materials (BC, TSP, and TSP+BC) were added gradually as required. No amendment material was added to the control treatment (CK). All pots were mixed to obtain homogeneous soil samples and then incubated at 25ºC for 14 days. During the incubation period, the soil samples were weighed every three days and moistened with deionized water to maintain constant moisture content. After incubation, the soil was air-dried and ground to pass through a 0.20 mm sieve for further analysis.

The untreated and treated soil samples were collected and air-dried for characterization using an X-ray diffraction (XRD) and scanning electron microscopy-energy dispersive spectrometer (SEM-EDS). The XRD patterns were obtained on a Rigaku D/Max-2500 PC (Rigaku Corporation, Japan) by scanning at a range from 20° to 55° at 2°min^{-1}. Soil morphology was determined using a Tescan Vega 3 LMH scanning electron microscope (Tescan, Czech Republic) equipped with an energy-dispersive X-ray micro analyzer. In addition, pH was measured using a pHS-3E meter.

Long-Term Remediation Experiment

In this study, a long-term remediation experiment was performed exactly as the incubation experiment described above, except for incubation time. In this experiment, the remediation effect was examined over 120 days.

BCR Sequential Extraction

The BCR sequential extraction method was used to differentiate the metal fractions and are described in detail in previous studies [14, 27]. Concentrations of metals in all the extraction solutions were determined through atomic absorption spectroscopy (WFX-210, Beifen-Ruili, China).

Toxicity Characteristics Leaching Procedure (TCLP) Test

Heavy metal solubility in the soil from each pot was estimated by the TCLP method (United States Environmental Protection Agency1311 [28]) as described in detail by Huang et al. [19]. The heavy metal immobilization efficiency (I,%) was calculated as follows:

$$I = \left(1 - \frac{C_T}{C_K}\right) \times 100\% \quad (1)$$

…where C_T is the heavy metal concentration in the extract (mg L^{-1}), C_K is the heavy metal concentration in the extract in CK soil (mg L^{-1}). In this study, the TCLP-extracted concentrations of Cd, Pb, and Cu from CK soil were 0.91, 295.55, and 340.24 mg L^{-1}, respectively.

Results and Discussion

Effect of Amendments on Soil pH

The soil pH values obtained after two weeks of incubation are listed in Table 1. The addition of BC, TSP, and TSP+BC (10 wt% each) resulted in significant increases in soil pH (by 1.24, 0.23, and 0.74, respectively) compared to the pH of CK soil.

Table 1. pH of the amended and non-amended soils.

Dosage	BC	TSP	TSP+BC (1:3)
CK	3.57	3.57	3.57
1%	3.64	3.62	3.63
3%	3.87	3.71	3.72
5%	4.37	3.73	4.03
10%	4.81	3.80	4.31

Some previous studies have also shown that soil pH increases after adding BC and TSP to contaminated soils [14, 29, 30]. Other studies have confirmed that elevated pH could reduce the leachability and exchangeable fraction of Cd, Pb, and Cu in soils, which might be attributed to increased precipitation resulting in the formation of their oxides, hydroxides, carbonates, and phosphates [30, 31].

Effects of Amendments on Heavy Metal Immobilization

The BC, TSP, and TSP+BC amendments reduced soil Cd, Pb, and Cu leachability in the TCLP extracts in comparison to the control (Fig. 1). Similar results were obtained in some previous studies [7, 32]. BC has a microporous structure and surface oxygen functional groups that may contribute to its high sorption to metals [26]. Correspondingly, P-induced metal immobilization was most likely due to precipitation or coprecipitation of metal phosphate minerals during the TSP remediation process [33]. In addition, Cd, Pb, and Cu leachability decreased significantly with increasing additions of amendments. For example, as the amount of BC increased from 1% to 10%, immobilization efficiencies increased for Cd (6.81-23.31%), Pb (16.04-35.80%), and Cu (9.07-48.49%).

Notably, the TSP amendment had a stronger fixing capacity than BC for Pb. The addition of 3% TSP significantly reduced the TCLP-extracted Pb by 98.00% compared to the control. In comparison, BC was less effective in immobilizing TCLP-Pb. However, BC had greater immobilization capacity for Cd and Cu compared with that of TSP. It is possible that BC and TSP have different immobilization mechanisms. Studies have shown that the addition of BC resulted in stable complexes with Cd, Pb, and Cu through specific surface adsorption [4]. However, in this study, minerals with lower solubility form first with phosphate. The solubility product of Cd and Cu phosphate is higher than that of Pb-P [34]. Thus, more soluble Pb was available to form precipitates in comparison to Cd and Cu. Consequently, Pb-P was possibly formed prior to Cd and Cu. In general, P most likely played an important role in metal immobilization, probably through the formation of metal phosphate precipitates. This assumption was further confirmed by XRD analysis (Fig. 2).

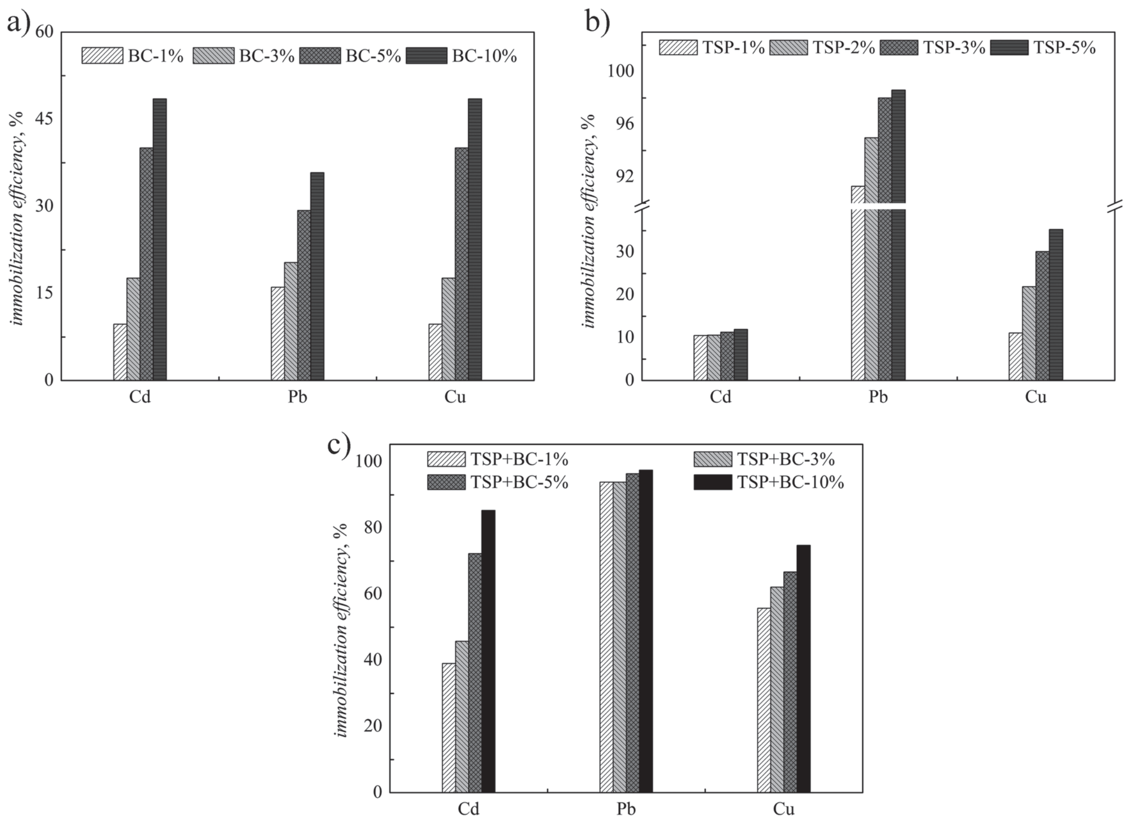

Fig. 1.Effects of amendments on the extractable Cd, Pb, and Cu using toxicity characteristic leaching procedure (TCLP). a) biochar (BC) amendment; b) triple superphosphate (TSP) amendment; c) BC and TSP mixture (at the mass rate of 1:1).

As shown in Fig. 2, the XRD patterns of the 10% TSP+BC-treated soils showed some new solid phases and indicated the presence of cadmium phosphate hydroxide, lead phosphate hydroxide, and copper phosphate hydroxide, confirming the formation of Cd-P, Pb-P, and Cu-P through precipitation or coprecipitation. However, the XRD patterns of the 2% TSP+BC-treated soils were very similar to those of the CK soils. This indicates that no new solid phases were formed. This might be due to precipitation of amorphous metal phosphate [35] or the low content (<2 wt%) of new crystalline minerals in the treated soils, which could not be detected by XRD [36].

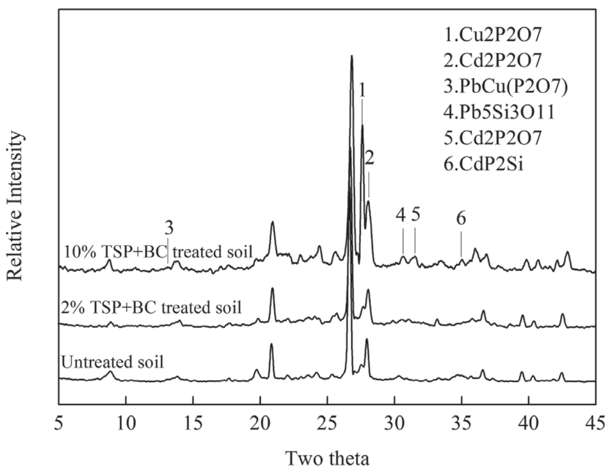

Fig. 2. X-ray diffraction patterns of contaminated soils with and without treatments (TSP and BC mass rate 1:1).

Furthermore, the formation of phosphate minerals in the TSP+BC-treated soils was supported by SEM elemental dot maps. As shown in Fig. 3, this evidenced the association of Cd, Pb, and Cu with P in the TSP+BC-treated soil, suggesting the possibility of coprecipitation.

Interestingly, as presented in Fig. 1c), the TCLP-extractable fraction of heavy metals was significantly decreased by the TSP+BC mixture (mass rate 1:1). Compared to the control, at 5% TSP+BC dose, the Cd, Pb, and Cu immobilization efficiencies were 72.21%, 96.37%, and 66.66%, respectively, which were higher than when both were used separately. The experiment results indicate a synergic effect between BC and TSP. It is likely that TSP+BC combine their respective advantages to limit the mobility of heavy metals in soil.

The different mass rates of TSP+BC amendments were investigated to select the optimum ratio for simultaneous remediation of heavy metals in soil. As shown in Fig. 4, the proportion of three different amendments showed a significant decline in the TCLP-extractable fraction of heavy metals, and

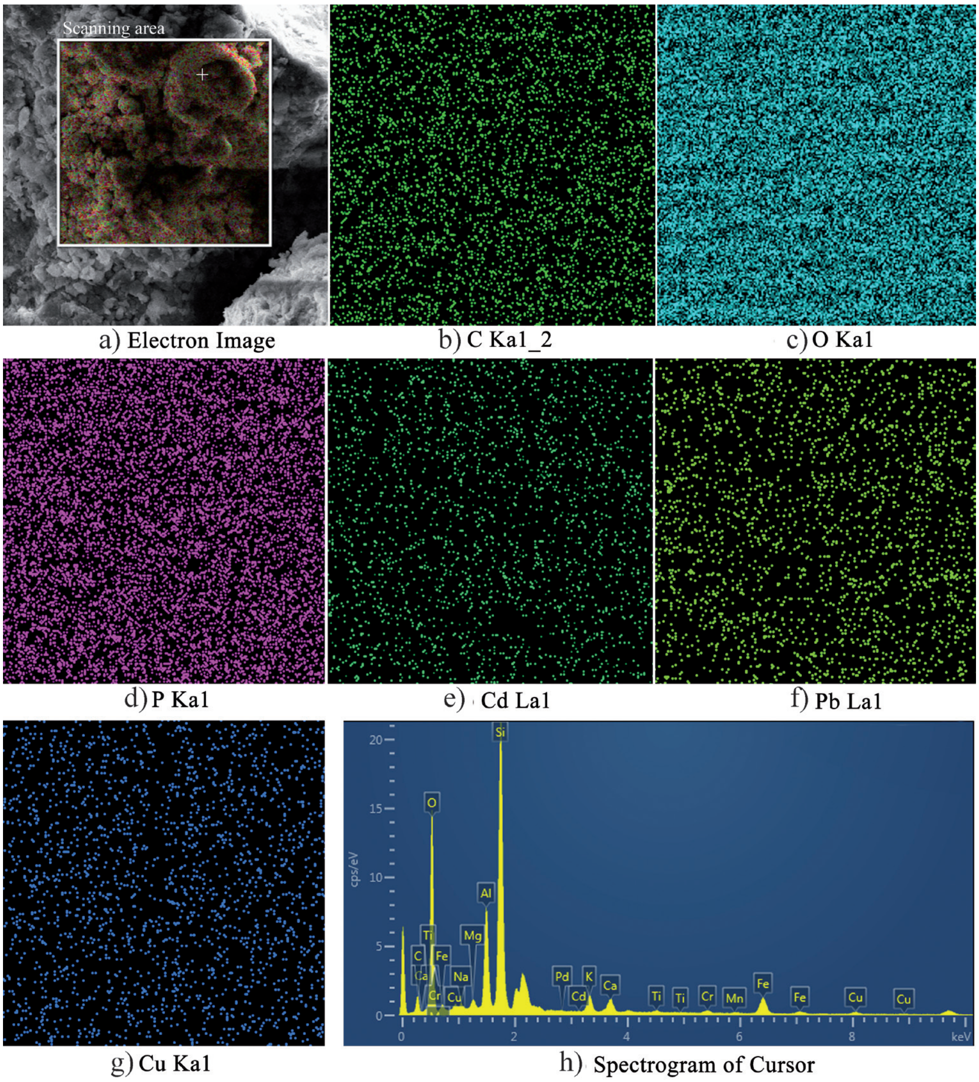

Fig. 3. Scanning electron microscopy-energy dispersive spectrometer and elemental dot maps of the residual solids in the TSP+BC amended soils after TCLP extraction (TSP and BC mass rate 1:1).

the mass rate of 1:3 TSP+BC indicated slightly better results. This might be attributed to competition and cooperation among the various reactions in the TSP+BC remediation process, such as including surface complexation, coprecipitation, sorption, and ion exchange [37, 38].

BCR Fractions of Cd, Pb, and Cu in TSP+BC-Treated Soil

The BCR sequence includes the acid-soluble, reducible, oxidizable, and residual fractions of metals, of which the acid-soluble fraction is regarded as the main mobile and bioavailable form [39], thereby representing a greater risk for agricultural productivity. Reducible and oxidizable fractions are considered slow-release fractions and can transform to acid-soluble species under acidic conditions, whereas the residual fraction is relatively immobile with low bioavailability [40]. The BCR analysis showed that the application of TSP+BC amendments (mass rate 1:3) at three different doses (3%, 5%, and 10%) induced the transformation of all three metals from soluble to stable forms. As shown in Fig. 5, Cd, Pb, and Cu in the untreated soil (CK) were mostly detected in the acid-soluble fraction, accounting for 90.02%, 74.24%, and 90.92% of the total Cd, Pb, and Cu in CK soil, respectively.

After the application of TSP+BC, the acid-soluble Cd, Pb, and Cu fractions significantly decreased, especially at the 10% dose. The relative distribution of Cd in the treated soil at the 10% dose is shown in Fig. 5a). As can be seen, Cd bound to the oxidizable fraction and residual fractions accounted for 53.36% and 36.17%, respectively, of the total Cd in soil. This indicates that the application of TSP+BC had an insignificant effect for immobilizing Cd in contaminated soils. However, the amendments significantly influenced redistribution, as shown in Fig. 5b). With an increase in the dosage of TSP+BC amendments, the concentrations of oxidizable, reducible, and residual Pb fractions

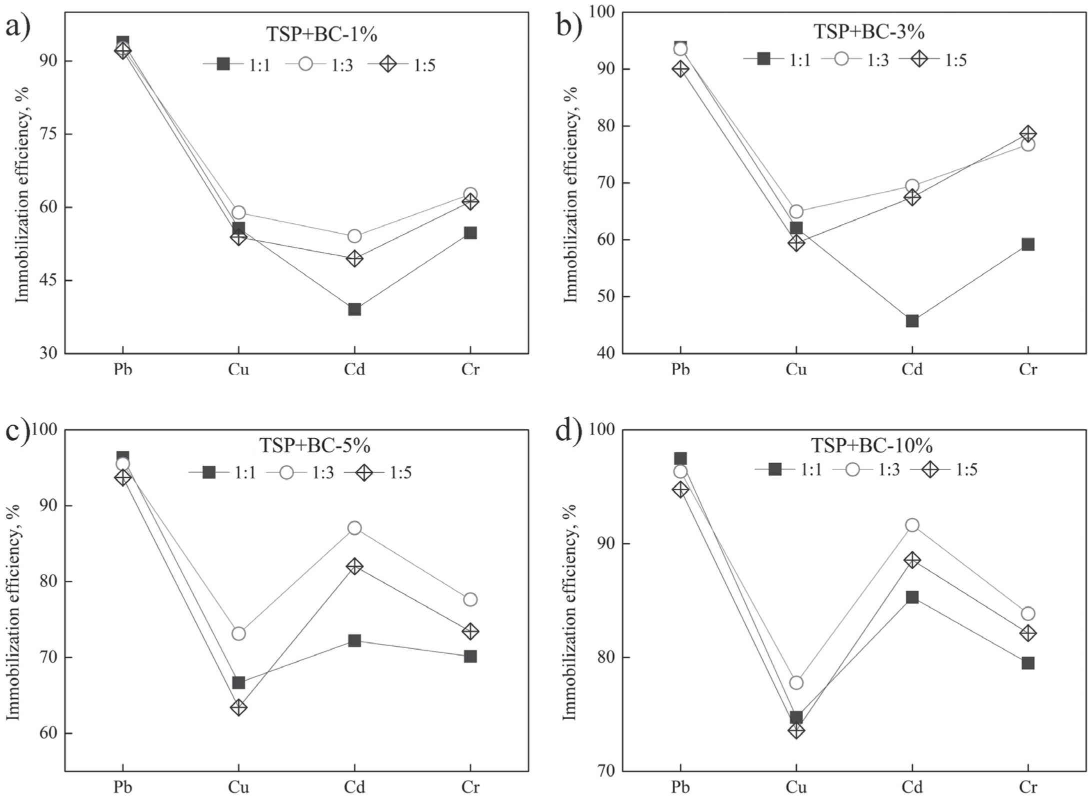

Fig. 4. Different mass rates of TSP+BC amendments on the extractable Cd, Pb, and Cu using TCLP. a) TSP + BC mixture at 1% dose, b) TSP + BC mixture at 3% dose, c)TSP + BC mixture at 5% dose, d) TSP + BC mixture at 10% dose.

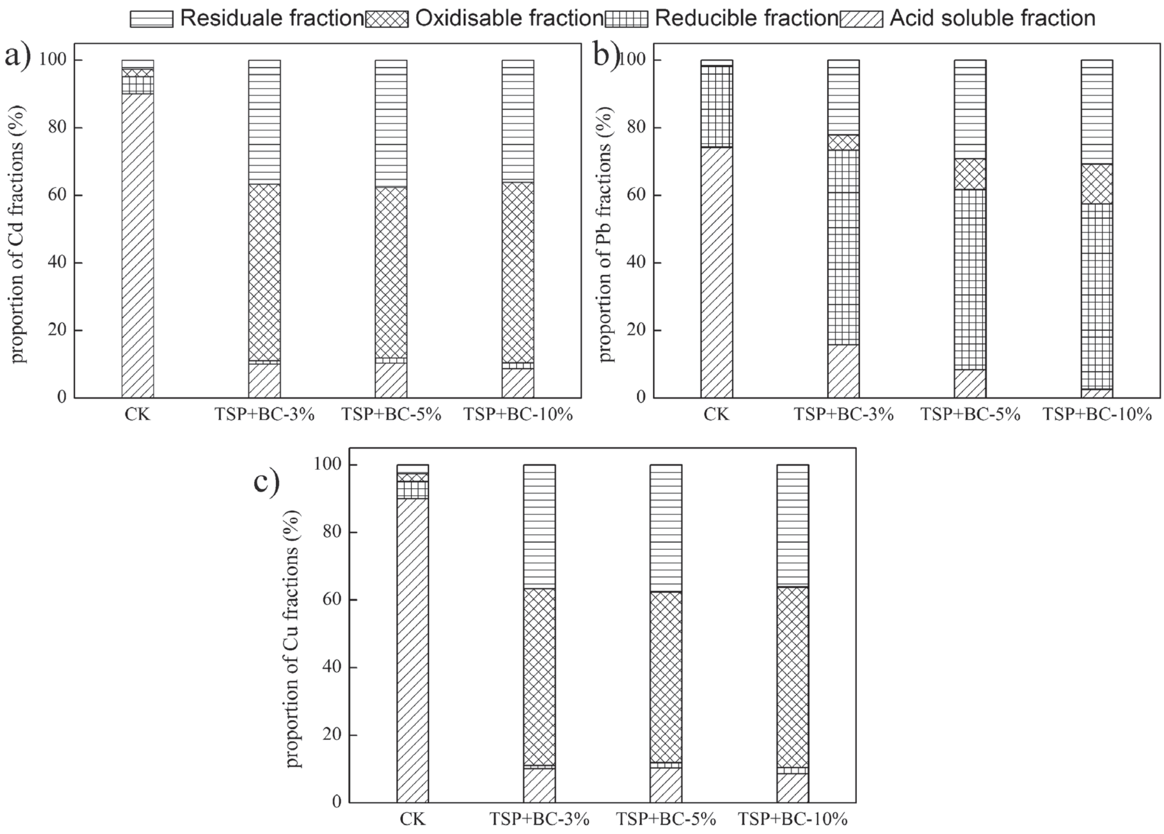

Fig. 5. Soil Cd, Pb, Cu speciation after treatment with TSP + BC amendments (at the mass rate of 1:3). a) Cd fractions in soil, b) Pb fractions in soil, c) Cu fractions in soil.

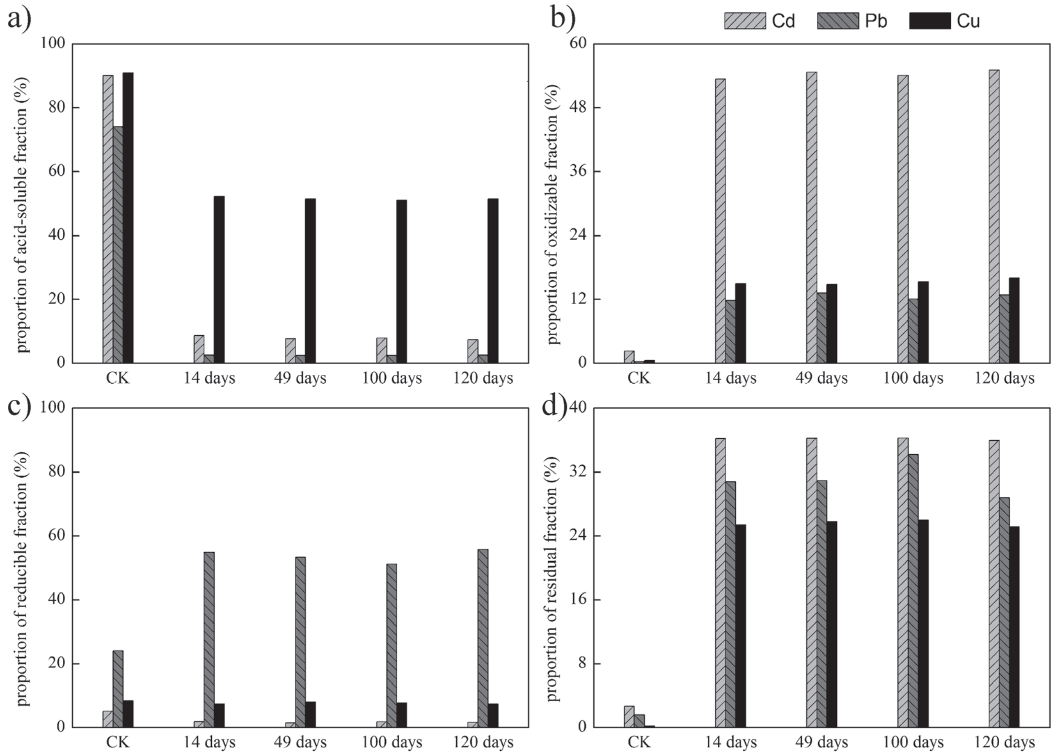

Fig. 6. Soil Cd, Pb, Cu speciation after treatment with TSP + BC amendments (at the mass rate of 1:3) for 120 days. a) acid-soluble fraction, b)oxidizable fraction, c) reducible fraction, d) residual fraction.

increased markedly, whereas the acid-soluble Pb fraction decreased sharply from 74.24% (CK) to 2.55% at 10% dose. Furthermore, in the treated soil, the acid-soluble and reducible Cu fractions decreased from 90.92% (CK) to 52.22% and from 8.37% (CK) to 7.41%, respectively (Fig. 5c), while the oxidizable and residual Cu fractions dramatically increased compared with those in the CK soil. The oxidizable and residual fractions of heavy metals were the dominant fractions and were strongly bound to the inner sphere in polluted soil. These results were also confirmed through SEM-EDC and XRD analyses.

Long-Term Remediation of TSP+BC

The long-term speciation of heavy metals in soils was investigated (Fig. 6). CK soils were treated with 10% TSP+BC (mass rate 1:3) and incubated for 120 days, after which their fractions of acid-soluble Cd, Pb, and Cu declined by 82.69%, 71.47%, and 39.43%, respectively; conversely the residual fractions of Cd, Pb, and Cu increased by 33.31%, 27.17%, and 24.95%, respectively. Meanwhile, the reducible and oxidizable fractions exhibited an increasing trend. The speciation variations of the four metals, especially the decreases in the acid-soluble fractions, further illustrated that the TSP+BC mixture effectively provides long-term stabilization of Cd, Pb, and Cu.

Conclusions

This study employed TCLP and BCR to analyze the effectiveness of BC, TSP, and TSP+BC amendments for remediating multi-metal-contaminated soils. Incubation experiments confirmed that the application of TSP and TSP+BC to co-contaminated soils can increase soil pH slightly and transform the acid-soluble fractions of heavy metals to more stabilized (residual/oxidizable) fractions. Additionally, TSP+BC was considered the best amendment for immobilization of multiple metals. This may be attributed to the synergic effect of TSP and BC and the increase in soil pH. Rational application of phosphate incorporated with BC may be effective for the immobilization of multiple metals and for reducing the availability of excess-P pollution.

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Conflicts of Interest

The authors declare no conflict of interest.

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