Immobilization of heavy metals (Cd, Zn, and Pb) in different contaminated soils with swine manure biochar

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**ABSTRACT**

To explore the feasibility of biochar for reducing mobility and bioavailability of heavy metals in different contaminated soils, batch incubation experiments including column leaching and pot experiments were conducted to investigate the effects of biochar input on soil pH, the bioavailability of heavy metals (Cd, Zn, and Pb) and their species in three different contaminated soils treated with different swine biochar application rates. The results show that biochar has more potential for pH improvement in acidic soils than neutral and alkaline soil. After 42 d incubation, the pH values of the acidic soils increased from 5.90 to 7.23, while the pH values of neutral/alkaline soils did not change significantly. The available heavy metals showed a decreasing trend as the biochar application rate increases. The order of the immobilization effect is Pb>Zn>Cd. Possible immobilization mechanisms are mainly ion exchange, complexation, n bond action and precipitation on the surface of biochar.

1. Introduction

Heavy metals released into soil environment due to industrialization, mining activities, wastewater irrigation have caused serious soil pollution. Among them, heavy metal pollution caused by mining activities is the most prominent. The mining activities not only destroy and occupy a large number of land resources but also bring a series of serious environmental pressure and human health issues. Metal mine tailings wasteland generally faces heavy metal pollution problems, and the content of heavy metal obviously exceeds the soil background value. These heavy metals impose a direct or indirect effect on the heavy metal content of crops. When their concentrations reach a certain level, it will not only lead to soil quality degradation, crop yield decline but also even enter the food chain and endanger human health [1–3]. Consequently, the remediation of contaminated soil has become the environmental issues that are widely concerned by many environmental scientists and soil scientists [4–8].

Currently, a variety of physical, biological and chemical remediation technologies, as well as phytoremediation, have been established to remediate contaminated soils [9–11]. Among them, in situ immobilization is regarded as a cost-effective contaminated soil remediation approach with its advantages of low investment, short cycle, quick effect, and easy implementation [12]. There have been already many reports on the in situ remediation of heavy metal contaminated soils by different amendments, including lime, clay, fly ash, activated carbon, phosphates, silicates, carbonates, organic compost, polymer and microbial materials [13,14]. Biochar, a low-cost and high-efficiency soil conditioner, is generally considered as a good alternative to immobilize heavy metals due to its unique physicochemical properties, such as high specific surface area associated with porous structure, low cost, environmentally sustainable and high adsorption performance [15–19]. Because biochar is usually alkaline, the application of biochar to soil can improve the pH value of soil, thus affecting the mobility and bioavailability of heavy metals. It can adsorb various contaminants through ion exchange, precipitation or surface complexation [19–27]. Previous studies have shown that biochar can decrease heavy metals bioavailability in soil and uptake in plants [28–32]. Therefore, biochar has been extensively applied for the immobilization of various heavy metals for remediation of contaminated soils [33–35].

At present, numerous studies have been conducted with respect to how biochar affects the mobility and bioavailability of heavy metals in soils [15,28,36–39]. However, most studies only focused on one particular...
contaminated soil type and/or single heavy metal contaminated soil, whereas few studies focus on how biochar addition affects heavy metals bioavailability of different soils [34, 40]. The bioavailability of heavy metals is highly correlated with physicochemical characteristics of soil, including pH, organic matter, redox conditions and so on [41, 42, 33, 43, 44]. Biochar addition will inevitably change the microbial microenvironment and physicochemical properties of soil [45], thus changing the species of heavy metals to a certain extent. Therefore, it is necessary to figure out the bioavailability and mobility of different heavy metals in different types of contaminated soil amendment with biochar application to obtain a better understanding of the suitability of biochar in different soils.

To evaluate the reliability of biochar addition on immobilization of these hazardous metals in three naturally contaminated soils (yellow soil, paddy soil and purple soil with Cd, Zn and Pb compound contamination), column leaching and pot experiments were conducted to (1) investigate the effect of biochar on Cd, Zn and Pb leaching in columns under simulated rainfall conditions, and (2) evaluate the potential of biochar for immobilization remediation of Cd, Zn, and Pb.

2. Material and methods

2.1. Biochar preparation and soil collection

The swine manure was used as feedstock to prepare biochar. Swine manure was obtained from a pig farm in Chengdu, China. The fresh swine manure was dried at 105°C for 24 h before pyrolysis. The dried swine manure was pyrolyzed at 450°C using a muffle furnace (Shengli instruments, HMFI1100-50, China), were ground and sieved (<1 mm) to uniform particle size.

Three natural contaminated soil samples (yellow soil, paddy soil, and purple soil, named GL, SF and MY) were collected from agricultural fields in Gulin County, Luzhou City (south of Sichuan province), Shifang City of Deyang City (Chengdu Plain of Sichuan province) and Miyi County, Panzhuhua City (Pan-xi region of Sichuan province) respectively. The soils sampled from GL, SF and MY were three typical contaminated soils of south-western China which were polluted by mining and smelting of pyritic, indiscriminate discharge of industrial wastewater and gas from phosphor-chemical enterprise and mining and smelting of lead and zinc mine respectively. The topsoils were sampled from 0 ~ 20 cm. The air-dried soil samples were analyzed for physicochemical properties after passing a 2 mm sieve.

2.2 Biochar characterization

The pH of biochar was determined using a pH Meter (PHS-3CT) after shaking for 1 h with a solid-liquid ratio of 1:10 w/w. Elemental analysis (C H N S) was determined using an elemental analyzer (elementar Vario MACRO). The specific surface area (SSA) was determined by the Brunauer Emmet Teller (BET) method with N2 adsorption. The oxygen-containing functional groups were determined by Fourier Transform infrared spectroscopy (FTIR).

2.3. Column leaching and pot experiments

Soil column leaching experiment was conducted to estimate how biochar addition affects the mobility of Cd, Zn, and Pb. The experiment was conducted with 1000 g of soil (dry mass) with three replicates per treatment. There are a total of twelve treatments, including four biochar/solid ratios (w/w) of 0%, 1%, 3% and 5% (denoted by CK, BC1, BC3, and BCS) and three soils. After the biochar is fully mixed with the soil, the amended soil was placed in a polymethyl methacrylate column (5 cm in diameter and 30 cm length). A wild-mouth bottle (500 mL) was placed under each column to collect leachate. In the beginning, 500 mL deionized (DI) water was added to each column to saturate the soil from the bottom to the top. Then, 200 mL of DI water was added to each column at an interval of 7 ds and the leachates sample was collected. This process was repeated six times. The leachates were collected immediately and filtered with a 0.45 μm pore size filter for subsequent analysis.

To evaluate the effect of biochar addition on the migration and transformation of heavy metals in different soils over time. A pot experiment was conducted with 500 g soil with three replicates. The experimental treatments were the same as the column leaching experiment. After the biochar addition to the soils by mixing, the amended soil was transferred into a plastic pot. Each pot was incubated for forty-five days at room temperature. Loss of water was made up using DI water to reach 70% w/w of water-holding capacity. After the pot experiment, the pH, organic matter (OM), available Cd, available Zn, available Pb, the contents of different chemical species of Cd, Zn, and Pb of soil samples were determined by ICP-MS (ELAN DRC-e).

2.4. Soil analysis

The physicochemical characteristics of soil samples were determined by the standard method [46]. The pH was determined in the same method as biochar with a solid-liquid ratio of 1:2.5 w/w. Soil organic matter (SOM) was determined colorimetrically by sodium dichromate dihydrate (Na2Cr2O7·2H2O) method. The cation exchange capacity (CEC) was determined using the ammonium acetate method [47]. Soil samples were digested in an HNO3–HF–HClO4 solution to analyze the total Cd, Zn and Pb concentrations by ICP-MS (ELAN DRC-e).

After the pot experiment, the bioavailable concentrations of Cd, Zn, and Pb in soil samples were estimated using a 0.025 M HCl solution. 6.0 g of soil
samples were added into 30 mL of 0.025 M HCl solution and shaken for 1 h [48]. The Cd, Zn and Pb concentrations in the soil extraction solutions were detected by ICP-MS (ELAN DRC-e). All analyses were performed in triplicate, including blank samples. Chemical species of Cd, Zn and Pb were detected by Tessier continuous extraction method [49]. The extracts obtained from various extraction steps were analyzed by ICP-MS (ELAN DRC-e). Origin 8.0 and SPSS 17.0 were used to analyze the experimental results in this study. One-way ANOVA was performed to analyze the significant difference among different treatments, and the significance level was 0.05.

3. Results and discussion

3.1 Physicochemical characterization of soil and biochar

Some physicochemical characteristics of tested soil are listed in Table 1. The SSA of biochar was 12.37 m²/g. The pH of biochar is 9.92, which is highly alkaline. The elemental compositions C, N, H, S of biochar are 65.45%, 3.37%, 1.84% and 0.45% mg/kg respectively. Infrared spectra of Figure 1 show that there is hydroxyl (OH), carboxyl (−COOH) group-oxygen containing functional groups on the surface of biochar. The oxygen-containing functional groups on the surface of biochar can change the species of heavy metals by ion exchange, surface complexation, and precipitation. When the heavy metals in the soil contact with biochar, their hydrolysates undergo ion-exchange reactions under the effects of hydroxyl and carboxyl groups on the surface of biochar, resulting in the adsorption of heavy metals to the biochar.

3.2 Effect of biochar on soil pH

The activity of heavy metals in soil is mainly related to soil pH. The biochar input to the soil inevitably affects the pH of the soil [30]. As shown in Figure 2, compared with the control, the soil pH values of GL and SF after the pot experiment gradually increased as biochar addition increased. The reason that biochar can increase the pH of the soil is that biochar contains certain alkaline substances, which can increase soil pH by neutralizing soil acidity. In addition, the acidity and alkalinity of the soil are mainly dominated by salt ions, and the higher ash of biochar is rich in salt ions, these ions can reduce the exchangeable hydrogen ions or aluminum ions, thereby increase soil pH. Compared with the blank, the biochar application rate of 5% increased the pH of the blank soils from GL and SF by nearly 2.0. It reached about 7.0 or so. However, the soil pH of MY did not change significantly with the increase of biochar addition (P > 0.05). The reason for this phenomenon is attributed to the pH of the three soils itself and the pH of biochar. The soils from GL and SF

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**Table 1. Physicochemical properties of tested soil.**

| Soil | pH  | Organic Matter (g/kg) | CEC (cmol/kg) | Total Cd (mg/kg) | Total Pb (mg/kg) | Total Zn (mg/kg) |
|------|-----|-----------------------|---------------|------------------|------------------|------------------|
| GL   | 5.85| 16.36                 | 16.1          | 5.63             | 228.0            | 989.1            |
| SF   | 5.90| 35.52                 | 15.5          | 18.71            | 247.9            | 1680.1           |
| MY   | 7.13| 25.16                 | 14.2          | 70.47            | 6993.2           | 20,526.0         |

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**Figure 1.** FTIR spectrum of oxygen-containing functional groups on the biochar surface.
Figure 2. The pH values of soils in GL, MY, and SF after the pot experiment. Different small letters denote significant differences for different treatments at $P \leq 0.05$ (n = 3).

are acidic (pH<6.0), while the soils in MY belong to neutral or weakly alkaline soil (pH>7.0), indicating that biochar has a significantly better adjustment function on acidic soil than neutral soil or alkaline soil. The physicochemical properties of soil leaching filtrate are a reflection of the composition characteristics of the soil solution, and the pH value of soil leachates is directly related to the species and bioavailability and toxicity of heavy metals in soil. The results of six rounds of leaching experiments with different biochar application rates showed that the biochar input increased the pH of the soil solution in all treatments. During the leaching process, the pH values of the leachates in the three soils showed a phenomenon of increasing first and then began to show a downward trend at the sixth leaching (Figure 3). The average pH values of the leaching filtrate in the C0, C1, C3, and C5 treatments were from 7.29 to 8.80 for GL, and from 6.60 to 8.54 for MY and from 6.50 to 9.70 for SF, respectively. The reason for this is that biochar contains a large number of basic ions and aromatic compounds such as K, Ca, Mg, etc., and has an -OH group on the aromatic compound. These ions or groups are alkaline after being dissolved in water. During the leaching experiment, as the rainfall increased, the basic groups and alkaline ions in the biochar dissolved in water and eluted, resulting in an increase in the pH of the leachate. Therefore, the chemical nature of biochar itself is an important factor affecting the amendment soil pH.

The soil dry-wet cycle makes the soil physical and chemical properties vary greatly, which has a great influence on the soil redox potential [50]. The alternating process of soil from dry to wet will cause the reduction reaction of $\text{NO}_3^-$, $\text{Fe}^{3+}$, $\text{Mn}^{4+}$ ions, which consumes $H^+$ and leads soil pH increased. Accordingly, it can be considered that the change in pH during leaching is the result of an ion reduction reaction in the soil wetting process [50]. Although biochar increased the pH of the soil, it did not change this characteristic, indicating that biochar application did not significantly affect the above basic reaction during soil wetting. The change of the above pH value is about 1000–1200 mm simulated precipitation, which indicates that the reduction reaction of $\text{NO}_3^-$, $\text{Fe}^{3+}$, $\text{Mn}^{4+}$ in the soil is basically completed, and the amount of alkaline ions in the soil gradually decreases.

### 3.3 The effect of biochar addition on heavy metals mobility in soils

There was a gradual decline in heavy metal contents in leachates over time in all treatments. As shown in Figure 4, biochar reduced the concentration of heavy metal in the leachate during the soil column leaching process. The highest heavy metal leaching occurred within the first 14 days. After biochar was added, the heavy metal content in the leachates decreased, indicating that biochar reduced the mobility of heavy metals. As the proportion of biochar increases, the concentration of leached heavy metals decreases. It is the precipitation and surface complex with biochar which results in the reduction of heavy metal leaching [51]. In general, biochar input reduces the leaching of heavy metals. As the proportion of biochar added
increases, the amount of heavy metal in leachate decreases. This result is constant with previous studies [30,52]. Among them, biochar has a more significant reduction of Pb in three soils (P ≤ 0.05), while the reduction in Zn and Cd is not significant. This may be attributed to the higher affinity of Pb on biochar than Zn and Cd. Other factors that may affect the mobility and effectiveness of heavy metals include pH and soil organic matter [34,52,53]. The different immobilization effects of different heavy metals by biochar indicate that the distribution of heavy metals in soil depends on the type of heavy metals, the interaction between heavy metals and soil, and the factors of biochar itself, such as biomass raw materials, pyrolysis temperature, application rate, and biochar pH. As the pH increases, the equilibrium concentration of Pb in the soil

Figure 3. Effect of biochar on pH of leachates for soils from MY, GL and SF.
3.4 Effect of biochar on different species of heavy metals in soil

The total amount of heavy metals in the soil can be used to evaluate the level of soil pollution in an area, but it cannot accurately reflect the actual situation of soil pollution. Therefore, it is necessary to analyze the distribution of heavy metals after biochar addition. In this study, the Tessier classification continuous extraction method was used to classify heavy metals into the acid extractable state, reducible state, oxidizable state, and residual state. Among them, the acid extractable state has strong mobility and is easily utilized by microorganisms; the reducible and oxidizable states can be converted into the acid extractable state under certain physical and chemical conditions and can be indirectly utilized by microorganisms. The residual state mainly exists in the soil crystal lattice, which is not easy to release in a short time, is the most stable, and has little mobility and cannot be utilized by organisms.

After 42 d of pot incubation experiment, the proportion of different species of Cd, Zn, and Pb in the soil are shown in Figure 5. The addition of biochar significantly reduced the proportion of three acid extractable heavy metals (P ≤ 0.05). For the soils from GL, compared with CK treatment, the soil acid extractable Cd decreased by 25.35%, 45.34% and 61.90% after the addition of biochar. Compared with CK, the residual Cd increased by 4.71%, 6.19%, and 17.55%, respectively. For the soils from MY, the soil acid extractable Cd decreased by 46.97%, 65.64% and 72.90% after the addition of biochar. For the soils from SF, the soil acid extractable Cd decreased by 24.17%, 38.45%, and 48.87% compared with CK.

For the soils from GL, the acid extractable Zn decreased while biochar addition increased. Compared with CK treatment, the soil acid extractable Zn decreased by 59.02%, 86.63% and 90.10% after the addition of biochar. The acid extractable Zn in the soil with 5% biochar was significantly lower than that of the control (P ≤ 0.05). For the soils from MY, due to the influence of soil pH, most of the Zn exists in the organic-bound state and the iron-manganese oxidation state and the residual state, and the exchangeable Zn is almost negligible. For the soils from SF, the soil acid extractable Zn decreased by 39.26%, 62.22%, and 82.74% compared with CK.

For the soils from GL, the acid extractable Pb in the soil decreased by 81.35%, 94.35%, and 97.00% compared with the control CK, and the residual increased by 3.66%, 5.46%, and 32.30%, respectively. For the
soils from MY, the soil acid extractable Pb decreased by 43.01%, 51.29% and 68.49% after the addition of biochar and the residual Pb increased by 29.10%, 43.36%, and 58.63%, respectively. For the soils from SF, the soil acid extractable Pb decreased by 60.24%, 88.89%, and 97.40% compared with CK and the residual Pb increased by 28.38%, 45.36%, and 52.53%, respectively. The residual state Pb in three soils increased significantly as biochar addition increased (P < 0.05). The effect of biochar on different heavy metals immobilization is not the same. We calculated the immobilization rates of different heavy metals in three soils after biochar addition [54]. The results show that the higher the proportion of biochar addition to the soils, the higher immobilization rates of heavy metals in all three soils. This is consistent with the results of other studies [55]. The ability order of immobilization rates of the three heavy metals is Pb > Zn > Cd.

In general, biochar input changed the distribution of heavy metals, and the acid extractable content of Cd, Zn and Pb decreased significantly in all contaminated soils (P < 0.05). This is consistent with the results of previous studies [32,56]. The immobilization effect on Cd and Zn was significantly higher in the alkaline soil from MY than that of neutral and acid soil from SF and GL (P < 0.05), while the immobilization effect on Pb was higher in alkaline soils from SF and GL than that of neutral and acidic soil from GL and SF. The change of heavy metal species in the soil is not only controlled by the nature of biochar but also related to the change of soil physicochemical properties (pH, CEC, etc.) [57]. With the increase of pH, the negative charge on the surface of clay minerals, hydrated oxides, and organic matter will increase, and the negative charge of soil colloid increase, which enhances the affinity and adsorption capacity of soil for heavy metal cations and reduce the desorption of heavy metals [58]. The soil pH is also closely associated with the solubility of heavy metals. With the increase of soil alkalinity, heavy metal ions in the soil will form insoluble Pb(OH)\(_2\), Cd(OH)\(_2\), Zn(OH)\(_2\) and other precipitation. The mobility of ions is weak, and biochar can be combined with precipitation, thus reducing the mobility of heavy metals in the soil. The increase in pH alsoWeakens the competition of H\(^+\), resulting in a tighter combination of iron-manganese oxide, organic matter and heavy metals in the soil. Biochar input also causes an increase in CEC, so that the electrostatic adsorption of heavy metals is stronger, and heavy metal ions are firmly adsorbed on the surface of the soil, reducing its mobility. The cations such as Ca\(^{2+}\) and Mg\(^{2+}\) released from the surface of the biochar are ion exchanged with Pb\(^{2+}\), Cd\(^{2+}\), and Zn\(^{2+}\) [26,59].

Under the effect of intermolecular hydrogen bond, the hydroxyl group and carboxyl group on the surface
of biochar combine with heavy metals to form complexes, and the complexation reaction make the heavy metals adsorbed on the surface of biochar and immobilized in the soil, affecting the migration and transformation of heavy metals and playing a role in the immobilization of heavy metals to a certain extent [59]. The strong absorption peak in the infrared spectrogram 1027 cm\(^{-1}\) is C-O-C pyranoid ring skeleton vibration, indicating that the biochar has a highly aromatic and heterocyclic structure. These functional groups have an electron structure with a highly dense electron cloud and are prone to bond with heavy metals forming π, which belong to typical chemical adsorption [60]. In addition, biochar has a large specific surface area and abundant surface pore structure, which can enhance the immobilization of heavy metals through adsorption.

The mechanism of swine manure biochar immobilization of heavy metal in soil mainly includes ion exchange, complexation, π bond action and precipitation [34,61] (Figure 6). Among them, the adsorption of heavy metals by soil colloids is usually divided into two types, which are specific adsorption and non-specific adsorption. The specific adsorption is the adsorption generated by the surface of the soil colloid and the adsorbed metal ions through covalent bonds and coordination bonds. Non-specific adsorption is generated by electrostatic attraction, which occupies the normal cation exchange point of soil colloid, also known as cation exchange adsorption. Specific adsorption and non-specific adsorption may occur in the process of biochar fixation of heavy metal ions in the soil, but mainly by specific adsorption. The study indicates that the specific adsorption is related to the hydrolysis ability of ions. The first-order hydrolysis constant of ions can predict the competitive adsorption capacity of soil colloids for heavy metal ions. The adsorption affinity decreases with the increase of the first-order hydrolysis constant negative logarithm pK1. The values of three heavy metals pK1 are Cd (10.1)>Zn (9.0)>Pb (7.8), respectively [62], and the immobilization effect of soil on heavy metal ions is Pb>Zn>Cd. With the increase of ion hydrolysis constant, the specific adsorption of ions to the soil is reduced, which is consistent with the previous studies [63]. Therefore, the mechanism of swine biochar immobilization of heavy metals is mainly based on adsorption and precipitation.

4 Conclusions

Batch incubation experiments were carried out to investigate the effects of swine manure biochar on the soil properties and availability and species of Cd, Zn, and Pb in different contaminated soils. Compared with neutral soil, biochar has more potential for pH improvement in acidic soils. Biochar addition changes the distribution and increases immobilization of heavy metals in soils. The immobilization effect between different treatments was 5% biochar> 3% biochar > 1%
biochar. Biochar input changed the species of heavy metals in the soil, and the weak acid extraction state migrated easily which changed to a more stable residue state, and the larger the amount of biochar added the more significant immobilization effect. The immobilization effect of three heavy metals is in the order of Pb>Zn> Cd. The mobility of Cd, Zn and Pb are significantly negatively correlated with soil pH. Possible immobilization mechanisms are mainly ion exchange, complexation, π bond action and precipitation on the surface of biochar.

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