Effects of magnetic particle proportion and additive amount on the extraction of Pb and Cd from soil by magnetic biochar

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Abstract: Due to the high sorption capacity for heavy metals, magnetic biochar (MBC) has the potential to adsorb heavy metals in soils, which are then removed together with MBC from soils by a magnetic field. However, little research on the magnetic particle (MP) proportion and the addition amount of MBC. In this study, different magnetic particle proportion and addition amount of MBC were evaluated by a batch experiment. The most suitable MP proportion of MBC was 0.2 mol/L Fe²⁺, under this MP proportion, the extraction rates of Pb and Cd were 42.9% and 37.2%, respectively. The most suitable addition amount was 2.5% under low pollution condition, and 7.5% under severe pollution condition.

1. Introduction

Heavy metal (HM) pollution to soils affects food security and environmental health. Among heavy metals, lead (Pb) and cadmium (Cd) are of most concern due to their highly persistent and toxicity[1]. Lead and Cadmium are nonessential elements for plant growth, can be taken up by crops without biochemical degradation processes[2]. Lead and cadmium can transfer from soils to plants and then are exposed to human beings through the food chain. Therefore, much attention has been paid to the remediation of heavy metal contaminated soils[3].

In recent years, modification has been widely used for biochar to improve its sorptive capacity and separation from aqueous solution[4, 5]. In addition to being recovered from contaminated water easily and cheaply, magnetic biochar (MBC) has enhanced metal sorption in numerous studies [6-8]. However, there are still few studies on the extraction of Pb and Cd from the soil by MBC.

In this study, different magnetic particle (MP) proportion of MBC was prepared, and the optimal MBC additive amount was also found in the process of extraction of Pb and Cd in contaminated soil. The study provided an optimized condition for using MBC to extract Pb and Cd in the contaminated soil.

2. Experimental

2.1.Materials

In this study, naturally Pb and Cd polluted paddy soil was collected from Henan Province (N 35⁰08'35", E 112⁰31'28"), China. The soil samples were air-dried and then sieved through a 2-mm mesh. Soil basic characteristics are given in Table 1.

The MBC samples were produced from wheat straw according to the procedure of Mohan[4]. Briefly, wheat straw chips were pyrolyzed at 300 °C for 4 h. The products were grounded to pass through a
0.180-mm sieve and were named BC300. The 9.28 g biochar products were then mixed with 200mL FeCl3/FeCl2 solution and stirred for 30 min. The concentrations of Fe^{2+} in magnetized solution were 0.1 mol/L, 0.2 mol/L and 0.4 mol/L, respectively. The concentration of Fe^{3+} were 0.2 mol/L, 0.4 mol/L and 0.6 mol/L, respectively. The solution pH was adjusted to 10-11 by sodium hydroxide and was stirred again for 1 h. After that, the mixture was aged for 24 h, filtered (PTFE, 0.45μm), washed and then dried at 50°C for 12 h. The MBC samples were named as 0.1mMBC300, 0.2mMBC300, 0.4mMBC300, respectively. MP without biochar addition was produced by the same procedure.

2.2. Experimental methods
Sorption isotherms of Pb and Cd were obtained using a batch equilibration technique. Briefly, 0.12 g of the biochars or MBCs was added to 40-mL PE tubes with PTFE sealing caps. Then, 40 mL of deionized water containing 50-2500mg/L Pb and 10-800 mg/L Cd (pH=5) was added into the tubes, respectively. The pH was adjusted by 0.1mol/L HCl or 0.1 mol/L NaOH solutions. The PE tubes were horizontally shaken in a shaker at 110 rpm (25°C) for 24 h, which was sufficient to reach sorption equilibrium. Thereafter, all tubes were centrifuged at 1600 g for 10 min and filtrated (PTFE, 0.45μm). Concentrations of Pb and Cd in the filtrate were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, 7400 Series, Thermo Fisher Scientific, US).

The extraction experiment was carried out by mixing 35 mL of deionized water with a mixture of 5 g soils and MBC (addition dose of 2.5-15.0%, w/w) in 40-mL PE tubes. Besides, PE tubes containing 35 mL of deionized water and 5 g soils served as control. The tubes were then shaken at 110 rpm in a horizontal shaker (25°C). The tubes were withdrawn in triplicate. After the measurement of pH and Eh, the mixtures were treated with a magnetic rod to separate MBC. Recovery percentages of MBC and residual concentrations of Pb and Cd in soils were measured.

2.3. Sample analysis
Values of pH and Eh were measured by a multi-parameter meter (PHSJ-4F, INESA, China). The pore volume, pore size and specific surface area (SSA) were measured by the Brunauer-Emmett-Teller (BET) method (NOVA-2000E, USA). Pb and Cd in soil samples were determined by ICP-OES after HNO3-HF-HClO4 digestion[9].

| Samples   | pH      | CEC (cmol/kg) | TOC (%) | Sand (%) | Silt (%) | Clay (%) | Pb (mg/kg) | Cd (mg/kg) | Soil texture |
|-----------|---------|---------------|---------|----------|----------|----------|------------|------------|--------------|
| He-soil   | 6.36    | 5.37          | 0.97    | 10.2     | 74.7     | 15.1     | 126.83     | 3.17       | Silty loam   |

### 3. Result and Discussion

3.1. Basic characteristics and adsorption isotherm models
Basic characteristics of different MP proportion of MBC is shown in Table 2. The result showed that with the increase of MP proportion, the pH value and specific area of MBC increased gradually. The fitting results of adsorption isotherm models with different MPs of MBC300 are shown in Table 3. The result showed that the Freundlich model fitted the experimental data better than the Langmuir model for Pb adsorption (r>0.90). However, for Cd adsorption, the Langmuir model fitted better (r>0.95). Hence, the adsorption of Pb by MBC was a multi-layer sorption process with the heterogeneous energetic distribution of active sites[10]. While the Langmuir model assumes that monolayer adsorption occurs on the homogeneous surface of all identical sites that are energetically and sterically independent of the adsorbed quantity[11]. The Langmuir parameter Qmax is the monolayer adsorption capacity. As the amount of MPs gradually increased, the adsorption capacity first increased and then decreased. The results showed that the specific surface area was not the only limiting factor for Pb and Cd adsorption. Previous studies have reported that excessive MP addition would increase the positive surface charge of MBC, thus affecting the adsorption of Pb and Cd[12].
3.2. Extraction experiment
During the extraction experiment, the change of MBC recovery rate and pH value was shown in Table 4. The result showed that the pH value of the MBC group increased compared with the original group on day 0. After 7 days, the change of pH value was less significant than that of 0 days due to the buffering effect of the soil. With the higher proportion of MP, the recovery rate was on the increase but when the proportion of Fe2+ over 0.2 mol/L, the recovery rate of MBC did not change significantly.

The results of Pb and Cd content in the soil before and after 7 days of extraction were shown in Figure 1. As can be seen from Figure 1, MBC in the soil had a more obvious extraction effect on Pb than Cd. It has been reported that Pb would preferentially occupy the adsorption point of MBC in the case of the coexistence of multiple heavy metals [13]. Besides, we found that MBC and Pb can be specifically adsorbed, resulting in a relatively close binding compound. As same as aqueous adsorption, 0.2 mol/L was the best MP proportion. The extraction rate of Pb and Cd can reach 42.9% and 37.2%, respectively.

3.3. Additive amount experiment
In the previous experiment, 0.2mMBC300 had the best comprehensive performance, so the sample was used to evaluate the optimal additive amount experiment in the soil. The removal rate of Pb and Cd after extraction with the different additive amount of MBC was in Figure 2. As can be seen from Figure 2, for Pb and Cd, the removal rate increased rapidly within the range of 2.5%-7.5%. When the addition amount was greater than 7.5%, the removal rate was not significantly increased. The result indicated that 2.5% of MBC can be added to the soil with a low pollution condition, which has a relatively good removal effect. If the soil was under moderate or severe pollution condition, 7.5% of MBC addition amount can be chosen for extraction.

4. Conclusion
The most suitable MP proportion of MBC was 0.2 mol/L Fe2+, under this MP proportion, the extraction rate of Pb and Cd was 42.9% and 37.2%, respectively. The most suitable addition amount was 2.5% under low pollution condition, and 7.5% under severe pollution condition.

Table 2 Characteristics of different MP proportion of MBC samples

| Sample          | Yield (%) | pH  | S_mic (m²/g) | S_meta (m²/g) | S_total (m²/g) | S_mic/S_total (%) | APD* (nm) |
|-----------------|-----------|-----|--------------|---------------|----------------|-------------------|-----------|
| 0.1mMBC300     | 151.1     | 8.34| -            | 44.78         | 44.78          | 0.00              | 13.27     |
| 0.2mMBC300     | 189.2     | 8.37| -            | 65.86         | 65.86          | 0.00              | 15.42     |
| 0.4mMBC300     | 293.1     | 9.32| -            | 87.26         | 87.26          | 0.00              | 21.91     |
| MP             | -         |    | -            | 86.48         | 86.48          | 0.00              | 12.33     |
| BC300          | 42.12     | 7.31| 0.93         | 2.39          | 3.32           | 28.01             | 13.37     |

APD: average pore diameter.

Table 3 Regression parameters of sorption isotherms of lead and cadmium on BC and different MBC samples

| Metal | Samples       | Qₑ | K_L | r² | K_f | n  | r²  |
|-------|---------------|----|-----|----|-----|----|-----|
| Pb    | BC300         | 145.98 | 0.005 | 0.969 | 15.28 | 0.350 | 0.938 |
|       | 0.1mMBC300    | 140.28 | 0.003 | 0.922 | 14.94 | 0.388 | 0.928 |
|       | 0.2mMBC300    | 150.78 | 0.037 | 0.870 | 18.15 | 0.210 | 0.981 |
|       | 0.4mMBC300    | 146.07 | 0.035 | 0.850 | 15.47 | 0.167 | 0.968 |
|       | BC300         | 6.91 | 2.602 | 0.979 | 3.92 | 0.143 | 0.860 |
| Cd    | 0.1mMBC300    | 13.58 | 2.035 | 0.940 | 7.82 | 0.164 | 0.891 |
|       | 0.2mMBC300    | 15.15 | 5.287 | 0.947 | 8.46 | 0.133 | 0.680 |

Langmuir: 
\[
Q_e = \frac{Q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}
\]

Freundlich: 
\[
Q_e = K_F \cdot C_e^n
\]
Table 4 Characteristics of soils with different MP proportions of MBC during the extraction experiment

| Day   | Sample       | pH         | Recovery Percentage (%) |
|-------|--------------|------------|-------------------------|
|       | Original     | 8.00±0.13C | /                       |
| Day 0 | 0.1mMBC300   | 8.33±0.07B | /                       |
|       | 0.2mMBC300   | 8.32±0.02B | /                       |
|       | 0.4mMBC300   | 8.67±0.06A | /                       |
|       | Only Water   | 7.34±0.01D | /                       |
| Day 7 | 0.1mMBC300   | 7.46±0.03D | 84.52±6.23B             |
|       | 0.2mMBC300   | 7.43±0.01D | 97.61±4.49A             |
|       | 0.4mMBC300   | 7.17±0.02E | 97.43±4.92A             |

Fig. 1. Lead and cadmium in soil samples after MBC recovery. CK indicates the control treatment (i.e. treatment without MBC). MBC300 indicate treatments with MBC300.

Fig. 2. Removal rate of Lead and cadmium in soil samples after MBC recovery.

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