Immobilization of soil Cd (II) by modified biochars

Ming Li1,2*, Tingting Fan1,2, Jianbo Huang1,2, Qi Liu3, Yifei Ding3, Han Zhang3 and Zhiwang Feng3

1Nanjing Institute of Environmental Science, Ministry of Ecology and Environment, Nanjing 210042, PR China.
2Key Laboratory of Soil Environmental Management and Pollution Control, Ministry of Ecology and Environment, Nanjing 210042, China;
3Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes, Ministry of Education, College of Environment, Hohai University, Nanjing 210098, PR China.

*Corresponding author’s e-mail: liming@nies.org

Abstract: Adsorption kinetics and isotherms of Cd2+ onto different types of biochar are studied in batch experiments. Three types of biochar (rice, wheat and corn straw biochar) and their phosphate or chitosan modified materials were used in this study. Results showed that Langmuir equation can better describe the adsorption isotherms of Cd2+ onto these biochars ($r^2 > 0.960$). Among different types of biochars, rice straw biochar (RB) and its chitosan modified biochar (CRB) had highest adsorption capacity of Cd2+. RB, wheat straw biochar (WB) and their modified biochars were used to remediate Cd-contaminated soil. Soil pH values increased with the increasing of biochar dosage and chitosan modified biochar amended soil had the highest soil pH values. Contents of DTPA extractable Cd in soil decreased with the increase of biochar dosage and incubation time. Among different types of biochars, 5% CRB amended soil at 60 days of incubation had the lowest content of DTPA extractable Cd. This study showed that the application of modified biochars can effectively alleviate soil Cd contamination.

1. Introduction
Among heavy metal pollutants, cadmium (Cd) has been a major specie in the farmland soil in China [1]. Cd speciation in soil could distribute into ionic, organic matter associated, Fe-Mn oxides associated and residue states [2]. Among them, Cd2+ in soil pore water is the most easily absorbed by plant roots, then can be accumulated in plant tissues and transfer along the terrestrial food chain, causing serious crop safety problems [3]. Therefore, remediation of soil heavy metal contamination has been an urgent problem to be solved.

Biochar is produced by anaerobic pyrolysis of waste materials under high temperature. Studies have shown that biochar always have high specific surface area, high pH value and oxygen functional groups such as -COO and -OH [4]. These physical and chemical properties enabled the adsorption of Cd2+ onto biochar through various mechanism, such as the electrostatic effect, surface precipitation and complexation, ion exchange [4,5]. The adsorption behaviors of Cd2+ onto biochar reduced the bioavailability of Cd2+ in both soil and water environment [4,6]. Recently, many studies focused on functionally modified biochar by various chemical agents, acid or alkali etc. due to their higher sorption capacities than pristine biochar [4,7]. Until now, functionally modified biochar has been increasing used in soil pollutants remediation. Therefore, in our study, we aimed to: (1) compare adsorption behaviors
of Cd\(^{2+}\) onto pristine and modified biochars. (2) explore contents of soil pH and DTPA extractable Cd varied with biochar properties.

2. Materials and Methods

2.1 Cd contaminated soil preparation and characterization

Soil sample was collected from the vegetable field (0-20 cm depths) in Lanping county, Yunnan province, China. Soil physico-chemical properties were detected as listed: pH (7.05±0.05), Total N content (0.12%), organic matter content (22.7 g/kg) and CEC content (7.71cmol(+) /kg). Cadmium nitrate (Cd(NO\(_3\))\(_2\)) was dissolved in ultra-pure water and spiked to the homogenized soil to achieve the Cd contaminated soil. The spiked soil was aged in greenhouse for two months. Soil available Cd were extracted by DTPA agent as described in the study of Xiao et al. [8], and then measured by ICP-OES.

2.2 Biochar preparation and modification

Biochar was pyrolyzed from three straw materials and then denoted as WB (wheat straw derived biochar), CB (corn straw derived biochar) and RB (rice straw derived biochar). These pristine biochars were then grounded and sieved through a 0.25-mm mesh before the remediation experiment.

Pristine biochar was modified with phosphate and chitosan, respectively. To obtain the phosphate modified biochar [9], pristine biochar was firstly impregnated with a 250 mL of 0.5 mol/L K\(_2\)PO\(_4\) solution with a mass ratio of 1:2. Then mixture was heated in a water bath with stirring for 6 h at 80 °C. Finally, the mixture was filtered and washed with deionized water, and dried at 60 °C in a vacuum oven. All obtained biochars were denoted as PWB, PCB and PRB. To obtain the chitosan modified biochar [10], chitosan (1g) was added in 400 ml of 2% acetic acid solution and stirred 3 h at 40 °C and 450 rpm. 1 g of the pristine biochar was added to the solution and stirred 1 h at 40 °C and 450 rpm. The pH of the mixture was adjusted to 12 using NaOH and HCl, and further stirred for 2 h at 40 °C and 400 rpm. Finally, the mixture was filtered and washed with deionized water, and dried at 60 °C in a vacuum oven. All obtained biochars were denoted as CWB, CCB and CRB.

2.3 Biochar amendment on Cd-spiked soil and DTPA extractable Cd

In our experiment, we designed the incubation time and biochar dosage to examine the remediation efficiency of Cd. 0.5%, 2% and 5% (w/w) pristine and modified biochar were separately mixed fully with Cd-spiked soils to obtain the biochar amended soil. After 15 and 60 days of incubation, we collected the amended soils and detected contents of DTPA extractable Cd in all spiked soils.

2.4 Sorption isotherms of Cd\(^{2+}\) onto biochar

Sorption kinetics and isotherms of Cd\(^{2+}\) onto soil were performed by adding 25 mL Cd(NO\(_3\))\(_2\) solution to 1.00 g pristine or modified biochar samples, 0.01 mol/L NaNO\(_3\) was added as a background electrolyte solution. For the sorption kinetics tests, 10 mg/L Cd(NO\(_3\))\(_2\) was added to above solutions, and soil pH was adjusted at 6.0 by adding NaOH and HNO\(_3\) for several times and readjusted before use. After that, these bottles were continuously shaken for 1,2,4,8,12,24 h separately at 25 °C, then the supernatant solutions were separated by centrifugation at 9000×g for 10 min, and then filtered through a 0.45 μm filter. Contents of Cd\(^{2+}\) in solutions were detected by ICP-OES (Prodigy, Leeman, USA), and the amounts of Cd\(^{2+}\) sorbed onto biochar were calculated. Three replications for each treatment.

For the sorption isotherms tests, concentrations of added Cd\(^{2+}\) were 0, 2, 10, 20, 50 and 100 mg/L, respectively. Mixtures were stored in a 80 mL polypropylene bottle, and soil pH was adjusted at 6.0 by adding NaOH and HNO\(_3\) for several times and readjusted before use. After that, these bottles were continuously shaken for 12 h at 25 °C, then performed as the above operation. Finally, the amounts of Cd\(^{2+}\) sorbed onto biochar were calculated. Three replications for each treatment.

Langmuir and Freundlich models were introduced to simulate the sorption behavior of Cd\(^{2+}\) onto biochar. Equations are expressed respectively as follow.
Langmuir = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)

Freundlich = K_f C_e^n \quad (2)

where \( C_e \) denotes the equilibrium concentration of \( \text{Cd}^{2+} \) in solution (mg/L), \( q_m \) denotes the maximal monolayer sorption capacity of \( \text{Cd}^{2+} \) onto pristine or modified biochar (mg/g), \( K_L \) denotes a constant related to sorption energy (L/g). \( q_e \) denotes the sorbed (mg/g) quantity of \( \text{Cd}^{2+} \); \( K_f \) and \( n \) denote the estimated constants of the sorption capacity and intensity, respectively.

2.5 Data analysis
Data are presented as mean ± SD (n = 3). Charts and graphs were drawn by Sigmaplot 10.0.

3 Results and Discussions

3.1 Sorption behaviors of \( \text{Cd}^{2+} \) onto biochar
As shown in figure 1a, sorption kinetics and isotherms of \( \text{Cd}^{2+} \) onto pristine and modified biochars were analyzed. Results showed that adsorption capacity of \( \text{Cd}^{2+} \) onto different biochars increased with the incubation time. The curve of sorption kinetics indicated that sorption behaviors of \( \text{Cd}^{2+} \) by biochar generally achieve equilibrium at 12h. Similar results were reported by Wang et al. [11], adsorption of \( \text{Cu}^{2+} \) onto calcium hydroxyapatite (HAP) occurs quickly and 12h was chosen for the adsorption isotherm experiment. As shown in figure 1b, the quantity of \( \text{Cd}^{2+} \) adsorbed onto biochar increased with the increase of \( \text{Cd}^{2+} \) contents in equilibrium solutions. The adsorption mechanisms for \( \text{Cd}^{2+} \) onto biochar included the electrostatic attraction of \( \text{Cd}^{2+} \) by negative charged biochar. Langmuir and Freundlich equations were applied to model the sorption isotherm of \( \text{Cd}^{2+} \), and shown in table 1. Data showed that Langmuir rather than Freundlich equation is better to analyze the sorption isotherms of \( \text{Cd}^{2+} \) onto investigated biochars. Values of \( q_m \) for different biochars indicated PRB has the highest sorption capacity of \( \text{Cd}^{2+} \), followed by RB, CWB, RB, CRB and PWB. As detected, CB and its modified materials such as PCB and CCB were not suitable for \( \text{Cd} \) stabilization, and we would not use them in our later experiments. Phosphate and chitosan modified biochar could enhance the adsorption capacity of metal ions through electrostatic effect, precipitation and surface complexation [9,10].

Figure 1. Sorption kinetics (a) and isotherms (b) of \( \text{Cd}^{2+} \) onto pristine or modified biochars.
Table 1. Data of Cd isothermal sorption on soils fitted with different equations.

| Model | Parameter | WB | CB | RB | PWB | PCB | PRB | CWB | CCB | CRB |
|-------|-----------|----|----|----|-----|-----|-----|-----|-----|-----|
|       | \( q_m (\text{mmol/kg}) \) | 5.16 | 0.99 | 219.97 | 14.23 | 2.33 | 302.89 | 104.04 | 6.81 | 90.36 |
|       | \( K_L (L/kg) \) | 0.0278 | 0.0875 | 0.0016 | 0.0268 | 0.1051 | 0.0013 | 0.0059 | 0.0488 | 0.0075 |
|       | \( r^2 \) | 0.9963 | 0.9786 | 0.9912 | 0.9948 | 0.9643 | 0.9910 | 0.9982 | 0.9941 | 0.9990 |
| Freundlich | \( K_f (\text{mmol/kg}) \) | 0.27 | 0.15 | 0.36 | 0.69 | 0.45 | 0.50 | 0.83 | 0.61 | 0.94 |
|       | \( n \) | 0.6123 | 0.436 | 0.977 | 0.6295 | 0.3831 | 0.9299 | 0.8551 | 0.5314 | 0.8315 |
|       | \( r^2 \) | 0.9965 | 0.9125 | 0.9928 | 0.9923 | 0.9106 | 0.9923 | 0.9987 | 0.9720 | 0.9988 |

3.2 Soil pH and DTPA extractable Cd respond to biochar amendment

As detected in section 3.1, WB, RB and their modified biochars were chosen to remediate Cd-contaminated soil in this study. As shown in table 2, RB and its modified biochars (PRB and CRB) amended soils had higher pH values than soil amended with WB and its modified biochars. Soil pH values increased with the increasing of biochar dosage. However, soils amended with phosphate modified biochars always had lower pH than their pristine biochars, and soil amended with chitosan modified biochars had the highest values of pH. Soil pH played an important role in regulating heavy metal bioavailability, mainly through the dynamic of precipitation-dissolution process [2].

Contents of DTPA-extractable metals always have better correlations with metal accumulated in plants, than contents of total metals in soil [12]. Thus, we compared the stabilization efficiency of biochars (types, rates and incubation time) on soil Cd, based on the contents of DTPA-extractable Cd in soils (figure 2). Results showed that contents of DTPA-extractable Cd decreased with biochar addition and the increase of biochar rates, which is in accordance with soil pH. Chitosan modified biochars (CWB and CRB) had higher immobilization efficiencies than the phosphate modified biochars, followed by the pristine biochars. During 15 days of incubation, the highest immobilization efficiency of 46.5% was found in soil amended with 2% CRB biochar. DTPA-extractable Cd significantly decreased with the increase of incubation time, as shown in figure 2b. However, no significant decrease was found in soils amended with modified biochars. Among different types, soils amended with CRB always had the lowest contents of DTPA-extractable Cd, also decreased with the increase of biochar rates. During 60 days of incubation, a highest immobilization efficiency of 43.8% was found in soil amended with 5% CRB biochar. Therefore, we suggested that CRB can be a suitable type of biochar for soil Cd immobilization in our study. However, further studies still needed to decrease the content of DTPA-extractable Cd to meet the soil environmental quality standard.

Table 2. Data of soil pH responded to soil amended with pristine or modified biochar, at different dosage and incubation time.

|       | 0.50% | 2% | 5% |
|-------|-------|----|----|
|       | 15d   | 60d | 15d | 60d | 15d | 60d |
| Control | 6.95±0.049 | 7.09±0.052 | 6.95±0.049 | 7.09±0.052 | 6.95±0.049 | 7.09±0.052 |
| WB     | 7.04±0.059 | 7.06±0.021 | 7.19±0.062 | 7.24±0.024 | 7.51±0.030 | 7.58±0.008 |
| RB     | 7.09±0.086 | 7.22±0.030 | 7.53±0.066 | 7.60±0.026 | 8.58±0.014 | 8.47±0.030 |
| PWB    | 6.95±0.087 | 7.22±0.103 | 7.04±0.131 | 6.70±0.506 | 8.06±0.015 | 8.13±0.050 |
| PRB    | 7.02±0.014 | 7.24±0.105 | 7.77±0.140 | 7.65±0.141 | 8.85±0.149 | 8.93±0.055 |
| CWB    | 7.51±0.029 | 7.44±0.189 | 8.47±0.529 | 8.64±1.057 | 9.81±0.004 | 10.04±0.039 |
| CRB    | 8.44±0.013 | 8.43±0.071 | 9.86±0.044 | 10.16±0.055 | 10.01±0.028 | 10.50±0.060 |
4. Conclusions
Our study showed that adsorption of Cd$^{2+}$ onto different types of biochar fit Langmuir equation better than Freundlich equation ($r^2 > 0.960$). The adsorption capacity of Cd$^{2+}$ onto biochars followed the order of PRB < RB < CWB < CRB < PWB < CCB < WB < PCB < CB. Chitosan modified biochar (CWB, CRB) treated soils had higher pH values than phosphate modified biochar treatments. In accordance with soil pH values, chitosan modified biochar treated soils had the lowest contents of DTPA-extractable Cd than phosphate modified and pristine biochar treatments. The immobilization efficiency of biochar increased with the increasing of biochar dosage. Among different types of biochars, CRB was the most suitable for the remediation of Cd-contaminated soil.

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References
[1] Chen, HY., Teng, YG., Lu, SJ., et al. (2015). Contamination features and health risk of soil heavy metals in China. Science of The Total Environment, 512-513: 143-153.
[2] Chen, Q., Peng, PQ., Hou, HB., et al. (2019). Effects of soil properties on the Cd threshold in typical paddy soils using BCR sequential extraction. Human and Ecological Risk Assessment: An International Journal, 25(8): 2160-2173.
[3] Louzon, M., Pelfrêne, A., Pauget, B., et al. (2020). Bioaccessibility of metal(loid)s in soils to humans and their bioavailability to snails: A way to associate human health and ecotoxicological risk assessment? Journal of hazardous materials, 384:121432-121432.
[4] Ahmad, M., Rajapaksha, A.U., Lim, J.E., et al. (2014). Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere, 99: 19-33.
[5] Xu, D., Zhao, Y., Sun, K., et al. (2014). Cadmium adsorption on plant- and manure-derived biochar and biochar-amended sandy soils: Impact of bulk and surface properties. Chemosphere, 111: 320-326.
[6] Ma, SC., Zhang, HB., Ma, ST., et al. (2015). Effects of mine wastewater irrigation on activities of soil enzymes and physiological properties, heavy metal uptake and grain yield in winter wheat. Ecotoxicology and Environmental Safety, 113: 483-490.
[7] Deng, JQ., Liu, YG., Liu, SB., et al. (2017). Competitive adsorption of Pb(II), Cd(II) and Cu(II) onto chitosan-pyro-mellitic dianhydride modified biochar. Journal of Colloid and Interface Science, 506:355-364.

[8] Xiao, WD., Ye, XZ., Zhang, Q., et al. (2018). Evaluation of cadmium transfer from soil to leafy vegetables: Influencing factors, transfer models, and indication of soil threshold contents. Ecotoxicology and Environmental Safety, 164:355-362.

[9] Zhang, H., Shao, JG., Zhang, SH., et al. (2019). Effect of Phosphorus-Modified Biochars on Immobilization of Cu (II), Cd (II), and As (V) in Paddy Soil. Journal of Hazardous Materials, 390: 121349-121349.

[10] Zhou, YM., Gao, B., Zimmerman, A.R., et al. (2013). Sorption of heavy metals on chitosan-modified biochars and its biological effects. Chemical Engineering Journal, 231: 512-518.

[11] Wang YJ., Chen JH., Cui YX., et al. (2009). Effects of low-molecular-weight organic acids on Cu(II) adsorption onto hydroxyapatite nanoparticles. Journal of hazardous materials, 162(2-3):1135-1140.

[12] Dai J., Thierry B., James H.R., Georges R., et al. (2004). Heavy metal accumulation by two earthworm species and its relationship to total and DTPA-extractable metals in soils. Soil biology & biochemistry, 36(1): 91-98.