Sorption of cadmium by rice husk char, bamboo char, and coconut shell char in aqueous solutions

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Abstract. Cadmium (Cd) is a byproduct of zinc production. It has a high solubility, mobility and biological accumulation leading to a risk of bone and kidney damage after long-term exposure. Sorption is an effective method to treat Cd-contaminated water. As a great potential contaminant sorbent, biochar can be produced from rice husk, coconut shell and bamboo under their respective optimum conditions for the sorption of toxic metal ions were used as representatives. Sorption models of kinetics and isotherms were used to fit the experimental results. Pseudo-first-order models fitted the data better than pseudo-second-order for all types of biochar. The Cd$^{2+}$ sorption capacity of coconut shell char and bamboo char was higher than rice husk char (7.3723 mg/g ≈ 7.3835 mg/g > 5.0345 mg/g). Freundlich model fitted the results of coconut shell biochar and bamboo biochar better than Langmuir model, which indicate a strong bond for Cd$^{2+}$ sorption. In contrast, for rice husk biochar Langmuir model fitted the results better than Freundlich model indicating monolayer sorption mechanism dominated the sorption.

1. Introduction
As a byproduct of zinc production. Cd$^{2+}$ has a high solubility, mobility, and biological accumulation [1]. It may lead to bone and kidney damage after long-term exposure [2, 3]. Thus, Cd has become a significant concern for human health and ecological safety [2]. Methods such as coagulation, chemical precipitation, ion exchange and electrokinetic method have been developed to remove Cd$^{2+}$ from water or soil. However, all these methods either need high cost or generate a significant amount of sludge which is required to treat for safety. For a better choice, sorption is widely used to treat Cd-contaminated water, especially at low concentrations.

Recently, techniques have been developed to produce biochar with enhanced sorption ability to Cd$^{2+}$ in water [4-6]. Biochar produced from waste biomass such as agricultural and forestry residues have shown good sorption ability to Cd$^{2+}$ in both aqueous solutions and soil environment. In Ehsan et al.’ study [7], extractability of Cd$^{2+}$ and its mobility in soil was reduced using biochar derived from...
unfertilized dates. Broiler litter-derived biochars also may enhance the immobilization of Cd\textsuperscript{2+} in soil by positive effect of chars on pH [8]. Solution chemistry, such as pH and ionic strength, may affect the sorption of organics onto biochar. Cheng et al. [9] found that the peanut husk biochar has an optimum condition for Cd\textsuperscript{2+} removal (99.9\%) at pH 5. Therefore, different biochar has not equally effective for sorbing Cd\textsuperscript{2+} in soil and water systems. They should be tested in model aqueous solutions before their application on a large scale. Additionally, the properties of target contaminants should also be considered carefully.

The objective of this study is to investigate the influence of feed type of biochar on sorption capacity of the selected biochars to Cd\textsuperscript{2+} under different water systems. The biochar combusted from the rice husk, coconut shell, and bamboo stem were employed as examples for the most used feed types of biochar production. A range of experiments was conducted to evaluate the sorption ability of three selected biochar to Cd\textsuperscript{2+}. Sorption kinetics and isotherms were determined, and sorption models were fitted to study the sorption mechanisms between biochar and Cd\textsuperscript{2+}.

2. Material and methods

2.1. Materials

Stock solutions of 0.1 M Cd\textsubscript{(NO\textsubscript{3})\textsubscript{2}} were prepared by dissolving analytical-grade Cd\textsubscript{(NO\textsubscript{3})\textsubscript{2}} in Millipore water. Cd\textsuperscript{2+} stock solution was prepared by dissolving Cd\textsubscript{(NO\textsubscript{3})\textsubscript{2}} in ultrapure water, and the Cd\textsuperscript{2+} concentration in the stock solution was 200 mg/L.

2.2. Biochar production

Coconut shell char, bamboo char, and rice husk char were used in the experiments. The coconut shell char used in the study was a commercial product from a local producer using a batch pyrolysis temperature at 900 \degree C. The bamboo biochar produced by pyrolysis process with the temperature at 750 \degree C and three h retention. The rice husk char was produced using a continuous slow pyrolysis at a final temperature of 350 \degree C with a retention time of 30 min. Before use, all three biochars were crushed and sieved to obtain particles with sizes less than 2 mm.

2.3. Biochar characterization

Carbon (C), hydrogen (H), and nitrogen (N) contents in the samples were analyzed using a CHN Elemental Analyzer (Carlo-Erba NA-1500). Surface areas of the samples were determined with a Quantachrome Autosorb-1 surface area analyzer using Brunauer–Emmett–Teller (BET) method. Surface morphology of the samples was determined using scanning electron microscopy (SEM) (JEOLJSM-6400, Japan) equipped with an energy dispersive X-ray fluorescence spectroscopy (EDS, Oxford Instruments Link ISIS) for analyzing surface elements. The pH of the used biochar was measured by addition 100 mg biochar into 10 ml deionized water after 5 min shaking.

![SEM image of the biochar used in the study](image)

**Figure 1.** SEM image of the biochar used in the study.
Table 1. Physicochemical properties of the biochars

| Property              | Coconut shell char | Bamboo char | Rice husk char |
|-----------------------|--------------------|-------------|---------------|
| pH (H₂O)              | 9.8                | 9.16        | 9.3           |
| Total C (g/kg)        | 923                | 834         | 512           |
| Total N (g/kg)        | 5.6                | 11.5        | 11.6          |
| Total H (g/kg)        | 32.1               | 16.9        | 19.2          |
| Ash (%)               | 10.3               | 9.9         | 38.3          |
| Surface area (BET) (m²/g) | 285.8              | 258.8       | 71.8          |

2.4. Sorption kinetics and isotherms

Sorption kinetics of Cd were investigated by adding 50 mg biochar into the centrifuge tube containing 10 ml Ca(NO₃)₂ solution (36 mg/L Cd²⁺) at room temperature (25± 0.5°C). The centrifuge tubes were then shaken at 50 rpm in a mechanical shaker. At different time intervals (5 min, 20 min, 30 min, 40 min, 50 min, 60 min and 120 min), vessels were withdrawn, and the mixtures were subsequently filtered through 0.22 µm pore size nylon membrane filters (GE cellulose nylon membrane). Cd²⁺ concentrations in the filtrates were determined by inductively coupled plasma-atomic emission spectrometry (ICP-OES, Optima 2300, Perkin-Elmer SCIEX, USA). The amount of Cd²⁺ adsorbed onto biochar was calculated from the differences between initial and final aqueous concentrations.

Sorption isotherms of Cd²⁺ onto biochar were determined by adding 50 mg sorbent to 10 mL centrifuge tubes 10 ml containing Ca(NO₃)₂ solution at room temperature (22 ±0.5°C). Cd²⁺ concentration in the centrifuge tubes ranged from 5 to 200 mg/L. The vessels were shaken in the mechanical shaker for 24 h, and the samples were then withdrawn and subsequently filtered to determine Cd²⁺ concentrations in the filtrate by ICP-OES measurement.

3. Results and discussion

3.1. Sorption kinetics

![Figure 2. Sorption kinetics data and fitted models of Cd²⁺ onto biochar](image-url)
A rapid initial phase and a much slow sorption phase were observed for the Cd\(^{2+}\) sorption onto biochar (Fig. 2). The maximum sorption capacities for all biochars were reached within the first hour of the experiments. Pseudo-first-order and pseudo-second-order were used to simulate the data of sorption kinetics (Table 2). Pseudo-first-order models fitted the data better than pseudo-second-order for all biochars (Table 1). The modeling results suggested that multiple mechanisms might control the sorption of Cd\(^{2+}\) onto the tested biochars. This phenomenon was probably because both the Cd\(^{2+}\) and functional groups on biochar surface can serve as sorption sites for the cations of toxic metal.

Based on the fitting parameters of pseudo-second-order, coconut shell biochar and bamboo biochar had very similar maximum sorption capacity for Cd\(^{2+}\) (7.3723 mg/g and 7.3835 mg/g respectively) after equilibration, but relatively low for rice husk biochar (5.0345 mg/g). This can be explained by the differences in surface area of the selected biochars. From our BET test, the higher surface area of coconut shell biochar (285.8 m\(^2\)/g) and bamboo char (258.8 m\(^2\)/g) than that of rice husk char (71.8 m\(^2\)/g).

### 3.2. Sorption isotherms

| Sorbent          | Kinetics and isotherm models/equation | Parameter-1 | Parameter-2 | R\(^2\)  |
|------------------|---------------------------------------|-------------|-------------|---------|
| Coconut shell char | Pseudo-first-order \( q_t = q_e(1 - e^{-k_1t}) \) | \( q_e=7.1750 \) | \( k_1=0.3711 \) | 0.9437  |
|                   | Pseudo-second-order \( q_t = \frac{k_2q_e^2}{1 + q_ek_2t} \) | \( q_e=7.3723 \) | \( k_2=0.1246 \) | 0.9982  |
|                   | Langmuir \( q_e = \frac{KQ_{\text{max}}C_e}{1 + KC_e} \) | \( K=0.4236 \) | \( Q_{\text{max}}=21.9609 \) | 0.9555  |
|                   | Freundlich \( q_e = K_fC_e^{1/n} \) | \( K_f=6.7484 \) | \( 1/n=0.4090 \) | 0.9886  |

| Bamboo char       | Pseudo-first-order \( q_t = q_e(1 - e^{-k_1t}) \) | \( q_e=7.2966 \) | \( k_1=0.5205 \) | 0.9430  |
|                   | Pseudo-second-order \( q_t = \frac{k_2q_e^2}{1 + q_ek_2t} \) | \( q_e=7.3835 \) | \( k_2=0.2904 \) | 0.9957  |
|                   | Langmuir \( K=2.3878 \) \( Q_{\text{max}}=20.1463 \) | \( 1/n=0.3924 \) | 0.9638  |
|                   | Freundlich \( K_f=6.1341 \) \( 1/n=0.4090 \) | 0.9555  |

| Rice husk char    | Pseudo-first-order \( q_t = q_e(1 - e^{-k_1t}) \) | \( q_e=4.8171 \) | \( k_1=0.2915 \) | 0.9274  |
|                   | Pseudo-second-order \( q_t = \frac{k_2q_e^2}{1 + q_ek_2t} \) | \( q_e=5.0345 \) | \( k_2=0.1099 \) | 0.9964  |
|                   | Langmuir \( K=1.8515 \) \( Q_{\text{max}}=18.6875 \) | \( 1/n=0.3924 \) | 0.9711  |
|                   | Freundlich \( K_f=6.1088 \) \( 1/n=0.4677 \) | 0.9051  |

Sorption isotherms of Cd\(^{2+}\) onto biochars were investigated (Fig. 3). The maximum content of the sorbed Cd\(^{2+}\) increased with the initial Cd\(^{2+}\) concentration in solution. Isotherm equations of Langmuir and Freundlich were used to fit the experimental results (Table 2). The correlation coefficients (R\(^2\)) derived from the Freundlich equations for coconut shell char and bamboo char were above 0.96, indicating that Freundlich model fitted the results better than Langmuir model. The Freundlich model is a semi-empirical equation, which describes surface sorption and multi-layer sorption under various non-ideal conditions. The fitted parameter 1/n were both below 1 for coconut shell char and bamboo char, suggesting a strong sorption bond for Cd\(^{2+}\). This sorption may be introduced by heterogeneous media where high energy sites were occupied first, followed by sorption at lower energy sites. In contrast, the results of rice husk char had a better fitting for Langmuir model than Freundlich model. This is due to the monolayer sorption mechanism dominated the sorption.
4. Conclusion

Biochar produced from rice husk, coconut shell, and bamboo under their respective optimum conditions were used as representatives for the sorption of toxic metal ions in this study. The objective is to investigate the influence of feedstock type on sorption capacity to $\text{Cd}^{2+}$ under different water system conditions. Sorption models of kinetics and isotherms were used to fit the experimental results. Based on the fitting parameters of pseudo-first-order, the Cd sorption capacity of coconut shell char and bamboo char was higher than rice husk char ($7.3723 \text{ mg/g} \approx 7.3835 \text{ mg/g} > 5.0345 \text{ mg/g}$). Pseudo-first-order models fitted the data better than pseudo-second-order for all types of biochar. This suggested that the sorption of toxic metal ions onto the tested biochars might be controlled by multiple mechanisms. Freundlich model fitted the results of coconut shell char and bamboo char better than Langmuir model, which indicated a strong sorption bond for $\text{Cd}^{2+}$. In contrast, for rice husk char Langmuir model fitted the results better than Freundlich model indicating monolayer sorption mechanism dominated the experiments. Therefore, the feedstock type needs to be carefully considered before biochar’s application.

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References

[1] Y.Z. Liu, T.F. Xiao, Z.P. Ning, H.J. Li, J. Tang, G.Z. Zhou, High cadmium concentration in soil in the Three Gorges region: Geogenic source and potential bioavailability, Applied Geochemistry. 37 (2013) 149-156.

[2] K. Perronnet, C. Schwartz, E. Gerard, J.L. Morel, Availability of cadmium and zinc accumulated in the leaves of Thlaspi caerulescens incorporated into soil, Plant and Soil. 227 (2000) 257-263.

[3] M.B. Mcbride, B.K. Richards, T. Steenhuis, J.J. Russo, S. Sauvè, Mobility and Solubility of Toxic Metals and Nutrients in Soil Fifteen Years After Sludge Application, Soil Science. 162 (1997) 487-500.

[4] H. Wang, B. Gao, S. Wang, J. Fang, Y. Xue, K. Yang, Removal of Pb (II), Cu(II), and Cd(II) from aqueous solutions by biochar derived from KMnO4 treated hickory wood, Bioresource Technology. 197 (2015) 356-362.

[5] J. Zhang, M. Liu, T. Yang, K. Yang, H. Wang, A novel magnetic biochar from sewage sludge: synthesis and its application for the removal of malachite green from wastewater, Water Science and Technology. 74 (2016) 1971-1979.

[6] X. Zhang, Y. Wu, Application of coupled zero-valent iron/biochar system for degradation of chlorobenzene-contaminated groundwater, Water Science and Technology. 75 (2017) 571-580.

[7] M. Ehsan, M.A. Barakat, D.Z. Husein, S.M. Ismail, Immobilization of Ni and Cd in Soil by Biochar Derived From Unfertilized Dates, Water Air and Soil Pollution. 225(2014).

[8] M. Uchimiya, I.M. Lima, K.T. Klasson, L.H. Wartelle, Contaminant immobilization and nutrient release by biochar soil amendment: Roles of natural organic matter, Chemosphere. 80 (2010) 935-940.

[9] Q.M. Cheng, Q. Huang, S. Khan, Y.J. Liu, Z.N. Liao, G. Li, Y.S. Ok, Adsorption of Cd by peanut husks and peanut husk biochar from aqueous solutions, Ecological Engineering. 87 (2016) 240-245.