



# Comparison of rice husk- and dairy manure-derived biochars for simultaneously removing heavy metals from aqueous solutions: Role of mineral components in biochars



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## HIGHLIGHTS

- Dairy manure biochar was more effective than rice husk biochar in removing Pb, Cu, Zn, and Cd.
- Dairy manure biochar showed less competitive sorption of metals than rice husk biochar.
- Precipitation with  $\text{CO}_3^{2-}$  or  $\text{PO}_4^{3-}$  was mainly responsible for the metal removal by the manure biochar.
- Removal of metals by rice husk biochar was mainly due to their complexation with phenolic  $-\text{OH}$ .

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## ABSTRACT

Rice husk biochar (RHBC) and dairy manure biochar (DMBC) were prepared as sorbents for simultaneously removing Pb, Cu, Zn, and Cd from aqueous solutions. DMBC was more effective in removing all the four heavy metals than RHBC, with the removal capacities of above  $486 \text{ mmol kg}^{-1}$  for each metal, much higher than those of RHBC ( $65.5\text{--}140 \text{ mmol kg}^{-1}$ ). RHBC showed stronger competition for metal removal than DMBC when the four metals coexisted, with Pb the least affected and Cd the most inhibited. When each metal was 1 mM in the multi-metal system, the metal removal by RHBC was reduced by 38.4–100%, much higher than that reduced by 2–40.9% for DMBC. The stronger competition for metals removal by RHBC was due to the fact that all metals competed only for the ionized phenolic- $\text{O}^-$  groups, while the removal of metals by DMBC resulted not only from the complexation with ionized hydroxyl- $\text{O}^-$  groups but also from the precipitation of metals with  $\text{CO}_3^{2-}$  and/or  $\text{PO}_4^{3-}$  that were rich in DMBC, resulting in less competition. The different mechanisms for the removal of metals by the two biochars were evidenced by the instrumental analysis of XRD, FTIR, and SEM as well as chemical modeling of Visual MINTEQ. Results indicated the waste biomass can be converted into value-added biochar as sorbents for removal of heavy metals and the removal ability varies with different biochar feedstock sources where the mineral components such as  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$  originated from the feedstock play an important role in the sorption nature of biochar.

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## 1. Introduction

Turning biomass into biochar followed by its application into soil is receiving more and more attention due to its ability to increase the long-term soil carbon pool (Lehmann, 2007; Nguyen et al., 2009). Biochar has a relatively structured carbon matrix with high degree of porosity and extensive surface area, allowing that it may act as a surface sorbent which is similar in some aspects to activated carbon and thereby plays an important role in controlling contaminants in the environment (Chen et al., 2011; Beesley et al., 2011; Beesley and Dickinson, 2011).

A variety of waste biomass have been converted into biochar as a sorbent for removing contaminants from waste water (Ippolito et al., 2012). Biochars prepared from plant wastes such as pine wood, crop residue, hardwood, corn straw, and sugar beet tailing have been shown to sorb significant amounts of Pb, Cu, Zn, and Cr in aqueous solution (Qiu et al., 2008; Chen et al., 2011; Dong et al., 2011). Biochars derived from animal wastes such as broiler litter and dairy manure could immobilize Cu, Cd, Ni, and Pb (Cao et al., 2009; Uchimiya et al., 2010). The high sorption ability of biochar may be resulted from the three reasons (Sohi et al., 2010): (i) electrostatic interactions between metal cations and negatively charged carbon surface; (ii) ionic exchange between ionizable protons at the surface of acidic carbon and metal cations; and (iii) sorptive interaction involving delocalized  $\pi$  electrons of

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carbon. Uchimiya et al. (2010) attributed immobilization of Cd, Cu, Ni, and Pb in soil and water by broiler litter biochar to cation exchange and  $\pi$  electrons (C=C), while Cao et al. (2009) indicated that high affinities for Pb by dairy manure biochar is mainly due to precipitation of Pb phosphate and carbonate minerals. Oxidation-reduction could happen during the sorption process. For instance, Cr(VI) removal by sugar beet tailing biochar is due to reduction of Cr(VI) to Cr(III) ion followed by its complexation with biochar (Dong et al., 2011).

Most work has been done on the single metal sorption by biochars, however, due to a common geological source (Pierzynski et al., 2005), or co-disposal (Deprez et al., 1999), heavy metals such as Pb, Cu, Zn, and Cd often coexist in contaminated water (Mielke et al., 2000; Zwonitzer et al., 2003). Their association and interactions with one another and with other environmental components are known to influence their mobility (Mingorance and Oliva, 2006). Therefore, it would be desirable to develop a cost-effective sorbent that can remove metals from a multi-metal contaminated water. Our previous work demonstrated that dairy manure biochar was effective in individually sorbing Pb, Cu, Zn, or Cd from mono-metal aqueous solution (Cao et al., 2009; Xu et al., 2013). This study was conducted to determine the feasibility of dairy manure biochar for simultaneously removing the four metals from the multi-metal solution. Another biochar produced from rice husk was included for comparison. The mechanisms responsible for the metals removal by these two biochars were elucidated at molecular levels using fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), chemical speciation model, scanning electron microscopy (SEM), and X-ray dot mapping analysis.

## 2. Materials and methods

### 2.1. Preparation and characterization of biochar

The biochars used in this study were obtained from two waste biomasses, dairy manure and rice husk, through a typical slow pyrolysis process. The details on biochar preparation have been described previously (Cao and Harris, 2010). Briefly, the dried manure and rice husk were put in a stainless steel reactor and heated in a Muffle Furnace under  $O_2$ -limited condition at 350 °C for 4 h. The solid residue left in the reactor after heating was C-rich and called as biochar (Lehmann, 2007). The biochars derived from dairy manure and rice husk were referred to as DMBC and RHBC, respectively. The resulted biochars were ground and passed through 0.5-mm sieve for later characterization and sorption experiment.

The concentrations of C, H, and N in biochars were determined using the CHNS/O Analyzer. Minerals (P, Ca, Mg, K, Na, etc.) were analyzed using the USEPA Method 3050B (USEPA, 1986). Surface area was detected by nitrogen adsorption isotherms at 77 K using a Surface Area and Porosimetry Analyzer. The pH of biochar was measured using the pH/Ion 510 Bench Meter. Water soluble  $PO_4^{3-}$  and  $CO_3^{2-}$  were determined using ion chromatography. The morphology of biochar were analyzed using SEM. The surface organic functional groups present in the biochar were identified using FTIR.

### 2.2. Sorption test

The sorption experiment was performed in 60-mL polypropylene tubes by mixing 0.125 g biochar with 25 mL 0.01 M  $NaNO_3$  solution containing 0, 1, 2, 3, 4, and 5 mM Pb, Cu, Zn, and/or Cd for each which were used in the multi-metal and mono-metal systems, respectively. The mixture of biochar and metal solution was then shaken at 100 rpm until the equilibrium was reached. Preliminary experiment showed that sorption of DMBC and RHBC for all metals reached equilibrium after 8 h (data not shown). After

equilibrium, solid residue and liquid phases were separated by centrifugation at 4000 rpm for 15 min and the solution was filtered through a 0.22- $\mu$ m Millipore filter. The filtrate was immediately acidified to pH < 2 with concentrated  $HNO_3$  for determination of Pb, Cu, Zn, and Cd by atomic absorption spectroscopy (AAS). The solids retained on the filter were characterized by FTIR, SEM, XRD, and X-ray elemental dot mapping analysis (Cao et al., 2009; Xu et al., 2013).

### 2.3. Modeling of heavy metal speciation

25 mL of 0.01 M  $NaNO_3$  solution containing 5 mM Pb, Cu, Zn, and/or Cd was mixed with 0.125 g of biochar. After reaching equilibrium, separation of solid and liquid was conducted as done as in the sorption test section above. Half of the filtrate was collected for dissolved organic C (DOC) measurement using organic C analyzer and for anions ( $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $Cl^-$ ,  $NO_3^-$ , and  $CO_3^{2-}$ ) analysis using ion chromatography. Remaining filtrate was acidified to pH < 2 with  $HNO_3$  prior to analysis of Cu, Zn, Cd, Ca, Mg, Fe, Al, Mn, Na, and K using AAS. The analytical results including pH, DOC, anions, and cations were used in speciation model Visual MINTEQ (Gustafsson, 2010) to calculate metal species in both solid and liquid phases.

### 2.4. Quality control

All sorption experiments were conducted at ambient temperature and included three controls: de-ionized water, metal solution, and biochar + de-ionized water. Three replicates were used for each treatment. Solution pH was not controlled but recorded at the beginning and the end of the equilibration. Sorption of metals was calculated from the difference between initial and final solution concentrations after taking controls into account. Actually, the control effect was much less and can be negligible.

## 3. Results and discussion

### 3.1. Characteristics of biochars

The selected physical and chemical properties of the DMBC and RHBC biochars are shown in Table S1 in Supporting Information. RHBC had a higher specific surface area (SSA) than DMBC (27.8  $m^2 g^{-1}$  vs 5.61  $m^2 g^{-1}$ ). However, the SSA for both biochars were low, within the general range of biochars produced from various biomass (Shinogi and Kanri, 2003). SEM images revealed that both biochars were not homogeneous and RHBC had more pores than DMBC (Fig. S1 in Supporting Information), which is consistent with its relatively higher SSA (Table S1).

Both biochars were of alkalinity, but DMBC had higher pH than RHBC (9.81 vs 8.01) (Table S1). The difference in pH between two biochars may arise from their feedstock composition. Dairy manure contained a large amount of mineral elements (shown below) which may begin to separate from the organic matrix at the temperature of higher than 300 °C, increasing the biochar DMBC pH to almost 10 (Cao and Harris, 2010). Rice husk was rich in cellulose and hemicelluloses which could be decomposed around 300 °C, producing organic acids and phenolic substances that lowered the pH of the products (Abe et al., 1998).

As expected, both biochars were rich in C, especially RHBC which contained 38.6% C. However, DMBC contained higher mineral elements such as Ca, K, Mg, Fe, Al and Na, compared to the RH-biochar (Table S1). Richness of mineral elements originated from the dairy cow diet input for satisfying nutrient requirement of milk production (NRC, 2001). RHBC contained less amounts of mineral elements. For example, total P was only 0.26% in RHBC

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