



The sorption of heavy metals on thermally treated sediments with high organic matter content



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HIGHLIGHTS

- Sediment oxygen-containing functional groups decrease after pyrolysis.
- Cu(II) and Cd(II) sorption decrease with increasing pyrolysis temperature.
- Pyrolysis at 400 and 500 °C increases Pb(II) sorption.
- Small hydrated ionic radius of Pb(II) facilitate its diffusion into the pores.
- Treated sediments show higher sorption than natural adsorbents.

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ABSTRACT

A sediment sample with organic matter higher than 60% was thermally treated and the sorption of Cu(II), Cd(II), and Pb(II) was investigated and compared to evaluate the potential use of sediments with high organic matter content to produce biochar. Cu(II) and Cd(II) sorption generally decreased with increasing pyrolysis temperature, concurred with decreased oxygen-containing functional groups of the adsorbents. Sediment particles pyrolyzed at 400 and 500 °C showed higher sorption to Pb(II) than other temperatures. The small hydrated ionic radius of Pb(II) may enable its close contact with solid particles and thus facilitated the diffusion of Pb(II) into the pores and the formation of cation- π bond with aromatic structures generated by pyrolysis. The sorption of heavy metals in thermally treated sediment showed comparable sorption to or higher sorption than natural adsorbents and biochars from biomass, suggesting their possible significant impact on the transport and risk of heavy metals.

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1. Introduction

Biochar is a promising material for soil amendment (Atkinson et al., 2010; Sohi et al., 2010). Investigators have suggested that various source materials could be used for biochar production. These materials mostly were wasted particles with high organic matter content, including wood (such as sawdust) (Keiluweit et al., 2010), crop residues (such as straws) (Karaosmanoglu et al., 2000), and manures (Cao et al., 2009). Biochars produced from all these materials showed positive impacts to soil system. In addition, because of their large specific surface area, high pH values, microporous structure, active functional groups and rich cation exchange capacity, these biochars showed effective sorption to both organic and inorganic pollutants (Cao et al., 2009; Wang et al., 2011). Importantly, biochars were highly recalcitrant in soils, with reported residence time in the range of 100–1000 years. This

long residence time suggests that the above-mentioned positive impacts could be permanent.

Our previous studies have suggested that sediment particles with high organic matter content could be applied as an additional source for biochar production (Pan et al., 2012; Wu et al., 2013). For example, the sediment and peat around Dianchi Lake area (Yunnan, China) contain organic matter over 60% (Lu et al., 2009). Sediment dredging project produced tons of sediments. The local residence applied this sediment as solid fuel, or directly applied them in agricultural soil. The thermal treatment of these samples produced charred sample, and these treated samples showed higher effectiveness of carbon sequestration than the biochars produced from common biomass (Pan et al., 2012). The reason is that the formation of organo-mineral complex could protect carbon from been thermally or biologically oxidized. In addition, the sorption of both hydrophobic and ionic organic contaminants was strong and hysteresis (Wu et al., 2013), suggesting that these biochars could effectively retain organic pollutants. As one of the systematic study, this work focus on the sorption

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of heavy metals on these thermally treated sediment particles with high organic matter content.

Various mechanisms were proposed to describe heavy metal sorption on solid particles, such as cation exchange, complexation, electrostatic attraction, and cation- π bond (Bailey et al., 1999; Reddad et al., 2002). Among these mechanisms, the complexation between heavy metals and oxygen-containing functional groups is of great importance to retain heavy metals (Uchimiya et al., 2012). According to our previous comparison, sediment particles could retain more organic matter than common biomass during the pyrolysis, because of the interactions between organic matter and mineral particles. The protected oxygen-containing organic matter could provide additional sorption sites for heavy metals. Thus, our primary hypothesis is that these thermally treated sediment particles have high sorption to heavy metals.

Three heavy metals of Cu(II), Cd(II) and Pb(II), which are widely detected in the environment, were selected as model adsorbates to study their interaction mechanisms with biochars derived from Dianchi sediment with high organic matter content. The discussion regarding the difference between biochars from sediment and those from biomass will be highlighted. The sorption in natural adsorbents and biochars produced from different materials was compared based on literature summary.

2. Methods

2.1. Sample collection and thermal treatment of Dianchi Lake sediment

A sediment sample was collected from Dianchi Lake (24°51'N, 102°44'E; Fig. S1, Supplementary data). The sediment particles were freeze-dried and ground. Visible plant residues were picked out manually, and then the samples were passed through a 2 mm sieve. The prepared sediments were thermally-treated using a method analogous to biochar production using common biomass. Briefly, the pretreated sediment particles were heated at different temperatures in a muffle furnace. The oven was purged using continuously flowing pure nitrogen. The sediment particles (noted as YC) were spread on an aluminum foil and heated continuously for 4 h at 200 °C, 300 °C, 400 °C, and 500 °C and were designated as 2C, 3C, 4C, and 5C, respectively. After the 4-h heating process, nitrogen was kept continuously flowing until the temperature decreased to 50 °C. These thermally-treated sediments were then collected and contained in brown glass vials for further use.

The prepared samples were characterized for their physical and chemical properties. Their bulk elemental compositions were quantified using an elemental analyzer (MicroCube, Elementar, Germany) and the surface elemental compositions, with special focuses on C and O contents, were analyzed using an X-ray photoelectron spectrometer (PHI 5500). Their functional groups were characterized using a Fourier transform infrared spectrometer (Varian 640-IR, USA). The surface area, total pore volume, and pore size distribution were measured using both CO₂ and N₂ for comparison (Autosorb-1C, Quantachrome) (Table S1).

2.2. Batch adsorption experiments

NaCl was dissolved in ultrapure water (Milli-Q) at the concentration 10 mM as background solution. Cu(NO₃)₂·4H₂O, Cd(NO₃)₂·4H₂O and Pb(NO₃)₂ (all higher than analytical grade) were separately dissolved in the background solution at the concentrations of 200 mg/L as stock solutions. These stock solutions were sequentially diluted in background solution to eight different concentrations in the range of 10–100 mg/L. Specifically for the samples of 4C and 5C, Pb(II) sorption was one order of magnitude higher than the other samples based on preliminary experiment.

Therefore, for the adsorption experiment of Pb(II) on 4C and 5C, the stock solution was diluted to eight different concentrations in the range of 300–800 mg/L. Seven mg of the solid particles were weight and put into 8 mL vials, and then heavy metal solutions with different concentrations were separately added in the vials. All the vials were kept in dark and shaken in an air-bath shaker at 25 °C for 3 d. This equilibration condition was sufficient for the apparent sorption equilibrium according to preliminary experiments. The concentrations of heavy metals released from the original sediment particles and the thermally treated samples were below 0.05 mg/L, and thus will not significantly impact the sorption of the added heavy metals. The released heavy metals were subtracted from the aqueous phase during data processing.

2.3. Detection of heavy metals

After equilibrated for 3 d, all the vials were centrifuged at 1000g for 10 min and the supernatants were subjected to solute quantification. The concentrations of Cu(II), Cd(II) and Pb(II) ions in the supernatants were quantified using an atomic absorption spectrophotometer (AAS, Hitachi Z-2000). The amount of the metal ions adsorbed on biochars could be calculated by the difference between the initial concentration and the equilibrated aqueous-phase concentration. Solution pH at equilibrium was measured using a pH electrode (Leici Instruments, Shanghai, China).

2.4. Data analysis

Two widely applied models, Freundlich and Langmuir models, were used to fit the sorption isotherms in SigmaPlot 10.0. These models have the following expressions:

$$\text{Freundlich model: } Q_e = K_F C_e^n \quad (1)$$

$$\text{Langmuir model: } Q_e = Q_L^0 b C_e / (1 + b C_e) \quad (2)$$

In these models, Q_e (mg/kg) and C_e (mg/L) are equilibrium solid-phase and aqueous-phase concentrations, respectively. K_F [(mg/kg)/(mg/L) ^{n}] is the Freundlich sorption constant indicative of the relative adsorption capacity of the adsorbent, and n is the nonlinearity factor. Q_L^0 (mg/kg) is Langmuir adsorption capacity and b (L/kg) is Langmuir sorption coefficient (the constant related to the free energy of adsorption).

The single-point sorption coefficients were calculated using the following equations:

$$K_d = Q_e / C_e \quad (3)$$

where K_d (L/g) is the adsorption equilibrium constant at C_e . According to the experimental data, the representative aqueous concentrations of $C_e = 3.16$ mg/L and $C_e = 31.6$ mg/L were selected to calculate K_d based on isotherm modeling.

Because the number of data points used in model fitting was not the same for different sorption isotherms, the coefficient of determination (r^2) could not be compared directly. The adjusted r^2 (r_{adj}^2) was calculated and compared:

$$r_{adj}^2 = 1 - [(1 - r^2)(m - 1) / (m - a - 1)] \quad (4)$$

where m is the number of data points used for fitting, and a is the number of coefficients in the fitting equation.

3. Results and discussion

3.1. Sorption isotherms of heavy metals on biochars

The heavy metal sorption isotherms were fitted using Langmuir and Freundlich models and the resulted parameters along with the

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