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Cu(II) removal from aqueous solution by *Spartina alterniflora* derived biochar

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HIGHLIGHTS

- Biochar prepared from an invasive plant – *Spartina alterniflora*.
- 5 times higher removal capacity for Cu(II) was obtained.
- Surface complexation other than ions exchange contributes the Cu(II) removal.
- A 3-site model was proposed to characterize the complex surface of the char.
- Other mechanisms, such as Cπ–metal interaction, metal (hydr)oxide precipitation may involve.

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ABSTRACT

A cost-effective biochar (SABC) was prepared from *Spartina alterniflora* by pyrolysis at low temperatures ($\leqslant$500 °C) under anoxic conditions. The obtained biochar was examined for its ability to adsorb copper ions from aqueous solution and the Cu(II) removal mechanisms were explored. Cu(II) adsorption on SABC was found to fit well with Langmuir isotherm and pseudo-second-order kinetic model. The maximum Cu(II) adsorption capacity of SABC reached 48.49 mg g^{-1}, which is about 5 times higher than the raw biomass. Ion exchange had negligible effect on Cu(II) removal. Based on FTIR spectra and potentiometric titration, a complexation model including two acidic and one basic functional groups was proposed. However, metal ions complexation with the surface sites could not account for the uptake amounts of Cu(II) by SABC, alternative binding mechanisms might involve simultaneously.

1. Introduction

Heavy metals have become a particularly serious environmental issue because these contaminants can be accumulated by living organisms throughout the food chain as a non-biodegradable pollutant, causing adverse effects on human (Gündoğan et al., 2004). Copper is one of the most widely used toxic heavy metals and usually discharged from industrial effluents of metal cleaning and plating baths, paper, paperboard, refineries pulp and wood preservative-employing mills (Ajmal et al., 2005; Anirudhan and Radhakrishnan, 2008). In order to control the pollution caused by these emissions, numerous processes, such as chemical oxidation, precipitation, adsorption, ion exchange, reverse osmosis and membrane separation have been established (Eloussaief and Benzina, 2010). Among them, adsorption is an effective technology for the advantages of low cost and straightforward design (Mohammed et al., 2011). However, most commercial adsorbents (usually activated carbons) only have limited ability for heavy metals removal (Lima and Marschall, 2005). Moreover, the high cost of activated carbon hinders its practical application, which stimulates researchers to develop low-cost adsorbents (Velghe et al., 2012).

In recent years, adsorbents derived from agricultural and forest residues (usually biomass) received extensive attentions due to their wide availability, low cost and favorable physical/chemical surface characteristics for pollutants removal (Farooq et al., 2010; Chowdhury and Saha, 2011). Biomass derived biochar, usually generated from incomplete pyrolysis of carbon-rich materials, is regarded as a promising heavy metal adsorbent (Qiu et al., 2008) for its abundance of polar functional groups, such as carboxylic, hydroxyl and amino-groups which are favorable for heavy metals removal (Cao et al., 2009; Hsu et al., 2009; Wang et al., 2010).

Spartina alterniflora is a salt-marsh plant which is widely distributed in intertidal flats. In 1970–1990s, this species was introduced into the eastern coasts of China for land reclamation due to its great ability to reduce tidal wave energy, mitigate erosion and trap sediments. However, this plant can out-competes with native plants, threaten the natural ecosystems and coastal aqua-

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culture and cause declines in native species richness. Aims to make better use of these generous biomass materials, effort has been taken to transform *S. alterniflora* into activated carbon by pyrolyzing at 700 °C and subsequently activated by phosphoric acid (Li and Wang, 2009), but little information is available on the utilization of *S. alterniflora* biomass for biochar production by pyrolyzing under low temperature.

In this work, biochar derived from *S. alterniflora* was prepared under low temperature (400 °C) and the obtained adsorbent was tested for its ability to remove Cu(II) ions from aqueous solution. Equilibrium and kinetic experiments of Cu(II) adsorption on *S. alterniflora* derived biochar (SABC) were carried out. Furthermore, the mechanisms of Cu(II) removal by SABC were explored and discussed.

2. Methods

2.1. Preparation of adsorbent and adsorbate

S. alterniflora was obtained from Chongming Island, Shanghai, China. The collected material was washed by deionized water for three times and then air dried for several days. After the materials were oven dried at 105 °C for 24 h and ground to pass through a 50 mesh sieve, the raw biomass was (typically 5 g every time) pyrolyzed (at a heating rate 20 °C min^{-1}) in batch at 400 °C for 2 h and cooled to room temperature under a nitrogen flow rate of 50 mL min^{-1}. The obtained biochar was stored in a desiccator for experiment use.

All chemicals and reagents (Sinopharm Chemical Reagent Co., China) used in this experiment were AR-grade. Cu(II) solution was prepared by dissolving copper nitrate ($Cu(NO_3)_2$) in deionized water and pH values were adjusted by 0.1 M HCl or 0.1 M NaOH.

2.2. Characterization of adsorbent

TG-DTA-MS analysis of the raw biomass of *S. alterniflora* was performed using a Netzsch STA 449C thermoanalyzer under N_2 (140 mL min^{-1}) from 30 °C to 600 °C with a rate of 5 °C min^{-1}. The contents of C, H, N, and O in biochar were determined by elementary analysis (EuroVector EURO EA 3000 Elemental Analyzer). Specific surface area and porosity characteristics were analyzed by nitrogen adsorption at 77 K (Quantachrome, Quantasorb SI). Biochar sample was mixed with KBr at a ratio of 1:100 (w/w) and pressed into film. Infrared spectra were collected by a Thermo Scientific FTIR 380 spectrometer for wave numbers 400–4000 cm^{-1} at a scanning resolution of 4 cm^{-1}. The surface structure of biochar was characterized by a scanning electron microscopy (JEOLJSM6700). Potentiometric titration test was carried out in a HDPE reactor at 25 °C. At first, biochar sample was suspended in deionized water (0.5 g in 50 mL) and the suspension was fluxed by N_2 (50 mL min^{-1}) under magnetic stirring for 24 h. Subsequently, a known volume (50 μL) of 1 M NaOH was added to adjust the initial pH to 11, and then 0.1 M HCl was used to titrate the solution. After each addition of titrant (25 μL), the pH of the suspension was recorded (Delta320, Mettler Toledo) when a stable value is attained. Titration modeling was performed according to the method of Pagnanelli et al. (2008).

2.3. Adsorption experiments

Cu(II) adsorption on SABC was conducted by batch equilibrium test. Briefly, 50 mL Cu(II) solution and 0.5 g biochar sample were placed in a 150 mL HDPE bottle. The bottle was agitated in a temperature-controlled shaker (25 °C) at a rate of 100 rpm. At the end of adsorption, equilibrium pH was recorded (Delta320, Mettler Toledo) and the suspension was filtered through a 0.45-μm membrane using a syringe. The concentrations of Cu(II) and other metals in filtrate were determined by an inductive coupled plasma emission spectrometer (ICP-AES, Shimadzu, ICPS-7510). The amount of copper sorbed to biochar was calculated according to the following equation.

$$q_e = \frac{V(C_0 - C_e)}{W} \tag{1}$$

where q_e (mg g^{-1}) is the amount of Cu(II) adsorbed at equilibrium. C_0 and C_e (mg L^{-1}) are the initial and equilibrium Cu(II) concentration in solution. W (g) is the mass of biochar.

3. Results and discussion

3.1. Characteristics of SABC

Table 1 presents the results of BET and elementary analysis of SABC and the raw biomass of *S. alterniflora*. After pyrolysis, the specific surface area and average pore size of SABC increased significantly while the pore size kept almost unchanged. In addition, enrichments of C and N are found in SABC due to the release of volatile component during pyrolysis. Result of TG-DTA-MS analysis (Fig. S1) indicates *S. alterniflora* biomass experienced a significant weight loss (55%) at 200–400 °C. At the pyrolysis temperature (400 °C) employed in this experiment, most of hemicellulose and cellulose, as well as part of lignin in biomass are thermally decomposed (Hamelinck et al., 2005). The release of volatile components facilitated the generation of vascular bundles structure in SABC (Fig. S2) and thus improved the specific surface area and average pore size of biochar.

3.2. Cu(II) adsorption by SABC

3.2.1. Comparison between SABC and the raw biomass

Cu(II) adsorption by the raw biomass of *S. alterniflora* and SABC were tested under pH 6.0 and 25 °C. The results show these two things have significantly different adsorption behavior and capacity for Cu(II) (Fig. S3). At an initial concentration of 50 mg L^{-1}, Cu(II) uptake by the raw biomass of *S. alterniflora* was only 9.10 ± 0.38 mg g^{-1} and this value kept almost unchanged with the increase of the initial Cu(II) concentration. However, the amount of Cu(II) removed by SABC increased remarkably with the increase of Cu(II) concentration. When the initial Cu(II) concentration was 100 mg L^{-1}, the adsorption amounts of Cu(II) on SABC attained 43.83 ± 1.92 mg g^{-1}. Further elevating the initial Cu(II) concentration to 290 mg L^{-1} led to a tiny increase of Cu(II) removal by SABC (with a maximum of 49.14 ± 1.39 mg g^{-1}).

3.2.2. pH dependent Cu(II) adsorption on SABC

pH is a critical parameter in heavy metals adsorption as it affects both metal speciation and the protonation/deprotonation of

Table 1
Characteristics of *S. alterniflora* raw biomass and SABC.

	Unit	Raw biomass	SABC
BET analysis			
Specific surface area	m^2 g	1.926	2.365
Pore volume	cm^3 g	0.0030	0.0031
Average pore size	nm	5.98	9.15
Elemental analysis (w/w, dry base)			
C	%	46.44	63.60
H	%	10.37	4.29
N	%	14.24	21.07
O	%	28.94	11.06