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Improving abiotic reducing ability of hydrothermal biochar by low temperature oxidation under air

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HIGHLIGHTS

- 240 °C oxidization under air improving hydrochar reducing ability towards Fe(III).
- Carbonyl group supposed to be responsible for Fe^{3+} transformation to Fe^{2+}.
- Reducing ability be easily restored by further air-oxidization at 240 °C.
- Oxidized hydrochar + H_2O_2 show potential on organic degradation.

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ABSTRACT

Oxidized hydrothermal biochar was prepared by hydrothermal carbonization of *Spartina alterniflora* biomass (240 °C for 4 h) and subsequent oxidization (240 °C for 10 min) under air. Oxidized hydrochar achieved a Fe(III) reducing capacity of 2.15 mmol/g at pH 2.0 with 120 h, which is 1.2 times higher than un-oxidized hydrochar. Low temperature oxidization increases the contents of carboxyl and carbonyl groups on hydrochar surface. It is supposed that carboxyl groups provide bonding sites for soluble Fe species and carbonyl groups are responsible for Fe^{3+} reduction. A Fenton-like process was established with Fe^{2+} replaced by oxidized hydrochar and tested for methylene blue (MB) decoloration. Oxidized hydrochar achieved a MB decolorization (200 mg/L, pH 7.0) rate of 99.21% within 3 h and demonstrates prominent prevail over H_2O_2 absent control test. This study reveals low temperature oxidization is an effective way to improve and restore abiotic reducing ability of hydrochar.

1. Introduction

Biochar is the carbonaceous solid produced by thermochemical conversion of organic materials with the exclusion of oxygen and which has physiochemical properties suitable for safe and long-term storage of carbon in environment and, potentially, soil improvement (Shackley and Sohi, 2010). In recent years, biochar has attracted extensive attentions from environmental researchers due to its prominent benefit in contaminants elimination (Sun et al., 2011). Numerous studies reveal biochars obtained from slow pyrolysis of biomass and biowaste present excellent performance on the removal of heavy metals (Dong et al., 2011; Liu et al., 2013), phosphate (Yao et al., 2011) and organic pollutants (Sun et al., 2011) from aqueous phase, soil as well as sediment. The elimination of environmental contaminants by biochar involves multiple processes, such as complexation with surface functional groups, ions exchange, chemical precipitation, cation–π bonding for heavy metals (Uchimiya et al., 2010; Harvey et al., 2011) and partition onto noncarbonized organic medium as well as adsorption on carbonized phase *via* π–π interaction for organic matters (Ni et al., 2011). Apart from above mentioned mechanisms, recently published works indicate abiotic reduction by biochar also contributes to the removal of heavy metal ions. For example, Hsu et al. (2009a) suggested that Cr(VI) removal by biochar proceeds with two consecutive steps: (i) the sorption of Cr(VI) and (ii) the subsequent reduction of sorbed Cr(VI) to Cr(III). Dong et al. (2011) indicated that Cr(VI) reduction is highly related to hydroxyl and carboxylate groups on biochar while Shen et al. (2012) suggested that the transform of Cr(VI) to Cr(III) are mainly regulated by phenolic moieties in biochar, which both emphasize the important roles of oxygen-containing functional groups on abiotic reduction of oxidation state heavy metal ions.

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Hydrochar is a carbon-condensed material obtained from hydrothermal carbonization (HTC) of biomass/biowaste with deliberate purposes for fossil fuel substitution (Kang et al., 2012) or CO_2 biosequestration (Sevilla et al., 2011). Compared with other carbonization methods for biochar production, HTC receives more attention due to its mild preparation condition, easy operation (such as mechanical dewatering of biosolids) and low environmental impact (Kang et al., 2012). In addition, hydrochar and their derivatives were proven to have potential in soil amendment (Du et al., 2012), contaminants sorption (for heavy metal such as uranium (Kumar et al., 2011), copper, cadmium (Regmi et al., 2012) and organic matter such as bisphenol A, 17 α-ethinyl estradiol and phenanthrene (Sun et al., 2011)) and electrochemistry (Paraknowitsch et al., 2009), which are also interested by many investigators. In contrast to biochar produced from slow pyrolysis, hydrochar possesses more abundant oxygen-containing functional groups such as carboxyl, hydroxyl, phenolic hydroxyl, quinine and lactone on its surface due to aqueous environment of hydrothermal carbonization process (Sevilla et al., 2011). Therefore, it is supposed that hydrochar can serve as an effective reducing agent for environmental remediation. However, to our best knowledge, the information regarding to the reducibility of hydrochar is scarce.

In this paper, hydrochar were prepared from the biomass of *Spartina alterniflora* with the intention to evaluate their abiotic reducibility. Inspired by Chen et al. (2011), hydrochar samples were subjected to low-temperature oxidation under air to increase the quantities of oxygen-containing functional groups on HTC carbon surface. Hydrochar samples were characterized with elemental analysis, FT-IR and XPS and tested for its ability to reduce Fe(III) in aqueous solution under acidic pH. Fe(III) was chosen as the target of abiotic reduction process for two reasons: (i) the knowledge about reductive transform of Fe(III) to Fe(II) is well established; (ii) the information about the reducibility of hydrochar towards Fe(III) can be helpful to extend its practice application because most of contaminants degradation can be mediated or promoted by Fe redox transformation. Based on the result of Fe(III) reduction by hydrochar obtained in this experiment, a Fenton-like process was established and primarily tested for the decoloration of methylene blue (MB) with Fe being substituted by HTC carbon with the intention of developing possible application for the reducing ability of hydrochar.

2. Methods

2.1. Preparation of hydrochar samples

S. alterniflora biomass was obtained from Chongming Island, Shanghai, China. The collected biomass was washed by deionized water for three times to scour off impurity such as dust and air-dried for days. Raw biomass was cut into pieces, ground to pass through a 100 mesh sieve and oven-dried at 105 °C for 24 h.

For hydrochar preparation, biomass powder and deionized water were sufficiently mixed (10 g to 50 ml) and placed into a 100 ml poly(tetrafluoroethylene)-lined stainless steel autoclave. After nitrogen flow (100 ml/min for 10 min) purging through the mixed suspension (to get rid of oxygen dissolved in solution), hydrothermal carbonization reaction was performed at 240 °C for 4 h. Then, autoclave was cooled down to room temperature and the obtained solid powder (hydrochar) was centrifugally separated (3000 rpm for 10 min) and alternately washed by acetone and deionized water until aqueous pH was stable. Hydrochar powder was oven dried at 105 °C for 24 h and ground to pass through a 100 mesh sieve for further use. To acquire oxidized hydrochar, a 25 ml crucible laden with 1 g hydrochar was oven-heated in air at 240 °C for 10 min. After cooled to room temperature, oxidized hydrochar sample was ground to pass through a 100 mesh sieve for experiment use without further treatment.

2.2. Sample characterization

Elemental contents of C, H, N, and O in (oxidized) hydrochar and raw biomass were determined by an Elemental Analyzer (EA 3000 EuroVector EURO). BET surface area and pore structure of samples were determined by a Micromeritics ASAP 2020 using N_2 as adsorbate at −195.74 °C. Infrared spectra were collected by a Thermo Scientific FTIR 380 spectrometer for wave numbers at 400–4000 cm^{-1} with each sample mixed with KBr at a ratio of 1:100 (w/w). Surface morphology of samples were characterized by a scanning electron microscope (JEOL JSM6700) equipped with an energy dispersive spectroscopy detector. XPS (ESCALAB 250 Xi, USA) was used to determine elemental composition and chemical state of elements on sample surface. The contents of oxygen-containing functional groups on raw biomass and the resulting hydrochar were examined by Boehm titration, before which acidic and alkaline washing were performed for each sample to remove soluble species (Tsechansky and Graber, 2014). The structures of hydrochar and oxidized hydrochar were characterized by X-ray powder diffraction (XRD) by a D/max-2500 X-ray diffractometer with Cu-kα radiation (40 Kv, 250 Ma, λ = 0.1789 nm) at a scanning speed of 4°/min and a scan range 2θ of 5–80°.

2.3. Fe(III) reduction experiments

All chemicals and reagents (Sinopharm Chemical Reagent Co., China) used in experiment were AR-grade without further treatment. Fe(III) solution was prepared by dissolving ferric chloride ($FeCl_3$) in deionized water and pH values were adjusted by HCl and NaOH (0.1 M).

Fe(III) reduction by hydrochar was conducted *via* a series of batch equilibrium and kinetics tests. Typically, 50 ml Fe(III) solution and 0.05 g hydrochar sample were mixed in a 100 ml conical flask covered with aluminum foil. After high-purity N_2 purging (100 ml/min) for 10 min, each flask was airtightly sealed with stopper and agitated in a temperature-controlled shaker (25 °C) at a rate of 180 rpm. For predefined time interval, solid samples were separated from aqueous solutions by filtration and equilibrium pH was recorded by a pH meter (Delta320, Mettler Toledo). The concentrations of total iron and ferrous ions in solution were determined by phenanthroline spectrophotometry (752 N ultraviolet–visible spectrophotometer, China) and the difference between them is the concentration of Fe(III).

2.4. Fenton-like decoloration of methylene blue by hydrochar

Hydrochar based Fenton-like tests for MB decoloration were also performed in batch. In general, 0.1 g hydrochar, 50 mL Methylene blue solution (pH = 7.0, 200 mg/L) and 1 mL H_2O_2 (30%) were mixed in a 100 mL conical flask covered with aluminum foil. The flasks were agitated in a temperature-controlled shaker (25 °C) at a rate of 180 rpm. After predefined time intervals, solid samples were immediately separated from aqueous solutions by filtration and the concentrations of MB in solution were determined by spectrophotometry (752 N ultraviolet–visible spectrophotometer, China).