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Identifying the reducing capacity of biomass derived hydrochar with different post-treatment methods

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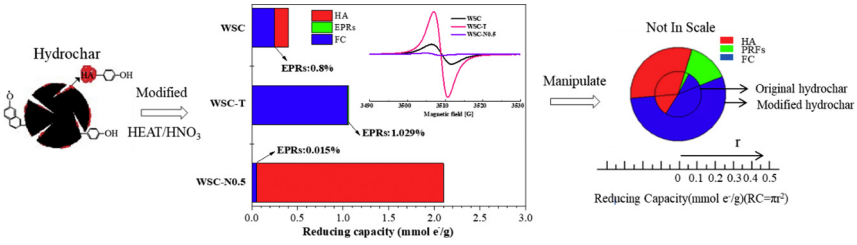
HIGHLIGHTS

- Major source of hydrochar reducing capacity (RC): oxygen-contained functionality (OFGs) and alkali-soluble substances;
- Persistent free radicals contribute less (~ 1%) to hydrochar RC;
- Thermal treatment increases hydrochar reducing capacity by developing oxygen-containing functional groups and persistent free radicals;
- HNO_3 oxidization increases hydrochar OFGs by generating alkali-soluble substances;

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, hydrochar was prepared from wheat straw (WS) and *Spartina alterniflora* (SA) biomass by hydrothermal carbonization, and further treated with HCl and NaOH washing, HNO_3 oxidization and low temperature thermal heating. The reducing capacity (RC) of sample was quantified by I_2 titration to explore how these modification methods affected the redox properties of hydrochar. The results indicated HNO_3 and thermal oxidization increased the RC of hydrochar by 2–5 folds while NaOH washing had the negative effect on samples' RC. By analyzing the excitation-emission matrix (EEM) fluorescence of alkaline extraction solution of sample, humic acid like substances generated from various methods were identified as one of the major sources for electron donating. HNO_3 oxidization could significantly increase the RC in hydrochar, which was likely resulting from the generation of alkali-soluble small molecule organic compounds. However, excessive oxidation by nitric acid with prolonged duration led to the gradual decrease in hydrochar's RC. Heating treatment caused a significant increase in the content of redox-active oxygen-containing functional groups and persistent free radicals (PFRs) in hydrochar. Even though both could donate electrons in the redox reaction with I_2, the former was considered a greater contributor for the RC of hydrochar. From this study, the origin of RC of hydrochar can be identified as: oxygen-containing functionality, humic-like matter and PFRs. By employing different modification methods, the RC of hydrochar could be tuned by regulating the above sources. This study provided fundamental knowledges and simple routes to manipulate the redox properties of hydrochar for different environmental applications.

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1. Introduction

Hydrochar is a type of carbon-condensed material obtained from the hydrothermal carbonization of biomass/biowaste (Sevilla et al., 2011). In recent years, hydrochar receives extensive attention due to its mild preparation condition and the ability to process wet feedstock without pre-drying (Kang et al., 2012). During hydrothermal carbonization, biomass/biowaste is heated with the presence of subcritical water and autogenous pressure and undergoes hydrolysis, dehydration, decarboxylation, aromatization and re-condensation reactions (He et al., 2013). Dependent on raw materials and reaction conditions, some genotoxic substances, such as polycyclic aromatic hydrocarbons, phenol and phenol derivatives, are likely to be produced during hydrothermal carbonization. These toxic substances can cause negative impact on seed germination and plant growth (George et al., 2012). However, Busch et al. (2013) revealed the toxic effect of hydrochar could be eliminated by chemical or biological methods and some post-treated hydrochars even showed positive stimulating effects. Owing to the aqueous circumstance of carbonization, the surface of hydrochar possesses abundant oxygen containing functional groups (Sevilla et al., 2011), which admits hydrochar with versatile functionalities and the great potentials in heavy metals and organic compounds immobilization. For example, Fang et al. (2015b) reported hydorchar can effectively remove methylene blue and lead via complexation with surface functional groups. Therefore, hydrochar is increasingly recognized as a promising environmental remediation material.

In recent years, a lot of experiments indicated that char can act as the electron shuttle to facilitate the biodegradation of organic compounds and take part in the abiotic reduction of heavy metals (Saquing et al., 2016; Xu et al., 2015). For example, the chemical transformation from Cr(VI) to Cr(III) was detected in Cr(VI) sorption by char, which was considered to be regulated by the phenolic moieties in carbonaceous materials (Dong et al., 2011; Shen et al., 2012). Kluepfel et al. (2014) characterized the redox properties of biochar and revealed that redox-active moieties are electron-donating phenolic groups for low temperature char, electron accepting quinone groups for intermediate temperature char, and quinones and condensed aromatics for high temperature char. However, to our best knowledge, little information is available on the redox property of hydrochar. In a recent work, Chen et al. (2017) reported hydrochar owns photochemical activity to generate reactive oxygen species for the degradation of organic contaminant which are associated with the surface redox active sites. Therefore, the elaborate application for pollution remediation requires sound knowledge on the redox property of hydrochars.

Hydrochar is different greatly from biochar in chemical properties. Published literatures revealed hydrothermal carbonization usually resulted in low degree carbonized char that mainly contained alkyl moieties with much less aromaticity (Cao et al., 2010). Therefore, the redox active conjugated π-electron system associated with condensed aromatic clusters can be ruled out from hydrochar. Our previous studies specified that hydrochar presented much more reducing capacity (RC) than oxidizing capacity (OC), and the RC was associated with the reductive moieties of hydrochar such as phenolic groups (Mai et al., 2017; Xu et al., 2014). This confirmed the surface functionality is one of the major source of electron donating in hydrochar. In addition, the characterization of char-derived dissolved organic matter (DOM) proved that humic-like substances are abundant in char, especially for those obtained under low temperature (Jamieson et al., 2014; Zhang et al., 2014). It is well known that humic-like substances are rich in reversible redox sites that can participate in a lot of redox transformation of organic and inorganic species in environment (Ratasuk and Nanny, 2007; Palmer and von Wandruszka, 2010). Therefore, DOM is supposed to make an important contribution to the redox property of hydrochar. In addition, recent studies reported that the carbonization process could produce a large number of persistent free radicals (PFRs) in char (Fang et al., 2014; Fang et al., 2015a; Liao et al., 2014). The content of free radicals was reported to have a direct relationship with the reduction of Fe (III) by natural organic matter (Palmer and von Wandruszka, 2010). Therefore, PFR is probably a candidate pool to donate electrons in hydrochar.

As such, the major objectives of this study were: 1) to identify the source of RC on hydrochar; 2) to elucidate how post-treatment affects the RC of samples. In this experiment, we prepared the hydrochars from two common biomass wastes and post-treated these samples by acid/base treatment, HNO_3 oxidization and heating treatment. These post-methods were selected because they are frequently used to modify the property (especially for surface functionality) of biochar/hydrochar for particular purposes. For example, HCl treatment was reported to increase the specific surface area (Ryu et al., 2015) and reduce surface negative charge (Dong et al., 2017) of char. NaOH treatment leads to the increase of lactone but the decrease of phenol, while HNO_3 treatment makes more carboxyl acid groups developed on char (Li et al., 2014). Our previous study revealed heating treatment can significantly improve the RC of hydrochar. The hydrochar samples from different post-treatment methods were further employed to reduce Cr(VI) to verify their environmental application.

2. Materials and methods

2.1. Preparation of hydrochar samples

2.1.1. Raw hydrochar

The biomass of wheat straw (WS) and *Spartina alterniflora* (SA) were used for the preparation of hydochar, respectively. Wheat straw is generated in a huge amount annually around the world. SA is an invasive herb widely distributed in the tidal stretch of coastal region in East and South China seas. Both WS and SA biomass were harvested from Chongming Island, shanghai, China. To prepare raw hydrochar, 10.0 g biomass powder (<100 mesh) were thoroughly mixed with 50 ml deionized water and loaded in a 100-ml poly(tetrafluoroethylene)-lined stainless steel autoclave. N_2 (99.99%, 100 ml·min^{-1}) was used to purge the mixture for 30 min to get rid of dissolved oxygen in solution. Hydrothermal carbonization was performed in an oven at 240 °C for 4 h. The pressure (3.4 MPa) in the hydrothermal processes was self-generated by closed chamber reactors. The solid sample was withdrawn by collecting the pellets after centrifuging (3000 rpm for 10 min) the autoclaved sample. Hydrochar powder was alternately rinsed with acetone and deionized water until the pH reached stable. The resulted sample was dried using an oven at 105 °C for 24 h, ground to pass through a 100-mesh sieve and stored under N_2 for experimental use. Samples derived from WS and SA biomass were marked with WSC and SAC, respectively.

2.1.2. HNO_3 oxidized hydrochar

HNO_3 oxidation of hydrochar was performed by soaking WSC or SAC (10.0 g) into 30% HNO_3 solution (10 ml) at boiling temperature (about 70 °C). After a predefined period, the oxidized sample was withdrawn and rinsed with deionized water until a constant pH was reached. After that, the sample was dried at 50 °C in a vacuum chamber overnight and stored under N_2. HNO_3 oxidized sample was labeled as WSC/SAC-NX, where X represents the oxidation time (i.e., 0.5, 2, 4 or 8 h).

2.1.3. Acid/base treated hydrochar

Acid/base treatment of hydrochar was carried out by soaking raw hydrochar (1.0 g) in 6 M HCl or NaOH (100 ml) for 24 h, followed by the same rinsing procedure as the HNO_3 oxidization treatment. Acid/base-treated samples were labeled as WSC/SAC-H and WSC/SAC-OH, respectively.

2.1.4. Thermal treated hydrochar

To prepare the thermal treated sample, 1.0 g hydrochar was heated by an oven in air at 240 °C for 10 min. After being cooled down to room temperature, sample was ground to pass through a 100-mesh sieve