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A novel porous carbon derived from hydrothermal carbon for efficient adsorption of tetracycline

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ABSTRACT

Increasing attention is being paid to hydrothermal carbonization (HTC) of waste biomass, due to energy shortages, environmental crises and developing customer demands. However, most research has been dedicated to the production of bio-oil, with few studies focusing on the application of hydrothermal carbon (hydrochar), a solid residue from HTC of biomass. In this study, a novel porous carbon (PC) was prepared from hydrochar, via pyrolysis at different temperatures (300–700 °C), the characteristics of PC as well as tetracycline (TC) adsorption behavior were investigated. The hydrochar and PC samples showed a remarkable range of surface properties, as characterized by Boehm titration, the Fourier transform infrared spectra and nuclear magnetic resonance spectra. The changes in characteristics suggested that the PC samples produced at high activation temperature (500–700 °C) were well carbonized and exhibited a high surface area (>270 m^2/g). Linear relationships were obtained between Freundlich adsorptive capacity (K_F) and elemental atomic ratios, surface area and pore volume. The high adsorption capacity of PC samples can be attributed to its low polarity and high aromaticity, surface area and pore volume. The molecular variations among the hydrochar and PC samples translated into differences in their ability to adsorb TC.

1. Introduction

In the last few years, the hydrothermal carbonization (HTC) of waste biomass has received increasing attention for several reasons: (1) the precursors are readily renewable and cheap, (2) it is a simple and environmentally friendly ("green") process, (3) bio-oil, chemicals and carbonaceous solids can be obtained simultaneously [1]. The advantage of HTC over the pyrolysis process of biomass is that it can convert wet input material into carbonaceous solids at relatively high yields [2].

Much attention has been focused on obtaining bio-oil from the HTC process; studies on the application of carbonaceous solids are very scarce. The carbonaceous solids, (i.e., hydrothermal carbon, hydrochar), have a less aromatic structure and thermal recalcitrance, a low surface area and poor porosity, hindering the effective exploitation of hydrochar for environmental and agricultural applications [2–5]. As a consequence, a post-activation method is required to increase the surface area and porosity of hydrochar.

The easiest possibility for the development of the surface area of hydrochar is thermal treatment under an inert atmosphere, where small organic molecules are removed to generate microporosity, thereby reaching a specific surface area are comparable to conventional carbon materials [3].

Hydrochar-derived black carbon (i.e., porous carbon, PC) can be considered structurally similar to pyrochar and

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activated carbon, consisting primarily of short stacks of graphite sheets with O-containing groups rimmed on the edge to form connected microporous networks [6]. Biomass-derived pyrochar shows an extraordinary strong affinity for hydrophobic and hydrophilic organic contaminants removal, due to its large specific surface area, pore volume and abundant functional groups [6–8]. Since activation of waste hydrochar with thermal treatment can change the surface area as well as the amounts and types of functional groups, its adsorption capability can be affected.

Tetracycline (TC) is widely used in aquaculture and veterinary medicines to improve growth rates and feed efficiencies [9,10]. TC is excreted through feces and urine as un-metabolized matter, and the most negative effect is the development of multi-resistant bacterial strains that can no longer be treated with presently known drugs [10]. Due to its potential risk, it is of great importance to explore efficient and cost-effective treatment technologies for TC removal. TC is amphoteric compound and contains multiple functional groups such as phenol and alcohol, which are active and can induce complex reactions with black carbon.

It has been reported that various adsorbents, including black carbon, can remove TC by means of surface adsorption, metal bridging, H-bonding and π–π interaction between TC and the corresponding structural components of the adsorbents [6,7,11]. However, no relevant studies have been performed to test the adsorption behavior of TC on waste hydrochar-derived PC.

In this work, PC samples were produced at different temperatures from real hydrochar that was obtained from a pilot-scale plant. To our knowledge, there is no research that discusses the characterization and adsorption behaviors of waste hydrochar-derived PC in the literature. The objective of this study was, therefore, the investigation of the effects of activation temperature on the characterization of waste hydrochar-derived PC and on the performance of PC in adsorbing TC from aqueous solutions. The materials produced in this study were then characterized in terms of porosity, structure, composition and functionality. It is expected that this work will enhance the production value of waste biomass HTC and promote the development of HTC in industry.

2. Materials and methods

2.1. Thermal conversion of waste hydrochar

The waste hydrochar was produced from *Salix psammophila* of HTC at 300 °C [12]. A more detailed procedure for the preparation of hydrochar is available in Supporting Information. The waste hydrochar was activated via thermal conversion under nitrogen gas (N_2) conditions at 300, 400, 500, 600 and 700 °C. In brief, the hydrochar samples of 5 g were packed into a ceramic pot and then pyrolyzed at different temperatures in a box-type resistance furnace (SLQ1100-30, Shengli Co., Ltd., Shanghai) under N_2 flow of 1 L min^{-1} for 4 h at a heating rate of 4 °C min^{-1}. The yield of the PC samples were recorded and then milled to pass through a 0.25 mm sieve (60 mesh) prior to further analyses. The activated samples are hereafter referred to as P300, P400, P500, P600 and P700, where the suffix number represents the activation temperature.

2.2. Characterization of samples

The elemental (C, H, N) analyses were performed with an Elemental Analyzer Vario EL 3 instrument. Ash content was measured by heating the samples at 200 °C for 1 h and then at 500 °C for an additional 4 h under an air atmosphere [13]. The pH of samples was measured in a suspension of 1:10 sample/deionized water using a combination electrode. The suspension was shaken for 1 h before measurement [14]. The oxygenated acidic groups and basic components of samples were determined using the Boehm's titration method [15]. A more detailed account of the Boehm's titration is available in Supporting Information.

The thermogravimetry (TG) and derivative thermogravimetric (DTG) of the hydrochar sample were analyzed by a thermo-gravimetric analyzer (Perkin Elmer, USA) under an N_2 atmosphere, by heating the sample from room temperature to 800 °C at a rate of 10 °C min^{-1}. The Brunauer–Emmett–Teller (BET) surface area of the samples was determined with a N_2 adsorption–desorption isotherm measured at 77 K using a Quantasorb SI instrument (Quantachrone, USA). The morphology of samples was examined by scanning electron microscopy (SEM) using a Philips (XL300) microscope. The functional groups and surface properties of samples were examined through solid state ^{13}C nuclear magnetic resonance (NMR) spectra with cross polarization magic angle spinning (Bruker DSX 300) and Fourier transform-infrared (FT-IR, Nexus 470) techniques. The samples were also characterized by X-ray diffraction (XRD) and X-ray photoelectron spectrometer (XPS) techniques; and, the binding energies for the high-resolution spectra were calibrated by setting C to 1 s at 284.6 eV.

2.3. Batch sorption experiment

Tetracycline (TC) was selected as the model compound. Adsorption isotherms were obtained at the concentration range of 5–50 mg L^{-1} TC, and the background solution was 0.02 M sodium chloride (NaCl) [6]. To initiate the experiments, a 60 mL amber glass vial with 40 mL sorption solution received a weighted amount of sorbent (0.04 g) and was then shaken at 150 rpm for 4 days at 30 °C. After reaching sorption equilibrium, the suspensions were filtered through a 0.45 μm polytetrafluoroethylene (PTFE) membrane filter, and aliquots of the filtrate were analyzed by UV–vis spectroscopy [16]. The absorbance of TC was measured at 360 nm.

3. Results and discussion

3.1. Characterizations of hydrochar and porous carbon samples

3.1.1. TG-DTG analysis of hydrochar sample

The pyrolysis characteristics, (i.e. both TG and DTG curves) are shown in Fig. S1. Weight loss of the hydrochar sample occurred between 130 and 700 °C, and the amount of solid