



Research article

One-step synthesis of a novel N-doped microporous biochar derived from crop straws with high dye adsorption capacity



Fei Lian ^{a, c, *}, Guannan Cui ^{a, b}, Zhongqi Liu ^a, Lian Duo ^b, Guilong Zhang ^a, Baoshan Xing ^c

^a Agro-Environmental Protection Institute, Ministry of Agriculture, Tianjin 300191, China

^b College of Life Science, Tianjin Normal University, Tianjin 300387, China

^c Stockbridge School of Agriculture, University of Massachusetts, Amherst, MA 01003, USA

ARTICLE INFO

Article history:

Received 8 January 2016

Received in revised form

24 March 2016

Accepted 25 March 2016

Available online 31 March 2016

Keywords:

Crop straw

N-doped biochar

Physicochemical property

Dye adsorption

Recyclability

ABSTRACT

N-doping is one of the most promising strategies to improve the adsorption capacity and selectivity of carbon adsorbents. Herein, synthesis, characterization and dye adsorption of a novel N-doped microporous biochar derived from direct annealing of crop straws under NH_3 is presented. The resultant products exhibit high microporosity (71.5%), atomic percentage of nitrogen (8.81%), and adsorption capacity to dyes, which is about 15–20 times higher than that of original biochar. Specifically, for the sample NBC800-3 pyrolyzed at 800 °C in NH_3 for 3 h, its adsorption for acid orange 7 (AO7, anionic) and methyl blue (MB, cationic) is up to 292 mg g^{-1} and 436 mg g^{-1} , respectively, which is among the highest ever reported for carbonaceous adsorbents. The influences of N-doping and porous structure on dye adsorption of the synthesized carbons are also discussed, where electrostatic attraction, π - π electron donor-accepter interaction, and Lewis acid-base interaction mainly contribute to AO7 adsorption, and surface area (especially pore-filling) dominates MB adsorption. The N-doped biochar can be effectively regenerated and reused through direct combustion and desorption approaches.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

With increasing demand of agricultural produces, a large number of crop straws are being generated every year around the world. For example, the total production of crop straws was 7×10^{11} kg in China in 2010 (Zhang et al., 2014a). However, these renewable resources are not effectively utilized due to various limitations including lack of facilities, high labor costs, and low economic benefit (Liu et al., 2014). Also, burning of crop residues, including burning on the field and as domestic fuel, is a common practice of land preparation and disposal of crop wastes in many developing countries. Therefore, it is necessary to develop environmental friendly and economically feasible technologies to effectively utilize a large quantity of crop straws.

Thermochemical conversion technologies, such as gasification and pyrolysis, are considered as promising approaches to produce liquid/gas fuels and biochar (Liu et al., 2014). Currently, biochar is mainly used as a soil amendment and low-cost adsorbent due to its

environmental stability and porous structure (Jha et al., 2010; Sun et al., 2014). Compared to commercial activated carbon, however, the porosity of biochar is less fully developed due to relatively low pyrolysis temperature and the lack of activation process, which limits its pollutant removal efficiency and other high value-added applications. Hence, various approaches including activation (Ippolito et al., 2012), magnetization (Chen et al., 2011), and hydrothermal synthesis (Qi et al., 2013) have been explored to generate biochar with enhanced sorption capacity or selectivity for pollutant removal. For example, adsorption of methylene blue onto a biochar was reported to increase by more than eight times after chemical activation with ZnCl_2 (Angin et al., 2013).

Recently, nitrogen-doped (N-doped) porous carbons have been demonstrated having improved performances in adsorption (Bai et al., 2014a), catalysis (Gao et al., 2014), and capacitors (Zhou et al., 2014) relative to pure carbons. The synthesis of N-doped carbon is usually based on two strategies, i.e., direct pyrolysis or post-treatment. The doped N can be derived from NH_3 (Luo et al., 2014), urea (Florent et al., 2013), or N-containing precursors such as organic polymers and ionic liquids (Paraknowitsch et al., 2010). Annealing of carbon materials with NH_3 gas or NH_3 /steam mixture at elevated temperatures is a facile and efficient approach to enable

* Corresponding author. Institute of Agro-Environmental Protection, Fukang road 31, Nankai District, Tianjin 300191, China.

E-mail address: lianfei@caas.cn (F. Lian).

the formation of N-doped carbon structure. For example, NH_3 treatment of activated carbons at high temperatures has been used to introduce N-containing groups to the carbons (Boudou, 2003; Przepiorski, 2006). Besides N-doping, Luo et al. for the first time found that NH_3 , as a reducing agent, can further react with the N-doped carbon to generate N-doped porous carbons having large surface area (up to $1970 \text{ m}^2 \text{ g}^{-1}$) (Luo et al., 2014). Cellulose filter paper was used as the raw material in their study. This observation increases the possibility of synthesizing N-doped porous carbons in a one-step fabrication. Besides cellulose, biochar may be another promising carbon source to produce N-doped carbon due to its high carbon content (ca. 40–80%) (Singh et al., 2010) and abundant availability. Biochar is mainly composed of carbon, nitrogen, oxygen, and ash (e.g., Si, K, Mg) (Sun et al., 2014). During the pyrolysis in NH_3 atmosphere, N atoms can be doped into carbon surface of biochar at moderate temperatures (500–600 °C) (Luo et al., 2014; Przepiorski, 2006). In addition, it is expected that the N-containing components in biochar such as C–N and C=N groups, cyclic amides, and nitrile groups may react with NH_3 (Luo et al., 2014), which contributes to increasing the burnoff and surface area of the N-doped biochar. Moreover, the ash elements such as K and Mg could probably facilitate the reaction between carbon and NH_3 as catalysts during annealing process (Zhou et al., 2014). Therefore, we hypothesize that NH_3 activation would be an efficient method to produce N-doped carbon from biochar with highly elevated dye adsorption capacity.

The objectives of the present work were to (i) demonstrate the feasibility of synthesizing N-doped carbon with high surface area and N-doping level from biochar by NH_3 activation; (ii) examine chemical binding of the doped-N and biochar through characterization of the as-prepared carbons using a comprehensive set of techniques; and (iii) evaluate adsorption performance of the N-doped biochars using two different categories of dyes, i.e., anionic (acid orange 7, AO7) and cationic (methyl blue, MB) dyes as model adsorbates.

2. Materials and methods

2.1. Preparation of N-doped biochars

Corn straw, collected from the outskirts of Tianjin, China, was used as raw material to prepare the N-doped biochars. The biomass was first washed several times with tap water to remove the impurity and oven-dried at 105 °C overnight. The dried biomass was then crushed and sieved through a 2.0 mm mesh. 6.0 g of the biomass were fed into a quartz boat and loaded into a horizontal cylindrical furnace. The furnace was heated from room temperature to 600 °C at a ramp of $10 \text{ }^\circ\text{C min}^{-1}$ and held for 120 min under a N_2 flow (200 mL min^{-1}). After that, the atmosphere was switched from N_2 to NH_3 gas (200 mL min^{-1}) and different activation procedures were conducted: (1) held the furnace at 600 °C for another 1 h; or (2) elevated the temperature from 600 °C to 700 or 800 °C at a ramp of $20 \text{ }^\circ\text{C min}^{-1}$ and held for 1, 2, or 3 h. Then the furnace was allowed to naturally cool down to room temperature in N_2 atmosphere and the obtained samples were gently ground and passed through a 0.125 mm sieve. The carbons were notated as NBC-T-X, with T indicating the pyrolysis temperature and X indicating the holding time in NH_3 flow. For example, NBC800-3 was the sample prepared at 800 °C for 3 h under NH_3 . Pristine biochars, prepared at 600 or 800 °C for 120 min in N_2 flow without NH_3 treatment were also included as adsorbents for comparison, notated as BC600 and BC800.

2.2. Characterization

The physicochemical properties of the pristine and N-doped biochars were characterized in detail by complementary analytical techniques: X-ray photoelectron spectroscopy (XPS), N_2 adsorption/desorption, Raman spectroscopy, X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and Fourier transform infrared spectroscopy (FTIR). Thermal gravimetric analysis (TGA) was employed to examine the thermal stability of the carbons. The characterization methods are described in the Supporting Information. The point of zero surface charges (pH_{PZC}) of the samples was determined using the pH drift method (Valdés et al., 2002).

2.3. Adsorption experiments

Both AO7 and MB were purchased from Tokyo Chemical Ind. (TCI, Japan) with the purities higher than 98%. Their molecular properties are listed in Table S1. Adsorption experiments were conducted using a batch equilibrium technique in 40-mL vials at $25 \pm 1 \text{ }^\circ\text{C}$. Dye stock solution (1000 mg L^{-1}) was prepared by dissolving solid solute in deionized water and then sequentially diluted to seven different concentrations in the range of 5.0–35 mg L^{-1} for the original biochars and NBC600-700. Specifically for NBC800s, the initial concentrations of dyes were in the range of 75–300 mg L^{-1} due to their much higher adsorption capacities based on the preliminary experiment. Vials received 20 mg of the adsorbents and 40 mL of aqueous dye solution at a series of concentrations. All the vials were shaken at 150 rpm in a rotary shaking incubator for 24 h in the dark to reach apparent equilibrium based on the kinetic study. After equilibrium, the vials were centrifuged and filtered with $0.45 \text{ }\mu\text{m}$ membrane. The concentrations of solute in the supernatant were examined using a SPECORD S600 UV–vis spectrophotometer (Jena, Germany) at 497 nm for AO7 and 664 nm for MB. The calibration curves of UV absorbance with dye concentration were shown in Fig. S1. Control experiments without adsorbents in the vials were carried simultaneously. The mass of adsorbed dyes was calculated based on the reduction of the solute concentration in the aqueous phase. All the experiments were performed in duplicate. The pH was measured at the end of the experiments, and was approximately 8.5 ± 0.2 for all the combinations.

Separate sets of experiments were carried out to assess the adsorption kinetics of AO7 and MB on N-doped biochars with single-point adsorption. To ensure the data comparability and analytical accuracy, the initial concentration of AO7 and MB was 10 mg L^{-1} and 20 mg L^{-1} for BC600, NBC600-1, and NBC700-1, respectively; while 100 mg L^{-1} and 200 mg L^{-1} for BC800 and NBC800s, respectively. The solid to solution ratio was 20.0 mg/40 mL. The vials containing adsorbent-dye mixtures were shaken on a rotary incubator (150 rpm) for 1/6, 1/2, 1, 2, 4, 8, 12 and 24 h at $25 \pm 1 \text{ }^\circ\text{C}$. At selected time intervals, pairs of vials were sampled and the concentrations of dyes in aqueous phase ($0.45 \text{ }\mu\text{m}$ filtered) were examined using a UV–vis spectrophotometer with 497 nm for AO7 and 664 nm for MB.

2.4. Regeneration of N-doped biochars

Two different approaches (i.e., direct combustion vs. desorption) were employed to regenerate the dye-adsorbed carbons. 20 mg of the NBC800-3 or BC800 (for comparison) was added to 40 mL of AO7 or MB solution with a concentration of 100 mg L^{-1} for NBC800-3 and 50 mg L^{-1} for BC800 based on their K_d values, and the mixtures were shaken for 24 h to achieve apparent adsorption equilibrium. After separated by vacuum filtration, the carbons were

Download English Version:

<https://daneshyari.com/en/article/1055328>

Download Persian Version:

<https://daneshyari.com/article/1055328>

[Daneshyari.com](https://daneshyari.com)