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

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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.

Keywords: crop straw; N-doped **biochar**; **physicochemical property**; dye adsorption; recyclability

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 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 °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 °C min⁻¹ and held for 1, 2, or 3 h. Then the furnace was allowed to naturally cool down to room temperature in N₂ 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 NH₃ flow. For example, NBC800-3 was the sample prepared at 800 °C for 3 h under NH₃. Pristine biochars, prepared at 600 or 800 °C for 120 min in N₂ flow without NH₃ 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), N₂ 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

± 1 °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 $5.0\text{-}35 \text{ mg L}^{-1}$ for the original biochars and NBC600-700. Specifically for NBC800s, the initial concentrations of dyes were in the range of $75\text{-}300 \text{ mg L}^{-1}$ 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 $0.45 \mu\text{m}$ 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 ± 1 °C. At selected time intervals, pairs of vials were sampled and the concentrations of dyes in aqueous phase (0.45 μ 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 oven-dried at 50 °C overnight. For combustion treatment, the dye-adsorbed carbons were subjected to direct combustion for 1 h in air at 300 °C. Then the regenerated samples were weighted and applied in the next adsorption/combustion cycles. For desorption treatment, a certain amount of the dye-adsorbed carbons were applied to 200 mL of 60% ethanol and stirred for 12 h to regenerate the adsorbent. Then the filtered carbons were washed by deionized water, dried and used in the further adsorption/desorption cycles.

2.5 Data analysis

The adsorption isotherms were described by both Freundlich and Langmuir models.

The two models have the following equations:

$$\text{Freundlich model: } q_e = K_F C_e^n \quad (1)$$

$$\text{Langmuir model: } q_e = Q_{\max} K_L C_e / (1 + K_L C_e) \quad (2)$$

where $K_F (\text{mg}^{1-n} \text{L}^n \text{g}^{-1})$ and $K_L (\text{L mg}^{-1})$ are the Freundlich and Langmuir adsorption affinity parameters, respectively; n is nonlinear coefficient (unitless); and $Q_{\max} (\text{mg g}^{-1})$ is the Langmuir adsorption capacity.

The batch kinetic data were analyzed using both pseudo-first and pseudo-second order models. The linearized forms of pseudo-first and pseudo-second order models are shown below:

$$\text{Pseudo-first order: } \ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (3)$$

$$\text{Pseudo-second order: } t/q_e = 1/(k_2 q_e^2) + t/q_e \quad (4)$$

where $q_e (\text{mg g}^{-1})$ is the amount of dye adsorbed at equilibrium, $q_t (\text{mg g}^{-1})$ is the amount of dye adsorbed at time t , $k_1 (\text{min}^{-1})$ and $k_2 (\text{g mg}^{-1} \text{h}^{-1})$ are the first-order and second-order rate constants, respectively.

3. Results and Discussion

3.1 Characterization of N-doped biochars

N_2 adsorption isotherms and pore size distributions of the carbons are shown in Fig. S2, which reveals a significant difference in their pore structures and porosities. The adsorption isotherms of NBC800s do not have hysteresis loop and can be categorized into type I according to ICPAC classification, indicating the microporous nature (Rufete-Beneite et al. 2014). The isotherms of NBC600-1 and NBC700-1 are of type II, characteristic of a mixed micro-/meso-porous structure. The more striking hysteresis loop in NBC700-1 isotherm suggests its higher proportion of mesopores and probably different shapes of mesopores (Hines et al. 2004). Consistently, it can be

seen from pore size distributions (Fig. S2b) that NBC800s are very microporous with the majority of pores smaller than 2.0 nm and high contribution of ultra-micropores (<1.0 nm). The structural parameters of carbons calculated from N₂ adsorption isotherms are summarized in Table 1. Note that the BET surface area (S_{BET}) and degree of microporosity (ratio of $V_{\text{m}}/V_{\text{t}}$) increase from 72.7 m² g⁻¹ and 16.0% for NBC600-1 to as much as 418.7 m² g⁻¹ and 71.5% for NBC800-3, respectively, suggesting that highly microporous N-doped biochar with large surface area can be obtained by NH₃ activation under desirable conditions, e.g., 800 °C for 2 or 3 h in this study. Additionally, the significant higher burnoff for NBC800-2 (83.2%) and NBC800-3 (87.0%) relative to the other samples also indicates the strong activation effect of NH₃ at higher temperature and longer duration.

Table 1. Burnoff, surface elemental composition, surface area, pore volume, and pore size distribution of the pristine and N-doped biochars

Sample	Burnoff (wt%)	Surface elemental composition (%) ^a				$S_{\text{BET}}^{\text{b}}$ (m ² g ⁻¹)	V_{t}^{c} (cm ³ g ⁻¹)	V_{m}^{d} (cm ³ g ⁻¹)	$V_{\text{m}}/V_{\text{t}}$ (%)	D_{p}^{e}
		C	O	N	Si					
BC600	68.2	85.9	11.1	0.40	1.13	34.0	0.040	1.99×10^{-3}	4.98	4.08
BC800	72.8	79.4	10.1	0.25	1.77	61.0	0.036	7.38×10^{-3}	20.5	4.76
NBC600-1	67.6	76.7	12.9	3.24	1.75	72.7	0.081	1.31×10^{-2}	16.2	4.42
NBC700-1	67.6	73.4	11.2	7.11	1.73	102.0	0.106	2.25×10^{-2}	21.8	4.08
NBC800-1	71.1	76.8	7.75	8.56	1.69	139.1	0.088	2.11×10^{-2}	23.9	3.98
NBC800-2	83.2	75.6	9.76	8.81	1.17	152.6	0.093	4.42×10^{-2}	47.5	3.32
NBC800-3	87.0	77.6	10.1	5.69	0.31	418.7	0.277	0.198	71.5	2.65

^a Determined by X-ray photoelectron spectroscopy (XPS). ^b Specific surface area determined by N₂ adsorption using the Brunauer-Emmett-Teller (BET) method. ^c Total pore volume, determined at $P/P_0 = 0.97$. ^d Micropore volume, determined by t-method. ^e Pore size distribution, determined by Barrett Joyner Halenda (BJH) method.

Surface elemental composition and N bond configurations in the N-doped biochars were examined by XPS (Table 1 and Fig. 1). NH₃ activation significantly increases N content of the biochars, which increases more than 20 times from 0.4% for BC600 to 8.8% for NBC800-2. For NBC800-3, however, the N content decreases to 5.7%, which probably due to the depletion of less heat resistant N-species. High resolution N_{1s} spectra of the N-doped biochars shed light on the nature of N-carbon bonds

formed under NH_3 (Fig. 1). The N_{1s} spectra can be deconvoluted into four peaks at 398.1-398.4 eV (pyridine-N), 399.1-400.5 eV (pyrrolic-N and/or pyridone-N), 400.8-401.3 eV (graphitic-N), and around 402.8 eV (oxidized-N), respectively (Sheng et al. 2011, Horikawa et al. 2012, Gu et al. 2013). As shown in Fig. 1 and Table S2, pyridine- and pyrrolic-like N are the main components (> 50 atom %) in the N-doped biochars. With increasing annealing temperature and activation time, the contents of pyridine- and pyrrolic-N gradually decrease, mainly due to the reaction between NH_3 and the N-doped carbon rings. A previous study found that the doped N is a key factor to facilitate the activation reactions (Luo et al. 2014). Meanwhile, it is observed that graphitic-N is formed on the carbon networks when the annealing temperature reaches to 800 °C, and the content of graphitic-N increases from 13.7 atom % (NBC800-1) to 46.4 atom % (NBC800-3) with longer duration (Table S2). Thus annealing temperature and duration could play a crucial role in modulating the chemical state of N in its doped carbons. Our results also suggest that the large amount of N atoms in the form of basic N in graphene sheet would provide numerous adsorption sites for dye molecules, especially acidic AO7.

Fig. 1. High resolution XPS spectra of N_{1s} for the N-doped biochars (a-e), and schematic illustration of various types of N-bonds in carbon sheet (f) including graphitic N, pyridonic N (N contained in pyridone), pyrrolic N (N contained in pyrroles), and pyridinic N (N contained in pyridines).

The structure, composition and chemical states of the N-doped **biochars** were further examined by Raman spectra, XRD, HRTEM, and FTIR (Fig. 2). Raman spectrum of carbonaceous material is typically characterized by two bands: the G band (1580 cm⁻¹) is associated with sp² C atoms and the D band (1350cm⁻¹) corresponds to sp³ C atoms, deriving from the defects and/or disorders of graphite crystal (Huang et al. 2008). Generally, the relative intensity ratio of D to G bands

(I_D/I_G) is a measure of disorder degree and average size of the sp^2 domains in graphitized structure (Akhavan 2010). The Raman spectra (Fig. 2a) of all samples exhibit two characteristic peaks related to the D band and G band, respectively. The I_D/I_G intensity ratio increases from 0.75 to more than 1.0 when the annealing temperature increases from 600 to 800 °C, implying the formation of more amorphous structures and a reduction of the sp^2 domains in the carbon structures. This observation is consistent with the XPS data. Generally, higher pyrolysis temperature often leads to higher degree of graphitization in inert gas atmosphere. The opposite phenomenon in this study is likely related to the reaction mechanism between NH_3 and carbon, where N_2 and CH_4 can be produced meanwhile the carbon becomes more defected and amorphous (Luo et al. 2014). The crystal structure of the samples was determined by XRD, as shown in Fig. 2b. The broad peaks around 22.8° can be indexed as the C (002) diffraction plane, and those sharp peaks including 28.5° and 40.6° are mainly derived from mineral crystals in the biochar such as quartz and sylvite. It is found that these samples have analogous diffraction patterns, suggesting that the introduction of N does not heavily alter the overall crystal structure of the carbons. However, a noteworthy trend is that the C (002) peak shifts from ~22.8° to 26.0° with higher annealing temperature and longer duration, indicating that increasing N atoms are introduced into the carbon skeleton. It is known that doping by atoms with smaller ionic radius could generally cause positively shifts of diffraction peak owing to the more narrowed interlayer space. Consistent with XRD, the HRTEM image of NBC800-3 (Fig. 2c) shows plenty of graphite microcrystallites separated by

nanometer spaces (i.e., micropores), which mainly constitute the amorphous carbon structure. In addition, the well-defined electron diffraction ring in Fig. 2c suggests that the graphite crystallites in NBC800-3 correspond to typical hexagonal lattice of carbon (Sheng et al. 2011). Moreover, FTIR spectra (Fig. 2d) reflect the variations of functionalities of the carbons after N-doping. The broad band at 3436 cm^{-1} is attributed to stretching of N-H. The band at 1605 cm^{-1} corresponds to $\text{C}(\text{sp}^2)=\text{N}$ stretching, and the peaks at 1228 cm^{-1} and 1052 cm^{-1} can be assigned to $\text{C}(\text{sp}^2)\text{-N}$ stretching mode (Bai et al. 2014b). It is evident that these absorption peaks of N-containing moieties are greatly enhanced from NBC600-1 to NBC800-3 (Yang and Jiang 2014, Zhang et al. 2014b). These results demonstrate that thermal annealing of crop straw biochar under NH_3 is a facile one-step methodology to fabricate N-doped nanoporous carbons.

Fig. 2. (a) Raman spectra and (b) XRD patterns of BC600, BC800 and N-doped biochars. (c) A HRTEM image and selected area crystal diffraction pattern (inset) of NBC800-3. (d) FTIR spectra of BC600, BC800 and NBC800s.

3.2 Adsorption kinetics

To examine removal efficiency of the N-doped **biochars** for dyes, adsorption kinetics of AO7 and **MB** were carried out. It is evident (Fig. 3) that the adsorption is faster on NBC800-3 than that on the rest of carbons. Given the tested conditions, approximately 90% and **70%** of adsorption is accomplished within 2.0 h **for AO7 and MB** on NBC800-3, **respectively**. The adsorption is characterized by two processes of different kinetics, i.e., a fast initial adsorption to outer surfaces, followed by a slow diffusion into inner pores of carbons. The photograph in Fig. S3 showed the color

changes of AO7 solutions ($C_0 = 40 \text{ mg L}^{-1}$, $S/L = 20 \text{ mg/40 mL}$) after treated with different carbons in 20 min, which clearly demonstrates much higher removal efficiency of NBC800-3 relative to NBC800-1 and original biochars (BC600 and BC800).

Fig. 3. Adsorption kinetics of AO7 and MB on pristine and N-doped biochars.

To quantitatively investigate the characteristics of adsorption process, the pseudo-first-order and pseudo-second-order models were used to fit the kinetic adsorption data by linear regression. The fitting parameters of adsorption kinetics are presented in Table S3 and S4. It can be seen that the pseudo-second-order model provides better fitting than the pseudo-first-order one for the experimental data. The much higher adsorption rate constants (k_2) of BC600, BC800, and NBC600-700 can

be explained by the fact that their less developed porous structures make it easier for dye molecule to reach apparent adsorption equilibrium, leading to a higher adsorption rate. Interestingly, we found that the k_2 values for MB follows an order of NBC800-1 > NBC800-2 > NBC800-3; however, an opposite trend was observed for AO7. Moreover, the difference in S_{BET} of NBC800s has much less effect on adsorption quantities for AO7 than for MB (justified by q_e values). These results indicate that the adsorption kinetics of MB is more related to the pore structures of the carbons, by contrast, the adsorption of AO7 is mainly controlled by surface adsorption other than pore diffusion process (see more discussion below).

3.3 Adsorption isotherms for dyes

Adsorption isotherms of AO7 and MB on the carbons are shown in Fig. 4. The adsorption data were fitted to Freundlich and Langmuir models, respectively. However, Langmuir model failed to capture the feature of the isotherms and hence only Freundlich fitting parameters are listed in Table 2. The better fitting of Freundlich model implies that the dye adsorption probably occurs on heterogeneous carbon surfaces. As discussed above, higher annealing temperature and longer duration can make the activation more complete and lead to superior physiochemical properties of carbons relative to the low-temperature samples. Thus, among the N-doped **biochars**, NBC800-3 exhibits the highest adsorption capacity for AO7 and MB, which is up to 292 mg g⁻¹ and 436 mg g⁻¹ respectively in the experimental C_e ranges. Comparison with the literature values (Table S5) shows that NBC800-3 has a great potential for dye removal from aqueous solution, higher than various porous

materials such as powdered activated carbons, polydopamine (PDA) microsphere (90.7 mg g⁻¹ for MB), magnetic graphene oxide (95.2 mg g⁻¹ for MB), and even nanocomposite hydrogel (358 mg g⁻¹ for MB).

Fig. 4. Adsorption isotherms of AO7 and MB on BC600, BC800 and N-doped biochars.

Table 2. Parameters of Freundlich model for the dye adsorption by BC600, BC800, and N-doped biochars.

Adsorbent	AO7			MB		
	K_F (mg ¹⁻ⁿ L ⁿ g ⁻¹)	n	R^2	K_F (mg ¹⁻ⁿ L ⁿ g ⁻¹)	n	R^2
BC600	3.34	0.416	0.885	7.88	0.218	0.828
BC800	8.29	0.258	0.867	10.9	0.182	0.883
NBC600-1	3.54	0.396	0.825	6.87	0.276	0.874
NBC700-1	3.14	0.415	0.892	8.34	0.209	0.925
NBC800-1	148	0.112	0.996	128	0.075	0.788
NBC800-2	224	0.147	0.962	221	0.044	0.876
NBC800-3	208	0.068	0.999	366	0.038	0.958

Dye adsorption on carbonaceous materials is mainly dependent on porous structure and surface chemistry. As shown in Fig. 4, the 800 °C N-doped **biochars** have similar adsorption capacity for AO7 although the significant difference in their BET surface area (Table 1). By contrast, the adsorption trend for MB is consistent with the order of their S_{BET} . This indicates that surface chemistry may play a more important role in AO7 adsorption, and surface area dominates MB adsorption by the carbons. The studied carbons are very positively charged during the adsorption experiment owing to their high pH_{PZC} (> 10.0) (Fig. S4). **Due to the alkaline nature of high-temperature biochars, N-doping exhibits limited effect to their pH_{PZC} in this study.** AO7 is a typical

anionic dye and negatively charged. Thus, electrostatic attraction could greatly contribute to the adsorption of AO7. Additionally, due to stronger electronegativity of nitrogen, the electron density of the graphite surface is decreased by the introduction of N atoms (Wang et al. 2010), which enhances π -electron accepting capacity of the N-doped biochars. AO7 and MB are ideal planar molecules, and their aromatic rings are π -electron rich and generally considered as a π -donor (Ma et al. 2012). Thus, π - π electron donor-accepter (EDA) interaction is likely another important mechanism for AO7 adsorption onto the N-doped **biochars**. Furthermore, the doped-N atoms on the carbon surface might serve as weak Lewis base, and can interact with O-containing moieties of AO7 via Lewis acid-base interactions. Overall, the doped-N contributes more to the adsorption of AO7 on the synthesized carbons than that of MB.

MB is a cationic dye and positively charged in aqueous solution at the tested pH. Thus, electrostatic interactions hardly contribute to MB adsorption by the N-doped biochars. To better illustrate the effect of adsorbent porosity, adsorbent surface area-normalized adsorption isotherms of AO7 and MB are compared between NBC800s (Fig. S5). The differences in normalized adsorption on the carbons are much less for MB than for AO7, showing a more important role of porosity in MB adsorption. MB has a planar shape with molecular dimensions of $1.43 \text{ nm} \times 0.61 \text{ nm} \times 0.40 \text{ nm}$ (Table S1), the planar MB molecule can diffuse into the micropores ($< 2 \text{ nm}$) in a flat form. Meanwhile, it is known that adsorption can be enhanced through overlapping adsorption potentials of opposite pore walls when the adsorbate molecular size is close to the pore size, i.e., pore-filling mechanism (Dubinin 1975).

The considerable amount of micropores in NBC800s probably takes a dominant role in adsorption of MB. Moreover, the π - π EDA interactions could also contribute to MB adsorption (Diagboya et al. 2014).

The lower normalized adsorption of AO7 on NBC800-3 cannot be explained by size-exclusion effect because AO7 and MB exhibit similar molecular sizes (Table S1). We suggest that it is mainly caused by strong electrostatic attraction between AO7 and carbon surfaces. Many reports demonstrate that electrostatic attraction is generally a more powerful adsorption mechanism when several interactions operate simultaneously such as Coulomb forces, van der Waals forces, and hydrophobic effect (Armanious et al. 2014). It is understandable that the positively charged sites on NBC800 surfaces would act as high energy sites for AO7 adsorption, and thus prevent many negatively charged AO7 molecules further diffusing into the inner portions of micropores. It is evidenced by the fact that the surface area-normalized adsorption of AO7 is higher than that of MB onto NBC800-1 and -2 especially at high dye concentrations (Fig. S5). The higher normalized adsorption of AO7 can be attributed to the strong electrostatic attraction of AO7 molecules onto carbon surfaces.

3.4 Reuse of the N-doped biochars

The recyclability of used adsorbents is of great importance for improving adsorption efficiency and economical feasibility. Two methods (direct combustion and desorption with 60% ethanol) were employed to regenerate the N-doped **biochars** using NBC800-3 as a representative. Both the methods were performed five runs of adsorption/recycling measurements, respectively, to examine the recyclability of the

adsorbent. Before the adsorption/combustion cycles, the weight loss analysis of AO7-adsorbed samples, as a representative, were conducted in N₂ atmosphere to determine the suitable combustion temperature and thermal stability of the adsorbents. TGA results for the exhausted BC600, BC800 and NBC800s (Fig. S6) show that the weight loss is mainly composed of two stages, i.e., from room temperature to ~200 °C and 200-800 °C. For the first stage, the significant difference in mass loss for NBC800s (~10%) and BC600 or BC800 (~4%) can be explained by the decomposition of adsorbed AO7 molecules. After the first stage, no distinct difference in mass change is observed from 200 °C to 800 °C for NBC800s and BC800. They exhibit same decreasing trend with mass loss of less than 10%, indicating their strong and similar heat-resistant property. Thus, 300 °C is considered suitable to regenerate the adsorbents in the adsorption/combustion treatment. As for BC600, the higher mass loss (~15%) can be explained by its relatively lower preparation temperature and more organic matters are still reserved.

Fig. 5. Recyclability of NBC800-3 and BC800 (for comparison) for AO7 adsorption by (a) direct combustion in air, and (b) desorption with 60% ethanol.

As shown in Fig. 5a, NBC800-3 maintains up to 65% of its original adsorption capacity after five adsorption/combustion cycles. Meanwhile, only slight mass loss (data not shown) of NBC800-3 occurs for each cycle because of its strong thermal stability as indicated by TGA (Fig. S6). These results suggest that direct combustion in air is a feasible method to regenerate the N-doped biochar adsorbent. Surprisingly, an evident increase of adsorption capacity of BC800 is observed after combustion treatment, which is probably due to the further development of porous structure when heated to 300 °C in air condition. Besides the combustion, desorption experiment was also used as an alternative method for recycling (Fig. 5b). It is desirable to note that

60% of its original adsorption capacity can be reserved for NBC800-3 after five adsorption/desorption cycles, similar to the adsorption/combustion result. Thus, both of the recycling methods can be used to regenerate the adsorbent. Similar result was also obtained for the reuse of MB-adsorbed carbons as shown in Fig. S7. These data clearly demonstrate the excellent recyclability of the N-doped biochar when used as an adsorbent.

4. Conclusion

We report a facile one-step thermal annealing method to produce novel N-doped microporous carbon using crop straws as raw material. The prepared N-doped biochars exhibit high adsorption capacity for both cationic and anionic dyes (MB and AO7), better than many other reported adsorbents, which is attributed to the doping of N and microporous structure. Moreover, the N-doped sample can be effectively regenerated by both combustion and desorption approaches. These results suggest that the N-doped biochars would probably have a high potential in a variety of environmental and chemical applications. More importantly, this study provides a feasible approach to produce N-doped carbons at relatively low cost and opens up a new way for comprehensive utilization of crop straws, and possibly other biomass wastes.

Appendix A. Supplementary data

Additional methods, figures, and tables are presented in Supporting Information.

Acknowledgements

This research was supported by Science and Technology Project of Chinese Academy of Agricultural Sciences, National Natural Science Foundation of China (41573127, 41203083), Central Public Research Institutes Basic Funds for Research and Development (Agro-Environmental Protection Institute, Ministry of Agriculture), Tianjin Natural Science Foundation (13JCYBJC25400), and USDA NIFA McIntire-Stennis Program (MAS 00028).

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Graphical abstract