Adsorption of nitrate onto biochar derived from agricultural residuals
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ABSTRACT
To develop low-cost adsorbents for aqueous nitrate, biochars were prepared from three types of agricultural residuals at different pyrolysis temperatures (300°C, 450°C, and 600°C). The corn cob biochar produced at 600°C (CC600) was the best nitrate adsorbent of all the tested biochars. Characterization results showed that CC600 had good thermal stability, porous structure, and abundant surface functional groups. Findings from batch adsorption experiments demonstrated that CC600 showed relatively fast adsorption kinetics to nitrate in aqueous solutions. In addition, the Langmuir adsorption capacity of CC600 to nitrate was 14.46 mg/g, comparable to that of other biochar-based adsorbents. Therefore, CC600 showed promising potential to be used as a low-cost adsorbent for the treatment of nitrate in water.

INTRODUCTION
With the rapid population growth and economy development, a large amount of nitrate has been released into surface water and groundwater through various ways (Burow et al. 2010; Archna et al. 2012; Kim et al. 2015). This has resulted in a number of environment problems, especially water eutrophication (Liu et al. 2005; Archna et al. 2012). Nitrate polluted water can also pose a threat to public health, such as causing cancer (Camargo & Alonso 2006; Song et al. 2015), infant methemoglobinemia (Camargo & Alonso 2006; Wongsanit et al. 2015), and nervous tissues and cognition damage (Lefferts et al. 2016). The development of effective treatment technologies that can reduce nitrate from wastewater discharges thus has attracted much attention recently (Liu et al. 2005).

Due to the good stability and high water solubility of nitrate, how to effectively and economically remove aqueous nitrate nitrogen becomes an issue (Archna et al. 2012). To resolve it, many researchers have carried out experiments to test different biological and physicochemical methods for the removal of nitrate from aqueous solutions.

The main principle of biological nitrate removal is using anaerobic denitrifying bacteria to reduce nitrate and nitrite under anaerobic conditions. This biological treatment has several advantages, such as wide sources of denitrifying bacteria, low cost of the process, and no secondary pollution to the environment. However, it also has too many restrictions and often fails to achieve the ideal removal efficiency of nitrate. In particular, biological methods have limitations for the treatment of high concentration nitrate wastewater at low temperatures (Demiral & Gunduzoglu 2010).

Compared with biological methods, physicochemical methods, such as ion exchange, electro dialysis, reverse osmosis, and adsorption, are more flexible and effective (Chatterjee & Woo 2009). Among the different physicochemical methods, adsorption has received extensive attention because its low cost and easy maintenance. Adsorbents with large specific surface area and pore volume thus have been developed for the removal of impurity ions from water. Recently, the development of novel, high efficiency, and environmentally friendly adsorbents has become one of hot topics in the field of water treatment. As an emerging engineered carbon material, biochar has been gradually applied as a low-cost adsorbent in water treatment to remove contaminants from wastewater (Yao et al. 2012b; Lou et al. 2016).

Previous studies have examined the sorption of nitrate onto biochars made from various agricultural and forest residuals including pine wood, bamboo, wheat straw, mustard straw, corn stover, and sugarcane bagasse (Mizuta et al. 2004; Mishra & Patel 2009; Yao et al. 2012b; Zhang
et al. 2012; Chintala et al. 2013; Xue et al. 2016). These experiment results show various results of effectiveness of biochar-based sorbents for the removal of aqueous nitrate. Nevertheless, some of the biochars showed better nitrate sorption ability than commercial activated carbon, indicating the promising potentials of biochar as a low-cost and environmentally friendly sorbent for nitrate treatment.

The overarching objective of this work was to further evaluate the effectiveness of biochar as an adsorbent for the removal of aqueous nitrate. Various types of biochars were prepared from three types of agricultural residuals through slow pyrolysis at different temperatures. Laboratory batch sorption and mathematical models were used to determine the sorption characteristics of nitrate onto the biochars. The specific objectives of this work were as follows: (1) optimize the production conditions of biochars from agricultural residuals; (2) determine the adsorption characteristics of nitrate onto biochars; and (3) explore the adsorption mechanism of nitrate onto biochar.

METHODS

Materials

Dry agriculture residuals were obtained locally from Wuhan in Hubei Province in China. Potassium nitrate (KNO₃) was purchased from Sinopharm Chemical Reagent Co., Ltd. Reagent in this work were of analytical grades and solutions purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water (18.2 MΩ) was collected and ground in a mortar with a pestle, and then sieved to a uniform size fraction of 0.9–1.2 mm. After further rinsing with deionized (DI) water several times to remove impurities and drying at 80 °C (Creamer et al. 2016), the final biochar samples were stored for later experiments. The samples were named after their feedstock and temperature. For example, the biochar prepared from CC and pyrolyzed at 600 °C was named CC600.

Characterizations

Basic physical and chemical properties of biochars were determined using method reported previously (Inyang et al. 2010; Yao et al. 2011a; Wang et al. 2015). Briefly, carbon (C), hydrogen (H), oxygen (O), and nitrogen (N) contents of the samples were analyzed using a CHN Elemental Analyzer (Elementar Analysen systeme GmbH). Surface morphology of the samples was determined using a scanning electron microscopy (SEM). X-ray diffraction (XRD) analysis was used to detect crystalline minerals on either pre-or post-sorption samples using a computer controlled X-ray diffract meter. Fourier transform infra-red (FTIR) analysis was used to verify the presence of surface functional groups on the samples. In the thermogravimetric analysis (TGA), the physical and chemical changes in the combustion process of a microcomputer based thermogravimetric differential thermal analyzer (HCT-1).

Batch sorption

About 0.1 g of the selected biochars were mixed with 50 mL sodium nitrate solutions (Xue et al. 2012). The mixtures were then shaken in the mechanical shaker (150 r/min) at 30 °C. After 24 h (predetermined equilibrium time), the mixtures were filtered through 0.22 μm membrane filters to measure the nitrate concentrations in the supernatants. Nitrate concentrations were determined by ion chromatograph (Metrohm) using ion chromatographic column (Metrosep A Supp 4). Sorbed nitrate concentrations on the biochar and removal rate were calculated based on the difference between the initial and final aqueous concentrations. Nitrate adsorption amount of q (mg/g) and adsorption removal rate of R (%) were calculated by formula (1.1) and formula (1.2):

\[ q = \frac{(C_0 - C_e)V}{m} \]  \hspace{1cm} (1.1)

\[ R = \frac{C_0 - C_e}{C_0} \times 100 \]  \hspace{1cm} (1.2)

where V is the volume of solution (mL) and m is the weight of biochar adsorbent, and \( C_0 \) and \( C_e \) are the initial concentration and equilibrium concentration of nitrate ion solution, respectively (mg/L).

The biochar sample with the best sorption performance for nitrate was selected for the rest of the batch sorption experiments to determine the adsorption kinetics and isotherms using similar experimental procedures. The kinetics
were measured at different time intervals (0–24 h) and isotherm was determined using different initial concentration (0–2,000 mg/L).

**Mathematical models**

Pseudo-first-order, pseudo-second-order, and Elovich models were used to simulate the adsorption kinetics data. Governing equations for these models can be written as (Yao et al. 2016b):

Pseudo-first-order: 
\[ q_t = q_e(1 - e^{-k_1t}) \]  (2.1)

Pseudo-second-order: 
\[ q_t = \frac{k_2q_e^2t}{1 + k_2q_e^2t} \]  (2.2)

Elovich: 
\[ q_t = \frac{1}{\beta} \ln (\alpha \beta t + 1) \]  (2.3)

where \( q_t \) and \( q_e \) are the amount of sorbate removed at time \( t \) and at equilibrium (mg/g), respectively. \( k_1 \) and \( k_2 \) are the first-order and second-order sorption rate constants (h\(^{-1}\)), respectively. \( \alpha \) is the initial sorption rate (mg/g) and \( \beta \) is the desorption constant (g/mg).

The Langmuir and Freundlich models were used to simulate the adsorption isotherms. Their governing equations can be written as (Tian et al. 2011):

Langmuir: 
\[ q_e = \frac{K_S_{max}C_e}{1 + K_C e} \]  (3.1)

Freundlich: 
\[ q_e = K_f C_e^{1/n} \]  (3.2)

where \( K \) and \( K_f \) are the Langmuir bonding term related to interaction energies (L/mg) and the Freundlich affinity coefficient ((mg/g)/(1/mg)\(^{1/n}\)), respectively. \( S_{max} \) is the Langmuir maximum capacity (mg/g), \( C_e \) is the equilibrium solution concentration (mg/L) of the sorbate, and \( n \) is the Freundlich linearity constant. The Langmuir model assumes monolayer adsorption onto a homogeneous surface with no interactions between the adsorbed molecules. The Freundlich model is an empirical equation commonly used for heterogeneous surface.

**Effects of sorbent dosage, pH, temperature and co-existing anions**

The effect of adsorbent dosage was studied by adding different amounts of biochar (0.05 g, 0.10 g, 0.15 g, 0.20 g) to 50 mL nitrate solution. At the dosage of 0.10 g to 50 mL solution, pH (5–11), temperature (20–40°C) and co-existing anions (Cl\(^{-}\), SO\(_4^{2-}\), PO\(_4^{3-}\)) were determined respectively. After 24 h shaking in the mechanical shaker, the same procedures were then used to determine the nitrate concentrations in the filtrates.

**RESULTS AND DISCUSSION**

**Effects of pyrolysis conditions on nitrate adsorption onto biochar**

The C, H, and N contents of the biochars showed variations among different feedstocks and temperatures (Table 1). For the same feedstocks, biochars produced at higher temperatures had higher C content, which is consistent with findings of previous studies (Sun et al. 2014). The H content of the biochars increased first and then decreased with temperature, which is also consistent with the conclusions of previous studies (Xue et al. 2014; Zhang et al. 2014; Liu et al. 2016). Both feedstock type and pyrolysis temperature showed strong effects on biochars’ sorption ability to NO\(_3^-\) in aqueous solutions (Figure 1). The CC and crop waste (CW) biochars showed higher sorption to nitrate than the PS biochars, indicating they are better feedstocks for this purpose. In addition, nitrate sorption abilities of the CC and CW biochars increased with pyrolysis temperature. The CC600 showed the highest sorption of nitrate from aqueous solution among all the tested biochars, it was thus selected as an example for further characterization and sorption investigations.

**Physiochemical properties of CC600**

The combustion process of CC600 showed three stages: dehydration, weight loss, and burnout (Figure 2(a)). The
first stage was from room temperature to 300 °C, where thermogravimetric (TG) curve showed small decline and the sample weight loss rate was only about 2%, mainly for the dehydration process. The second stage accompanied with a main weightlessness from 300 to 750 °C, mainly for volatile and fixed carbon combustion. The third stage was from 750 to 1,000 °C, where TG curve became smooth and the quality of the sample picked up slightly. This was probably because the same chemical composition had different crystal type with the temperature changing, so there was a crystal form of inorganic transformation. In other words, a small amount of stable compound was generated at the high temperature. SEM image of the CC600 showed porous structures with rough surfaces (Figure 2(b)). The average pore size of CC600 was about 30 μm. The relatively large pores would be beneficial for the adsorption process. The FTIR spectra of CC600 showed strong peaks 1,100 cm⁻¹ and 3,400 cm⁻¹ (Figure 2(c)), corresponding to C-O stretching vibration (three hydroxyl) and O-H stretching vibration (hydroxyl). The FTIR results indicated that the main functional group on the biochar surface was hydroxyl (–OH), which has strong affinity to polar compounds in water. Compared with the initial biochar after adsorption there were peak shifts at 1,100 cm⁻¹ and 3,400 cm⁻¹ and these shifts indicated that functional groups involved in the adsorption. The XRD spectra showed no evidence of diffraction peaks, suggesting CC600 might not have any crystal lattice structure on its surface.

**Adsorption kinetics and isotherms**

Nitrate adsorption kinetics onto CC600 showed two distinct phases: a rapid initial phase over the first few hours and a slow phase to reach maximum (Figure 3(a)). For the nitrate, nearly all the sorption occurred within the first several hours. Pseudo-first-order, pseudo-second-order, and Elovich models were used to simulate the sorption kinetics data (Figure 3(a)). Nitrate sorption onto CC600 were best fitted by the pseudo-second-order with R² equal to 0.94.
The experimental value of \( q_e \) was almost identical to the model-predicted value. The pseudo-second-order model assumes that the adsorption rate is controlled by the chemical adsorption mechanism that involves the electron sharing or electron transfer between the adsorbent and adsorbate. The model results of this work suggested that the adsorption kinetics of nitrate onto CC600 might be mainly controlled by the chemical adsorption (Ozacar & Sengil 2003). According to the Weber-Morris model, \( C \) was 1.4245 and it indicated that intra particular diffusion played a little role in the adsorption process.

Adsorption isotherms of nitrate onto CC600 showed relatively high equilibrium concentrations (Figure 3(b)). Two commonly used isotherm equations were used to describe the experimental isotherm, which is better fitted by the Langmuir model with \( R^2 \) equal to 0.968 (Table 3). The Langmuir maximum sorption capacity of CC600 to nitrate was 14.46 mg/g, comparable to the values reported in the literature on other biochar-based adsorbents (Mizuta et al. 2017; Mishra & Patel 2013; Yao et al. 2015b; Zhang et al. 2015; Chintala et al. 2015; Xue et al. 2015). This result confirmed that CC600 was good adsorbent for the removal of nitrate from water.

**Effects of sorbent dosage, pH, temperature and co-existing anions**

The removal rate increased with increasing biochar dose (Figure 4(a)). The adsorption capacity increased from 5.56 mg/g to 7.74 mg/g when the biochar dose went from 0.05 g to 0.20 g.

Changes of initial solution pH significantly affected adsorption effect (Figure 4(b)). When the pH increased, the adsorption capacity decreased. This is probably because when there were low pH (3–7) and high concentration of \( H^+ \) in the solution, a large number of \( H^+ \) attached to the biochar surface that was favorable to electrostatic adsorption. As the pH is over 7, there was a competition between \( OH^-/C_0 \) and \( NO_3^-/C_0 \), which led to the reduction of adsorption capacity.

When the reaction temperature increased from 20 °C to 40 °C, the adsorption increased from 5.83 mg/g to 7.59 mg/g (Figure 4(c)). This indicates that the adsorption process was endothermic and the increase of temperature was beneficial to the reaction. This made a great contribution to actual production application.

According to the test data (Figure 4(d)), the existence of three anions showed negative effect on the adsorption and even resulted in desorption (Figure 4(d)). Relatively speaking, the influence of \( SO_4^{2-} \) and \( PO_4^{3-} \) on adsorption were higher than that of \( Cl^- \). It is probably because the adsorption

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**Table 2** | Best-fit kinetic parameters of \( NO_3^- \) adsorption onto CC600

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( q_e ) (mg/g)</th>
<th>( k_1 ) (h(^{-1}))</th>
<th>( R^2 )</th>
<th>( q_e ) (mg/g)</th>
<th>( k_2 ) (g/mg min)</th>
<th>( R^2 )</th>
<th>( K ) (mg/g)</th>
<th>( C ) (mg/g)</th>
<th>( R^2 )</th>
<th>( \alpha ) (mg/g)</th>
<th>( \beta ) (g/mg)</th>
<th>( R^2 )</th>
</tr>
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<tbody>
<tr>
<td>CC600</td>
<td>6.4</td>
<td>0.381</td>
<td>0.886</td>
<td>7.1</td>
<td>0.079</td>
<td>0.940</td>
<td>1.3053</td>
<td>1.4245</td>
<td>0.838</td>
<td>12.933</td>
<td>0.7874</td>
<td>0.926</td>
</tr>
</tbody>
</table>

**Table 3** | Best-fit isotherm parameters \( NO_3^- \) adsorption onto CC600

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( K ) (L/mg)</th>
<th>( q_m ) (mg/g)</th>
<th>( R^2 )</th>
<th>( K_f ) (mg/g)(1/mg)(^{1/n})</th>
<th>( n )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC600</td>
<td>0.0014</td>
<td>14.46</td>
<td>0.968</td>
<td>0.249</td>
<td>0.503</td>
<td>0.917</td>
</tr>
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</table>
affinity of the high valence anion was generally higher than that of the low valence anion.

CONCLUSIONS

A range of biochars were produced from three types of agricultural residuals at three pyrolysis temperatures. Among them, CC600 had the best adsorption performance for aqueous nitrate with the Langmuir adsorption capacity of 14.46 mg/g. This biochar showed good thermal stability, porous structure, and abundant surface functional groups and thus had promising potential to be used as a low-cost adsorbent for the removal of nitrate from aqueous solutions.

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