ORIGINAL PAPER

Enhanced removal of ammonium from water by ball-milled biochar

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Abstract Novel biochar was prepared by ball milling using bamboo as raw material. The aim of this study was to find a good alternative way to improve the potentials of biochar for ammonium adsorption from aqueous solution. The sorption performance of ball-milled bamboo biochar (BMBB) was compared with that of bamboo biochar (BB) using batch adsorption experiments. Different adsorption kinetics models proved that the pseudo-second order was the best kinetic model for explanation of the adsorption kinetics characteristics, indicative of the energetically heterogeneous solid surface of the biochar. The Langmuir model could fit the isothermal adsorption data of BMBB well. The maximum adsorption capacity of BMBB (22.9 mg g^{-1}) was much higher than that of BB (7.0 mg g^{-1}). This study offers a relatively cost-effective and efficient methodology for the improvement in the adsorption capacity of biochar for ammonium nitrogen.

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Introduction

The use of nitrogen fertilizer increases the yield of grain, but leads to a series of environmental issues such as soil and water pollution (Erisman et al. 2007). The chemical nitrogen fertilizer enters the water through runoff and leaching after being applied to the soil, leading to the eutrophication of surface water (Carpenter et al. 1998). Meanwhile, a considerable amount of ammonium enters the water environment along with industrial and residential effluent discharge. These activities inevitably lead to the eutrophication of water and overshadow the dissolved oxygen (DO) in the water, causing the eutrophic water to become green and stinky. This not only increases the difficulty and cost of water treatment but also has a certain impact on human health. Ammonium can also cause harm to the human body through food chain to synthesize nitroso compound which is a strong carcinogen. Therefore, the synthesis and production of novel and high-efficiency adsorbents to remove ammonium are essential to ensure the quality and safety of water environment.

With the continuous development of sewage treatment technology, the removal efficiency of eutrophic elements (N and P) has been greatly improved. Some of the technologies known for the sorption of ammonium from contaminated water include precipitation, membrane separation, ion exchange, chemical oxidation, adsorption, etc. (Cruz et al. 2018; Huang et al. 2010, 2018; Karapınar 2009; Wang et al. 2015a). However, some of the shortcomings associated with these techniques include high operating cost and low treatment efficiency. Ion exchange is mainly used for the deep treatment of low-concentration inorganic ammonium in water, but the exchange capacity of the regenerative agent cannot meet the requirement of the technical and economic standards (Jorgensen and Weatherley 2003). The chemical precipitation method has high ammonium removal efficiency, but the chemical agents are relatively expensive (Li and Zhao 2001; Li et al. 1999; Zhang et al. 2009). The biological method is suitable for low-concentration ammonium treatment with organic matter, the treatment efficiency

is relatively stable, and there is no pollution, while the operating cost is high (Li and Zhao 2001). The adsorption technique is considered to offer a more sustainable, cost-effective and high removal efficiency in comparison with other techniques stated above (Ma et al. 2011; Wang et al. 2015a; Wang and Peng 2010). However, due to the wide variety of physicochemical properties among different adsorbents, the adsorption efficiency is largely different. The choice of adsorbent is the key to determine the efficiency of removing ammonium from wastewater. Therefore, the development of low-cost and high-efficiency adsorbent is urgently needed.

A variety of adsorbents have been used to remove contaminants from water and soils (Alshameri et al. 2014; Huang et al. 2010, 2018; Wang et al. 2006, 2019d; Yin and Kong 2014). Ammonium-adsorbing materials include both natural materials such as natural zeolite and bentonite, and artificial materials such as molecular sieves, activated carbon (AC) and nanomaterials. Natural materials are low in cost and easy to be obtained, but the adsorption efficiency is low. Artificial materials require high cost and complicated process, while the adsorption efficiency is high. Due to the cost-effectiveness and high adsorption efficiencies, biochar has been widely used in water treatment as adsorbents (Gao et al. 2015; Wang et al. 2016, 2018a, c, 2019a; Zheng et al. 2019). Studies have shown that biochar has the potential to hold nutrients for effective fertilizer preparation and mitigate greenhouse gas emissions (Ma et al. 2011; Manikandan et al. 2013; Spokas et al. 2012; Wang et al. 2018b, 2019b; Yang et al. 2016; Yao et al. 2012). However, the newly prepared biochar has relatively limited adsorption performance. Different modification methods have been developed to improve the adsorption performance of biochar (Li et al. 2017; Lian et al. 2019; Ma et al. 2009; Rajapaksha et al. 2016; Vikrant et al. 2018; Wang et al. 2017, 2019c).

Ball milling technology has been applied in the field of biochar research due to its cost-effectiveness and high adsorption efficiency (Peterson et al. 2012; Xu et al. 2019). The principle is to grind biochar into nanometer-sized particles, thereby increasing its adsorption capacity for contaminants. The ball milling technology plays a great role in increasing the porosity, specific surface area (SSA) and surface chemistry of biochar (Manikandan et al. 2013; Peterson et al. 2012; Richard et al. 2016; Zhang and Cue

2018). At present, there have been several studies on the removal of methylene, galaxolide as well as heavy metals in aqueous medium (Lyu et al. 2018a, b; Zhang et al. 2019). However, there has not been any report on ammonium removal from water using biochar obtained from ball milling. Although there have been a lot of studies on the adsorption of ammonium nitrogen by different biochars (Li et al. 2017; Wang et al. 2015a, b, 2016), the adsorption characteristics and mechanism of ammonium on biochar after ball milling are not very clear. Therefore, it is necessary to clarify the adsorption characteristics and behavior of ball-milled biochar on ammonium nitrogen.

The main objectives of this study were to compare the ammonium adsorption capacity of bamboo biochar (BB) and ball-milled bamboo biochar (BMBB) and to investigate the adsorption characteristics and mechanism of ammonium onto ball-milled biochar. The adsorption capacity of biochar on ammonium was expected to increase considerably after ball milling. To investigate the adsorption mechanism in line with kinetics and isotherms, batch adsorption equilibrium experiments were conducted to explore the adsorption mechanism from the perspective of kinetics and isotherms. The ultimate goal was to provide a technical reference for biochar obtained through ball milling techniques as a novel adsorbent for the removal of ammonium from contaminated water.

Material and methods

Chemicals and reagents

The reagents used in this study include ammonium sulfate ($(NH_4)_2SO_4$), potassium sodium tartrate ($KNaC_4H_4O_6 \cdot 4H_2O$), potassium iodide (KI), mercuric iodide (HgI_2), sodium hydroxide (NaOH) and hydrochloric acid (HCl). They are all of the standard grades and were purchased from the Sinopharm Chemical Reagent Co., Ltd.

Preparation of BB and BMBB

The preparation of BB and BMBB was completed at the University of Florida. Biochar was made from bamboo feedstock. Specific biochar and ball milling biochar preparation methods are consistent with the method we used before (Wang et al. 2018b). Briefly,

the raw feedstocks were pyrolyzed in an N_2 environment using a furnace (Olympic 1823HE) at a maximum pyrolysis temperature of 450 °C. The obtained biochar was later mechanically ground with the aid of a planetary ball mill.

Biochar characterization

The scanning electron microscopy (SEM) was used to investigate the structure and surface morphology of the biochar samples. Also, the BET methodology was adopted to measure the SSA of the sorbent with N_2 adsorption. The Fourier-transform infrared (FTIR) spectrometer (Thermo Fisher Scientific, USA) was used to characterize the surface functional groups of the biochar samples. The functional groups of the samples were recorded between 400 and 4000 cm^{-1} spectral ranges. The Malvern Zeta meter (Nano ZSE + MPT2, Malvern Panalytical Instruments Ltd., UK) was used to analyze the surface zeta potential of the biochar samples.

Adsorption experiments

The stock solution of ammonium (1000 mg L^{-1}) was obtained by dissolving ammonium sulfate in deionized water. The adsorption experiments were performed in triplicate at room temperature, and the samples were shaken on a rotary shaker for 24 h. The kinetic experiments were conducted with the addition of 0.010 g adsorbent to a 50-mL centrifuge tube containing 40 mL of 50 mg L^{-1} ammonium sulfate solution. The samples were intermittently shaken between 0.083 and 24 h. 0.5 M hydrochloric acid or 0.5 M sodium hydroxide was used to adjust the pH of the initial solution to 6.0. In order to separate biochar from the solution, a syringe filter with a 0.22 μm size was used. The concentrations of ammonium in the filtrate were measured using Nessler's reagent spectrophotometry. The absorbance is determined at 420 nm. 0.010 g of each adsorbent was added to 40 mL of ammonium solutions with a concentration ranging from 0 to 100 mg L^{-1} in the sorption isotherms experiment. The procedure of the experiment was the same as that of the kinetics experiment. The ammonium concentrations were analyzed as described previously after shaking for 24 h. The adsorption isotherms and kinetic data were simulated by various models.

Results and discussion

BMBB and BB characterization

The images of BMBB and BB obtained from the SEM are shown in Fig. 1. After ball milling, the particle size of the BMBB becomes fine, reaching nanometer level. Also, there is an increment in the SSA from 18.2 to 298.6 m^2 g^{-1}. This increment may contribute to the adsorption of ammonium by the ball-milled biochar.

Both the pristine and ball-milled biochar's FTIR spectra are shown in Fig. 2. The most significant disparity of FTIR spectra between BB and BMBB was noted and recorded at 1635 cm^{-1}, 1315 cm^{-1} and 698 cm^{-1}, respectively. It was found that 1635 and 1315 cm^{-1} peak signifies the presence of carbonyl groups, and this actually increased significantly after ball milling processes. Also, the 698 cm^{-1} peak signifies the presence of an aromatic C–H stretching. The presence of these functional groups can react with ammonium, which may affect the ammonium adsorption process.

The zeta potential of two adsorbents at different pH is shown in Fig. 3; the surface charges of − 13 to − 46.2 mV represent BB, while those of BMBB start from − 29.9 to − 49.2 mV over the pH range of 3–12. More negative charge in the ball-milled biochar indicates the presence of more acidic oxygen-containing functional groups, and this corresponds with the results obtained from the Fourier infrared spec-
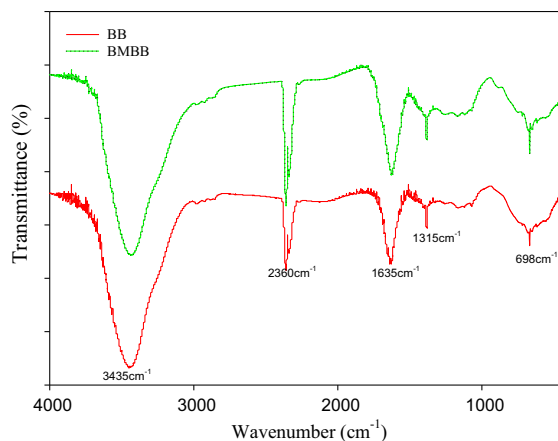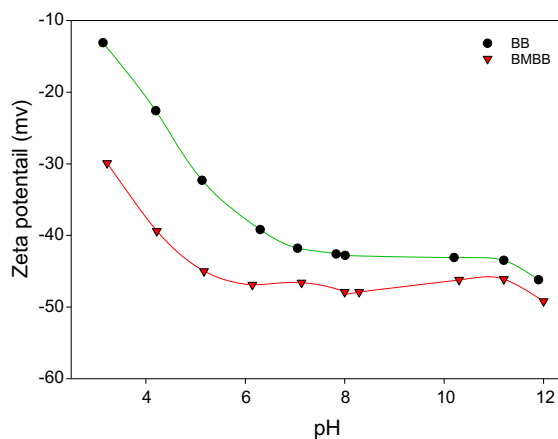

Fig. 2 The FTIR spectra of BB and BMBB
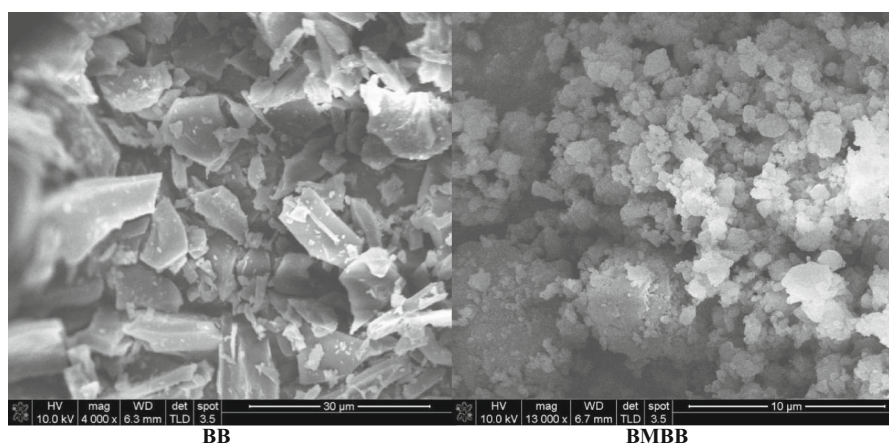

Fig. 3 Zeta potential of BB and BMBB

Fig. 1 The SEM images of BB and BMBB

troscopy. It is indicated that the presence of acidic oxygen-containing functional groups on the surface of biochar resulted from the ball milling exercises. These particular functional groups play a major role in the adsorption of ammonium when the oxygen-containing functional groups react with certain chemicals.

Adsorption kinetics

Adsorption kinetics helps in the total exploration of the potential adsorption process and mechanisms from the perspective of adsorption pathways. Figure 4 shows ammonium adsorption kinetics of BB and BMBB. Biochar adsorption of ammonium can be classified into two stages, namely a fast reaction stage and a slow reaction stage. The ammonium uptake by BB and BMBB displayed similar kinetics curves that show relatively fast reaction within 4 h and gradually reached equilibrium in 16 h, whereby ammonium removal was about 95% for BMBB. After 24 h, the adsorption amount did not increase anymore. That is, the adsorption equilibrium was reached. This is because the surface pore channels, surface functional groups and SSA of adsorbents are sufficient to provide more binding sites at the initial stage of adsorption, and ammonium ions attach themselves to the surface of the biochar easily. As time goes on, the electrostatic force of repulsion among the ions increases while the active binding sites decrease. This makes the adsorption reaction a little difficult to proceed, thereby achieving adsorption equilibrium. Although ball milling may not really alter the adsorption kinetic characteristics of the biochar, it significantly improved

Fig. 4 Adsorption kinetics of BB and BMBB on ammonium

the adsorption capacity of ammonium by 1.7-folds ($p < 0.05$). This is confirmed by the result obtained from the ANOVA (analysis of variance). A fast ammonium removal in the first 4 h is due to a large number of unoccupied adsorption sites and negatively charged functional groups on the surface of biochar in the initial stage of the reaction.

The adsorption process was described by several kinetic models as follows:

$$q_t = q_e\left(1 - e^{-k_1 t}\right), \quad \text{pseudo-first-order} \tag{1}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}, \quad \text{pseudo-second-order} \tag{2}$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta t + 1), \quad \text{Elovich} \tag{3}$$

$$q_t = q_e - \left(q_e^{1-n}\frac{k_n}{1-n}t\right)^{\frac{1}{1-n}}, \quad \text{Ritchie} \tag{4}$$

In comparison with the pseudo-first-order (1), Elovich (3) and Ritchie (4) models, the pseudo-second-order (2) model offers a better fitting experimental data for both adsorbents with high R^2 value (Table 1), implying that ammonium adsorption kinetics by BB and BMBB was mostly via chemical sorption through the formation of chemical bonds between the biochar surface and ammonium.

Adsorption isotherm

Isothermal adsorption models can help to shed light on the mechanism controlling the biochar adsorption process and to evaluate the maximum adsorption capacity of ammonium (Foo and Hameed 2010; Limousin et al. 2007). Two commonly used isothermal adsorption models were introduced in this study, namely Langmuir and Freundlich. According to the Langmuir isotherm model, the process of adsorption happens in the monolayer on a uniform surface. The Freundlich isotherm model is a multi-molecular layer adsorption process that does not consider adsorption saturation and occurs on a multi-layered heterogeneous surface.

$$\text{Langmuir isotherm}: q_e = Q_o k_L C_e / (1 + k_L C_e) \tag{5}$$

$$\text{Freundlich isotherm}: q_e = k_f C_e 1/n \tag{6}$$

Table 1 Fitted parameter values of ammonium adsorption onto BB and BMBB using various adsorption kinetics models

Adsorbent	Model	Parameter 1	Parameter 2	R^2
BB	Pseudo-first-order	$k_1 = 4.199$	$q_e = 5.7$	0.956
	Pseudo-second-order	$k_2 = 0.954$	$q_e = 6.1$	0.969
	Elovich	$\alpha = 692.2$	$\beta = 1.57$	0.851
	Ritchie	$k_n = 0.0000844$	$q_e = 5.75$	0.959
BMBB	Pseudo-first-order	$k_1 = 2.783$	$q_e = 9.7$	0.964
	Pseudo-second-order	$k_2 = 0.357$	$q_e = 10.3$	0.965
	Elovich	$\alpha = 262.8$	$\beta = 0.764$	0.883
	Ritchie	$k_n = 0.0000639$	$q_e = 9.66$	0.964

The equilibrium adsorption isotherms of ammonium are presented in Fig. 5. The best-fit parameter values for each of the models are shown in Table 2. The Langmuir model gives a better explanation of the equilibrium ammonium adsorption isotherms of BB and BMBB with high R^2 value, implying that the adsorption behavior between BMBB and ammonium ions was controlled by homogenous surface along with monolayer adsorption. The maximum adsorption capacities of BB and BMBB calculated by the Langmuir equation were 7.0 and 22.9 mg g^{-1},
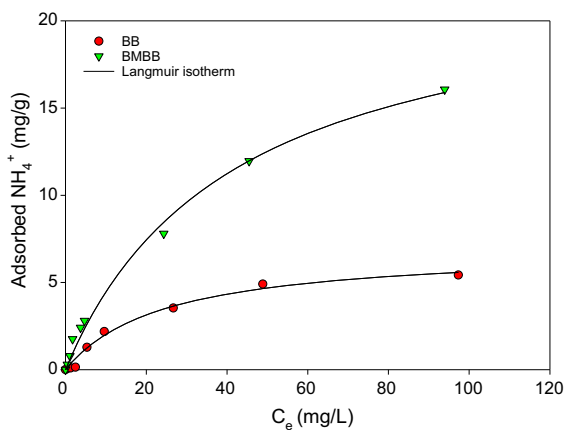
Fig. 5 Ammonium adsorption isotherms of BB and BMBB

respectively. The value suggests that the ammonium adsorption by BMBB was significantly improved. Because BMBB was rich in surface functional groups, the ammonium adsorption onto BMBB was primarily controlled through the interactions between the ammonium and the acidic oxygen-containing functional groups. The higher ammonium sorption capacity of BMBB may indicate that BMBB contains more surface functional groups than BB, therefore having more adsorption sites for cationic ion-exchanged ammonium (Lyu et al. 2018a). The presence of these functional groups plays a major role in binding the ammonium to the carboxyl groups of the BMBB. This is done through the bridging or complex formation processes. The adsorption of ammonium onto biochars could result majorly from the chemical bonding and polar interaction between ammonium and the surface functional groups. This enhanced the sorption ability of BMBB to ammonium by promoting the cation–π interaction between ammonium ion and the surface functional groups on the surface of biochar (Hale et al. 2013; Lyu et al. 2018b).

Compared with other adsorbents, the BMBB in this study show high ammonium adsorption capacity which is comparable to that of other modified biochars (Vu et al. 2017) (Table 3). It indicated that the BMBB henceforth has a good adsorption potential for the treatment of contaminated water.

Table 2 Fitted parameter values of ammonium adsorption onto BB and BMBB using different adsorption isotherm models

Adsorbent	Langmuir adsorption model			Freundlich adsorption model		
	Q_o (mg g^{-1})	k_L	R^2	k_f	$1/n$	R^2
BB	7.0	0.041	0.988	0.58	1.95	0.943
BMBB	22.9	0.024	0.994	1.13	1.678	0.992

Table 3 Comparison of the adsorption capacities of different adsorbents for ammonium removal from water

Adsorbent	Pyrolysis temperature (°C)	Q_m (mg g^{-1})	pH of solution	References
Rice husk biochar	600	3.24	7.0	Zhu et al. (2012)
Peanut shell biochar	400	10.52	–	Gai et al. (2014)
Giant reed biochar	500	1.490	7.0	Hou et al. (2016)
Oak sawdust biochar	300	5.31	–	Wang et al. (2015b)
Distillers' grains biochar	700	11.41	–	Zheng et al. (2018)
Modified corncob-biochar	400	22.6	7.0	Vu et al. (2017)
Pine sawdust biochar	300	5.38	7.0	Yang et al. (2018)
Wheat straw biochar	550	2.08	–	Yang et al. (2018)
Zeolite	–	9.41	8.0	Huang et al. (2010)
Halloysite	–	1.66	5.6	Jing et al. (2017)
Kaolinite	–	15.58	7.0	Alshameri et al. (2018)
Palygorskite	–	21.51	7.0	Alshameri et al. (2018)
Sepiolite	–	17.237	7.0	Alshameri et al. (2018)
BB	450	7.0	6.0	This study
BMBB	450	22.9	6.0	This study

Conclusions

Oxygen-containing functional groups are produced on the surface of biochar because of the ball milling processes. The adsorption kinetics, indicative of the energetically heterogeneous solid surface of the biochar, can be explained better with the pseudo-second-order kinetic model. The isothermal adsorption value of the BMBB corresponds to the Langmuir model. The maximum adsorption capacity of BMBB (22.9 mg g^{-1}) was much higher than that of BB (7.0 mg g^{-1}) due to the highly negatively charged functional groups. The ball milling can greatly promote the ammonium adsorption capacity and accelerate adsorption rate. This particular study offers a relatively cost-effective and efficient methodology for the improvement in the adsorption capacity of biochar for ammonium nitrogen.

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