Removal of aqueous ammonium by biochars derived from agricultural residuals at different pyrolysis temperatures

Fei Gao, Yingwen Xue, Pinya Deng, Xiaoru Cheng & Kai Yang

Taylor & Francis
Taylor & Francis Group

OPEN ACCESS

Removal of aqueous ammonium by biochars derived from agricultural residuals at different pyrolysis temperatures

Fei Gao[a], Yingwen Xue[a], Pinya Deng[b], Xiaoru Cheng[a] and Kai Yang[a]

[a]School of Civil Engineering, Wuhan University, Wuhan, China; [b]School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan, China

ABSTRACT

Water contamination by ammonium ions presents huge risks to the ecosystems. This work evaluated the potential of biochar as an alternative adsorbent to remove ammonium from aqueous solutions. Nine types of biochars were converted from three types of agricultural residuals at three pyrolysis temperatures. Batch sorption experiment showed that all the biochars effectively removed ammonium ions from water. The biochars produced at low pyrolysis temperatures, however, showed higher sorption of ammonium. The low-temperature biochars showed relatively fast sorption kinetics of ammonium, which reached equilibrium around 10 h. Sorption isotherms showed that the low-temperature biochars had high sorption capacities to the ammonium, and the Langmuir maximum capacities were all higher than 200 mg/g. Batch sorption experiments also showed the sorption of ammonium onto the biochar was affected by pH and temperature, but not by ionic strength. The biochar showed good sorption ability to ammonium in aqueous solutions under all of the tested conditions. Findings from this work indicated that biochar could be used as an alternative adsorbent for the treatment of ammonium in water.

1. Introduction

Aqueous ammonium ions are one of the most common nitrogen compounds that can cause serious pollution problems to water bodies.[1] Ammonium is released from municipal, industrial, agricultural practices, and imposes contamination risks on receiving waters by accelerating eutrophication, depleting dissolved oxygen, harming aquatic organisms.[2,3] While various treatment methods have been developed for the removal of ammonium from aqueous solutions, physical removal method using low-cost adsorbents is among the most competitive ways because of its performance and cost.[4,5]

Biochar is a pyrogenic carbon material that has attracted much attention recently.[6] When applied to soils as an amendment, biochar cannot only improve soil quality by increasing water and nutrient holding capacities and promoting beneficial microbial activities,[7] but also serve as carbon sink because of its good stability.[8] As a porous carbon material with relatively high surface area and pore volume, biochar also shows good sorption ability to various chemical compounds, including some of the common water pollutants. Previous studies have suggested that biochar can be used as a low-cost adsorbent for the removal of contaminants such as heavy metals and organic pollutants from water.[9,10] Biochars derived from agricultural residues such as straw, bagasse, and animal manure showed strong binding affinity to various heavy metal ions in aqueous solutions.[11–13] Several studies have also demonstrated that biochars have strong sorption ability to organic contaminants including pesticides and pharmaceuticals, and their sorption capacities are much higher than that of soils. [11,14,15]

Compared with heavy metals and organics, less research effort has been dedicated to investigate the removal of nutrients such as ammonium by biochars derived from agricultural residues.[16] Steiner et al. [17] found that biochar produced from pine chips can reduce the ammonium emissions from N-rich composts because the strong sorption ability of the biochar to gaseous NH_3 and aqueous ammonium ions. Yao et al. [18] tested the sorption of aqueous ammonium onto a range of biochars prepared from various biomass materials and found that all the tested biochars can somehow remove ammonium ions from water because the biochars have a net negative surface charge. The sorption of ammonium onto the biochar is reported to be reversible and thus is bioavailable and can be utilized by plants after being applied to soils as an amendment.[16,19] This makes biochar more attractive as an alternative adsorbent for the treatment of ammonium from water because the spent adsorbent

---

CONTACT Yingwen Xue ✉ ywxue@whu.edu.cn

may be applied directly to soils as a potential N-fertilizer. It is therefore crucial to conduct additional experimental investigations to test and evaluate the sorption ability of biochars, particularly the ones derived from waste biomass, to aqueous ammonium under various conditions.

In this work, biochars were made from three types of agricultural residuals at three pyrolysis temperatures. Sorption of ammonium ions onto the biochar was evaluated through batch sorption experiment under various conditions with following objectives: (1) determine the effect of pyrolysis temperature on the sorption of ammonium onto the biochars; (2) measure the sorption kinetics and isotherms of ammonium onto selected biochars; and (3) determine the effects of temperature, pH, and ionic strength on ammonium sorption.

2. Materials and methods

2.1. Biochar production

Three types of agricultural residuals: Peanut shells (PS), corncobs (CC), and cotton stalks (CS) were collected from local farms in Hubei Province in China as feedstock for biochar production. The feedstock was milled, washed, and air-dried. The feedstock was then added into a quartz tube reactor in a muffle furnace. High purify nitrogen gas was used to flush the reactor, and the furnace until oxygen content in the system was less than 0.5%. The temperature of the furnace was then raised to a peak temperature of 300, 450, or 600 °C and holed for 2 h. The furnace was then turned off and cooled down to the room temperature. The solid product (biochar) was collected, and yield of each samples was determined based the weight. The biochar samples were ground in a mortar with a pestle and sieved into a size range of 0.9–1.2 mm. The samples were washed several times with DI water and dried at 105 °C in an oven. The final biochar samples were labeled based on the feedstock type and peak pyrolysis temperature as PS300, PS450, and PS600; CS300, CS450, and CS600; and CC300, CC450, and CC600, and stored for later experiments.

2.2. Initial evaluation of ammonium sorption

To evaluate the sorption ability of the biochars to ammonium, about 0.1 g of the each biochar was mixed with 50 mL ammonia nitrogen solution (50 ppm) in a centrifuge tubes, the mixture was then shaken in a mechanical shaker (120 r/min) at 25 °C for 24 h. After that, the mixtures were filtered through 0.22-μm membrane filters and ammonium concentrations in the supernatants were determined using the phenate method with a UV/VIS spectrophotometer.[18] The sorption experiments were performed in triplicate, and the average values were reported.

2.3. Sorption kinetics and isotherms

Based on the initial evaluation, three biochars with the highest sorption of ammonium from each of the feed-stock types were selected for the kinetic and isotherm experiments. For sorption kinetics, about 0.1 g of the selected biochars was mixed with 50 mL ammonium solutions (50 ppm) in the centrifuge tubes. The mixtures were then shaken in the mechanical shaker (120 r/min) at 25 °C. At different time intervals (i.e., 0.5, 1, 2, 5, 10, 20, and 24 h), some of the tubes were withdrawn from the shaker. The mixtures were immediately filtered through 0.22-μm membrane filters to determine the ammonium concentrations in the supernatants. For the isotherms, about 0.1 g of the selected biochars was mixed with 50 mL ammonium solutions of different initial concentrations (i.e., 10, 25, 50, 100, 200, 300, and 500 mg/L). The mixtures were then shaken in the mechanical shaker (120 r/min) at 25 °C for 24 h. The mixtures were immediately filtered through 0.22-μm membrane filters to determine the ammonium concentrations in the supernatants. Sorbed ammonium concentrations on the biochar were calculated based on difference between the initial and final aqueous concentrations. The kinetic and isotherm experiments were performed in triplicate, and the average values were reported.

2.4. Effects of pH, temperature, and ionic strength

The biochar with the highest sorption of ammonium in the initial evaluation was selected to test the effects of pH, temperature, and ionic strength. For each condition, the biochar (0.1 g) was mixed with 50 mL ammonium solutions (50 ppm) in the centrifuge tube and the mixture was shaken in the mechanical shaker (120 r/min) for 24 h. Seven pH (1,3,5,7,9,10, and 12), three temperature (25, 40, 50 °C), and five ionic strength (25, 50, 100, 200, and 300 mg/L NaCl) values were tested in the experiments. The pH values of the solutions were adjusted with 1.0 mol/L NaOH and 1.0 mol/L HCl solutions. The ammonium concentrations in the aqueous and solid phases after the sorption were determined using the same methods as above. The experiments were performed in triplicate, and the average values were reported.

2.5. Mathematical models

Pseudo-first-order, pseudo-second-order, and Elovich models were used to describe the sorption kinetic data. The governing equations of these models can be written as [20]:

$$\text{First-order: } q_t = q_e(1 - e^{-k_1 t}) \qquad (1.1)$$

$$\text{Second-order: } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e^2 t} \qquad (1.2)$$

$$\text{Elovich: } q_t = \frac{1}{\beta} \ln(\alpha\beta t + 1) \qquad (1.3)$$

Table 1. Yield of the biochar (%) under different conditions.

	300 °C	450 °C	600 °C
PS	41.5	33.0	30.7
CC	34.8	25.4	22.6
CS	40.0	30.6	28.7

where q_t and q_e are the amount of ammonia nitrogen removed at time t and at equilibrium, respectively (mg/g), k_1 and k_2 are the first-order and second-order sorption rate constants (1/h), respectively, α is the initial sorption rate (mg/g), and β is the desorption constant (g/mg).

The Langmuir and Freundlich models were used to simulate the sorption isotherms. Their governing equations can be written as [20]:

$$\text{Langmuir: } q_e = \frac{KS_{max}C_e}{1 + kC_e} \quad (2.1)$$

$$\text{Freundlich: } q_e = K_f C_e^n \quad (2.2)$$

where K and K_f are the Langmuir bonding term related to interaction energies (L/mg), and the Freundlich affinity coefficient (mg$^{(1-n)}$L^n/g), respectively, S_{max} is the Langmuir maximum capacity (mg/kg), C_e is the equilibrium solution concentration (mg/L) of the sorbate, and n is the Freundlich linearity constant.

3. Results and discussion

3.1. Biochar yield

The yields of the biochars from the three feedstocks the three temperatures ranged from 22.6% to 41.5% (Table 1). For the same feedstock, biochar production decreased with the peak pyrolysis temperature with the highest yield at 300 °C and the lowest yield at 600 °C. This is consistent with the findings in the literature that high pyrolysis temperature decomposes more feedstock biomass.[21,22] The biochar yields also varied among the three types of feedstock with an order of: PS > CS > CC for all the three tested temperatures. This was mainly because the cellulose, hemicellulose, and lignin contents in the three feedstock materials were different. Under the same conditions, biomass has higher lignin content may produce more biochar.[21,23]

3.2. Initial evaluation

In the initial test, all the nine biochars effectively removed ammonium from aqueous solution (50 mg/L) with the adsorption rate ranged from 15.8 to 17.6 mg/g (Figure 1). Among all the samples, CS300 and PS600 showed the highest and the lowest ammonium sorption, respectively. The biochars converted from the CS and CC adsorbed more ammonium than their corresponding PS samples. For all the three types of feedstocks, the biochars produced at lower pyrolysis temperature showed better sorption ability and CS300, CS300, and PS300 were the best of their type (Figure 1). Previous studies have shown that low-temperature biochars tend to have more surface oxygen-containing groups, which can interact with cations including ammonium ions in aqueous solutions.[24,25]

3.3. Adsorption kinetics and isotherms

The three selected biochars showed relatively fast adsorption kinetics to ammonium in aqueous solutions (Figure 2). The adsorption was dramatic within the first 2 h and then slowed down to reach the equilibrium between 10 and 24 h. Simulations from the first-order, second-order, and Elovich models described the experimental data fairly well with R^2 values larger than 0.85 (Figure 2 and Table 2). The best-fit parameters of each model were listed in Table 2. Compared to the other two models, the Elovich model performed the best, suggesting the adsorption of ammonium onto the biochars might be controlled by multiple processes.[20]

The adsorption isotherms showed that the three biochars had relatively high sorption capacities (>100 mg/g) to ammonium in aqueous solutions (Figure 3). Compared to CS300, PS300 and CC300 had slightly high sorption to ammonium. Although the R^2 values were higher than 0.80 (Table 1), neither the Langmuir nor the Freundlich models matched the experimental data very well (Figure 3). This also suggested that the adsorption of ammonium onto the biochars could be controlled by multiple mechanisms. The best-fit parameters of the two models were listed in Table 1, which shows that the Langmuir maximum adsorption capacities of the three biochars were all higher than 200 mg/g. Findings from the kinetics and isotherms indicated that the low-temperature biochars were highly effective in removing ammonium from water because of their fast adsorption kinetics and high adsorption capacities.

3.4. Effects of pH, temperature, and ionic strength

The sorption of ammonium onto the selected biochar (CS300) was high at all the tested pH values (Figure 4(a)). The optimum pH for adsorption was found to be at 10, where the ammonium sorption reached 19.2 mg/g. As the temperature rose, ammonium adsorption onto the
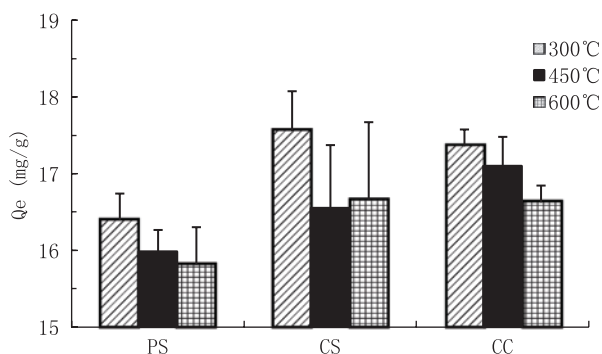
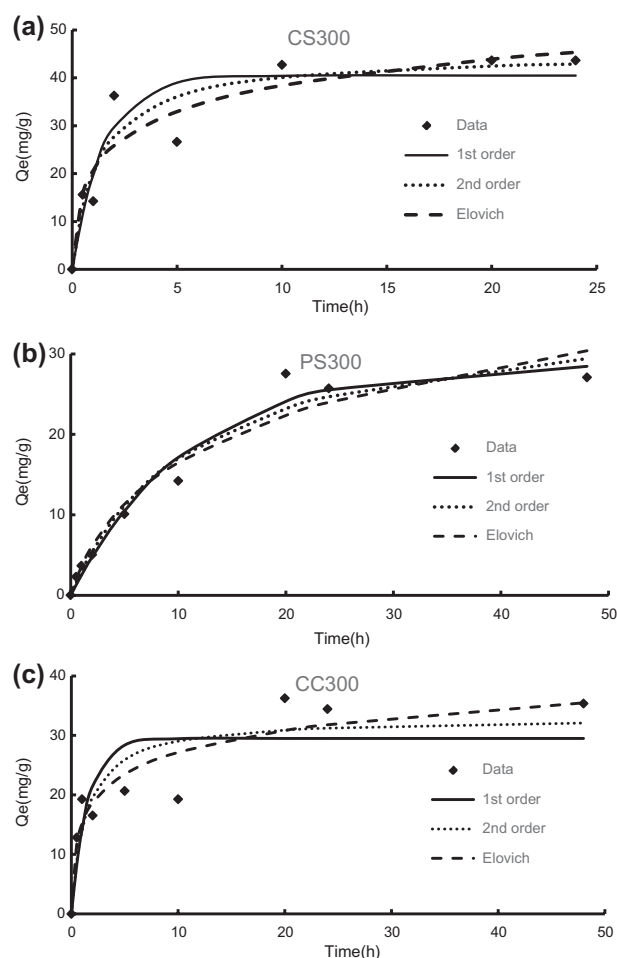**Figure 1.** Initial evaluation of ammonium adsorption onto the biochars.

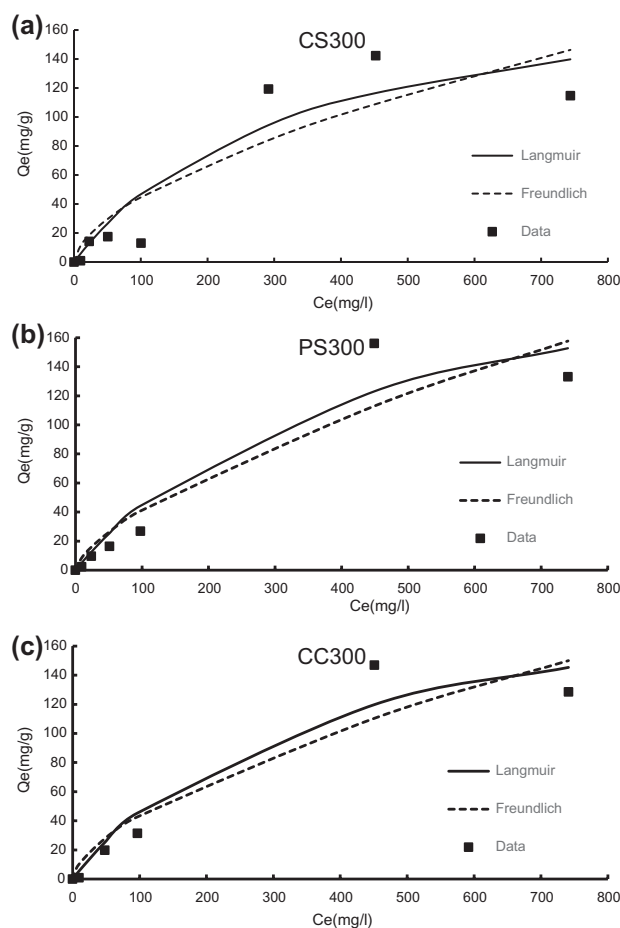**Figure 2.** Adsorption kinetics of ammonium onto three biochars produced at 300 °C.

Figure 3. Adsorption isotherms of ammonium onto three biochars produced at 300 °C.

biochar reduced (Figure 4(b)), indicating the sorption process was controlled by exothermic reactions. Even at 50 °C, the adsorption of ammonium was still close to 10 mg/g, suggesting the biochar can be used in high temperature environment to remove ammonium from water. Changes in ionic strength (NaCl) showed little influence on the sorption of ammonium onto the biochar (Figure 4(c)), suggesting the interactions between ammonium ions and the biochar surface might be selective or site specific. This may promote the real-world application of the biochar for the removal of ammonium ions from wastewater.
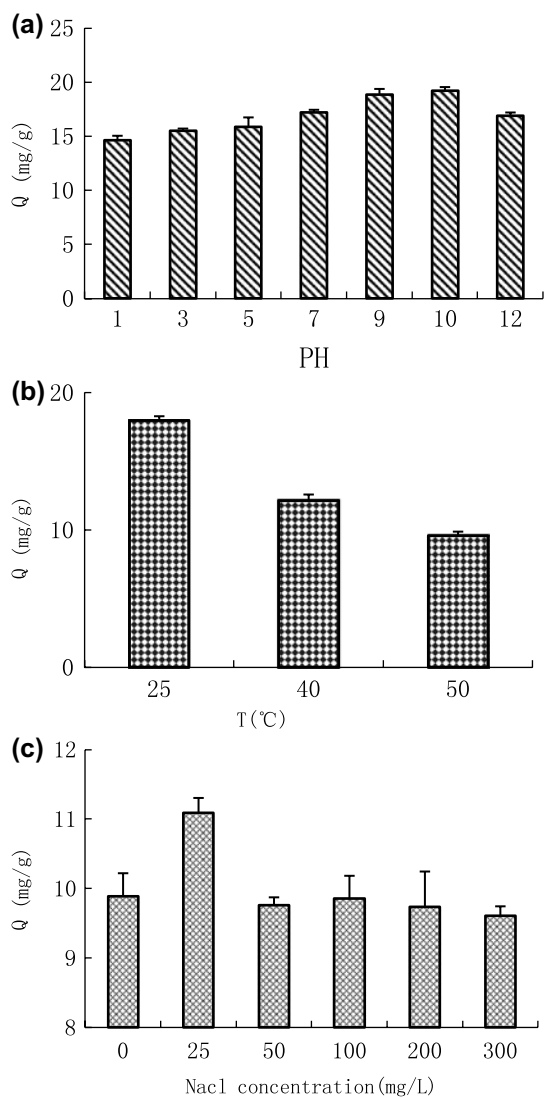
Table 2. Best-fit model parameters of ammonia sorption onto three biochars produced at 300 °C.

Biochar	Model	Parameter 1	Parameter 2	R^2
CS300	First-order	$K_1 = 0.662$	$qe = 40.5$ mg/g	0.867
	Second-order	$K_2 = 0.018$	$qe = 45.1$ mg/g	0.895
	Elovich	$α = 98.45$	$β = 0.126$	0.895
	Langmuir	$K = 0.003$	$S_{max} = 202.5$ mg/g	0.879
	Freundlich	$Kf = 2.92$	$n = 0.592$	0.822
PS300	First-order	$K_1 = 0.09$	$qe = 28.8$ mg/g	0.975
	Second-order	$K_2 = 0.0024$	$qe = 36.4$ mg/g	0.965
	Elovich	$α = 4.237$	$β = 0.101$	0.952
	Langmuir	$K = 0.002$	$S_{max} = 243.3$ mg/g	0.928
	Freundlich	$Kf = 1.91$	$n = 0.668$	0.892
CC300	First-order	$K_1 = 0.655$	$qe = 29.5$ mg/g	0.704
	Second-order	$K_2 = 0.022$	$qe = 33.0$ mg/g	0.803
	Elovich	$α = 86.19$	$β = 0.188$	0.887
	Langmuir	$K = 0.003$	$S_{max} = 217.4$ mg/g	0.942
	Freundlich	$Kf = 2.54$	$n = 0.617$	0.904

(a)

(b)

(c)

Figure 4. Effects of pH, temperature, and ionic strength on the adsorption of ammonium onto CS300.

4. Conclusions

Nine biochars were prepared from agricultural residuals at different pyrolysis temperatures. All of them showed good sorption ability to ammonium in aqueous solutions; however, the biochars produced at lower temperature were better. The low-temperature biochars showed fast and high sorption of ammonium with the Langmuir maximum sorption capacities higher than 200 mg/g. The sorption of ammonium onto the biochar was relatively high at various experimental conditions. All these results suggested that biochars, particularly low-temperature biochars, derived from agricultural residuals could be used as an alternative adsorbent to remove or reclaim ammonium ions from water.

Disclosure statement

No potential conflict of interest was reported by the authors.

Notes on contributors

Fei Gao is a graduate student in the School of Civil Engineering at the Wuhan University in China. Her research mainly focuses on water treatment and wastewater treatment.

Yingwen Xue is an associate professor in the School of Civil Engineering at the Wuhan University in China. He earned his PhD degree in Disaster Prevention and Reduction Engineering and Protective Engineering at Wuhan University. Xue has published more than 31 peer-reviewed journal articles. His research mainly focuses on water treatment, biochar, and nanotechnology for water treatment.

Pinya Deng is a graduate student in the School of Environmental Science and Engineering at the Huazhong University of Science and Technology in China. Her research mainly focuses on environmental science and engineering.

Xiaoru Cheng is a professor in the School of Civil Engineering at the Wuhan University in China. He earned his master's degree in Municipal engineering at Wuhan University of Technology. He has published more than 15 peer-reviewed journal articles. His research mainly focuses on water treatment, biochar, and nanotechnology for water treatment.

Kai Yang is a professor in the School of Civil Engineering at the Wuhan University in China. He earned his PhD degree in Hydrology and Water Resources at Wuhan University. Yang has published more than 39 peer-reviewed journal articles. His research mainly focuses on water treatment, water restoration, and water quality.

References

[1] Baldisserotto B, Martos-Sitcha JA, Menezes CC, et al. The effects of ammonia and water hardness on the hormonal, osmoregulatory and metabolic responses of the freshwater silver catfish Rhamdia quelen. Aquat. Toxicol. 2014;152:341–352.

[2] Glavan M, Pintar M. Impact of point and diffuse pollution sources on nitrate and ammonium ion concentrations in the Karst-influenced Temenica river. Fresen. Environ. Bull. 2010;19:1005–1014.

[3] Cheng C, Tan W, Liu LY. Numerical simulation of water curtain application for ammonia release dispersion. J. Loss Prev. Process Ind. 2014;30:105–112.

[4] Tekerlekopoulou AG, Pavlou S, Vayenas DV. Removal of ammonium, iron and manganese from potable water in biofiltration units: a review. J. Chem. Technol. Biotechnol. 2013;88:751–773.

[5] Jorgensen TC, Weatherley LR. Ammonia removal from wastewater by ion exchange in the presence of organic contaminants. Water Res. 2003;37:1723–1728.

[6] Kambo HS, Dutta A. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. Renewable Sustainable Energy Rev. 2015;45:359–378.

[7] Lehmann J, Rillig MC, Thies J, et al. Biochar effects on soil biota – a review. Soil Biol. Biochem. 2011;43:1812–1836.

[8] Zimmerman AR, Gao B, Ahn MY. Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. Soil Biol. Biochem. 2011;43:1169–1179.

[9] Xie T, Reddy KR, Wang CW, et al. Characteristics and applications of biochar for environmental remediation: a review. Crit. Rev. Environ. Sci. Technol. 2015;45:939–969.

[10] Inyang M, Dickenson E. The potential role of biochar in the removal of organic and microbial contaminants from potable and reuse water: a review. Chemosphere. 2015;134:232–240.

[11] Cao XD, Ma L, Gao B, et al. Dairy-manure derived biochar effectively sorbs lead and atrazine. Environ. Sci. Technol. 2009;43:3285–3291.

[12] Inyang M, Gao B, Yao Y, et al. Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. Bioresour. Technol. 2012;110:50–56.

[13] Jiang TY, Jiang J, Xu RK, et al. Adsorption of Pb(II) on variable charge soils amended with rice-straw derived biochar. Chemosphere. 2012;89:249–256.

[14] Kasozi GN, Zimmerman AR, Nkedi-Kizza P, et al. Catechol and humic acid sorption onto a range of laboratory-produced black carbons (biochars). Environ. Sci. Technol. 2010;44:6189–6195.

[15] Yao Y, Gao B, Chen H, et al. Adsorption of sulfamethoxazole on biochar and its impact on reclaimed water irrigation. J. Hazard. Mater. 2012;209–210:408–413.

[16] Spokas K, Novak J, Venterea R. Biochar's role as an alternative N-fertilizer: ammonia capture. Plant Soil. 2012;350:35–42.

[17] Steiner C, Das KC, Melear N, et al. Reducing nitrogen loss during poultry litter composting using biochar. J. Environ. Qual. 2010;39:1236–1242.

[18] Yao Y, Gao B, Zhang M, et al. Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. Chemosphere. 2012;89:1467–1471.

[19] Taghizadeh-Toosi A, Clough T, Sherlock R, et al. Biochar adsorbed ammonia is bioavailable. Plant Soil. 2012;350:57–69.

[20] Yao Y, Gao B, Inyang M, et al. Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings. J. Hazard. Mater. 2011;190:501–507.

[21] Sun Y, Gao B, Yao Y, et al. Effects of feedstock type, production method, and pyrolysis temperature on biochar and hydrochar properties. Chem. Eng. J. 2014;240:574–578.

[22] Liao R, Gao B, Fang J. Invasive plants as feedstock for biochar and bioenergy production. Bioresour. Technol. 2013;140:439–442.

[23] Demirbas A. Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. J. Anal. Appl. Pyrol. 2004;72:243–248.

[24] Uchimiya M, Wartelle LH, Klasson KT, et al. Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. J. Agr. Food Chem. 2011;59:2501–2510.

[25] Chen BL, Chen ZM. Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. Chemosphere. 2009;76:127–133.