Removal of nitrate from constructed wetland in winter in high-latitude areas with modified hydrophyte biochars

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Abstract−In high-latitude areas, nitrate treatment from constructed wetlands is often not so good in winter. The study aims to develop an efficient and economic technology to remove nitrate from constructed wetland under the conditions of winter temperature. We conducted laboratory experiments to investigate the removal of nitrate from aqueous solution and wastewater by modified hydrophyte biochars from constructed wetlands. The second-order model fit the nitrate desorption kinetics of modified hydrophyte biochars with a high coefficient of determination ($R^2 > 0.99$). Freundlich isotherms performed well to fit the nitrate sorption data ($R^2 > 0.98$) of modified hydrophyte biochars. Batch adsorption experiments also showed that both initial solution pH and coexisting anions could affect the adsorption of nitrate onto modified hydrophyte biochars. Our results suggested that modified hydrophyte biochars might be a promising alternative wastewater treatment technology for nitrate removal from constructed wetland in winter in high-latitude areas.

Keywords: Hydrophyte, Biochar, Constructed Wetland, Adsorption, Nitrate

INTRODUCTION

With the rapid development of social economy, a large quantity of wastewater and agricultural runoff is discharged into natural water bodies, leading to rising nitrate content as well as serious water eutrophication problems [1,2].

More recent applied research has focused upon ameliorating the nitrate contamination of surface waters as a drinking water supply [3]. Constructed wetlands have become increasingly favored as a simple and economical means for reduction of high concentrations of nitrate in both agricultural runoff and treated municipal wastewater [4]. Nitrate removal in constructed wetland occurs through plant uptake and by denitrification [5]. With high nitrate loading rates typical of constructed wetlands in high-latitude area, temperature is a very important factor [6].

In high-latitude areas, the temperature of constructed wetlands in winter is low, thus leading to the decreased denitrification effect and the slow removal rate of nitrate [7]. Moreover, the decomposition of aquatic plants in winter results in secondary pollution in water bodies [8,9]. The normal operation of constructed wetlands in winter in high-latitude areas remains a challenge.

Many studies have considered the adsorption of water pollutants from the plant waste [10-12]. A biochar is one class of carbon-rich solid mixture obtained through the pyrolysis of biological residues at a high temperature under the conditions of limited oxygen [13,14]. It is a new, inexpensive, adsorbent material. However, biochars are negatively charged groups and that cation exchange capacity is higher than anion exchange capacity. It has been believed that biochars mainly adsorbed cations other than anions and that the sorption capacity of nitrate by biochars itself was very limited [15,16].

Several methods have thus been developed to modify biochar to enhance its sorption of nitrate [17-19]. For example, biochar composites prepared by pyrolyzing iron chloride ($FeCl_3$) greatly enhance nitrate sorption ability of the biochars [20,21]. However, the iron ions of modified biochar may have some influence on the water body. Excessive iron levels can cause iron bacteria to multiply and block the pipeline. Thus, a method is needed which has little influence on the water body to modify biochars.

Our aim was to develop an efficient and economic technology to remove nitrate from constructed wetland in high-latitude areas under the conditions of winter temperature. The litters of the common aquatic plants (reed (*Phragmites australis* Trin. Ex Steud.) and cattail (*Typha orientalis* C. Presl)) in constructed wetland were used to prepare the biochars and then modified with hydrochloric acid. As a follow-up, laboratory adsorption experiments and mathematical models were used in this study to determine the mechanisms and characteristics of nitrate adsorption onto the modified hydrophyte biochars. Therefore this study was designed with the following objectives: (a) determine the surface characteristics of the modified hydrophyte biochars from reed and cattail; (b) measure the kinetics and equilibrium isotherms of nitrate adsorption onto the modified hydrophyte biochars; and (c) determine the effect of initial solution pH and coexisting anions on the adsorption of nitrate onto the modified hydrophyte biochars.

MATERIALS AND METHODS

1. Preparation and Modification of Biochars

Litter of reed and cattail were acquired in November 2014 from Mantanghe constructed wetland, Shenyang City, Liaoning Province,

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China. Then stalks were washed with deionized water and dried. After crushing with plant crusher, the crushed stalks passed through a 100-mesh sieve and were collected. The collected particles were put into a tubular resistance furnace. Nitrogen flow was purged into the furnace according to the flow rate of $400\,mL\cdot min^{-1}$ to maintain the low oxygen content in the furnace. The temperature in the furnace was increased to $700\,°C$ according to the program-controlled heating rate of $10\,°C\cdot min^{-1}$ and then maintained for 20-min pyrolysis. After the pyrolysis process, biochars were naturally cooled to room temperature and then removed from the furnace. Then biochars were washed with deionized water to neutral pH and dried at $105\,°C$. Finally, reed biochar and cattail biochar were obtained.

These biochars were activated by heating with concentrated hydrochloric acid (HCl). Air dried biochar (10 g) was placed in a conical flask covered with a watch glass and treated with 200 ml of concentrated HCl. The biochar mixed with concentrated HCl was heated on hot plate at $200\,°C$ (placed in laboratory hood) for 24 h. The treated biochars were washed repeatedly with deionized water and then dried at $80\,°C$. Finally, modified reed biochar (MRB) and modified cattail biochar (MCB) were obtained.

2. Sorption Experiments and Sample Analysis

2-1. Sorption Kinetics of MRB and MCB

First, 0.2 g of MRB was, respectively, weighed into a series of centrifuge tubes. Then, 10 mL of $20\,mg\cdot L^{-1}$ KNO_3 solution was added into each centrifuge tube, which was put on the shaking table under the conditions of $(10\pm0.5)\,°C$ and 150 rpm. The tubes were taken out, respectively, after 5, 10, 20, 40, 80, 160, and 320 min. Then the solution in the tubes was filtered through the membrane with the pore size of $0.45\,\mu m$ and the concentration of Nitrate in the filtered solution from each tube was measured in three replicates. The measurement results were averaged.

Nitrate adsorption kinetics experiments of MCB were designed as above.

2-2. Sorption Isotherms of MRB and MCB

First, 0.2 g of MRB was weighed into a series of centrifuge tubes. Then, 10 mL of 5, 10, 20, 40, 80, 160, and $320\,mg\cdot L^{-1}$ KNO_3 solution was added into different centrifuge tubes. Three duplicates were arranged for each KNO_3 concentration. Centrifuge tubes were vibrated for 2 h on the shaking table under the conditions of $(10\pm0.5)\,°C$ and 150 rpm. The tubes were taken out and the solution in the tubes was filtered through the membrane with the pore size of $0.45\,\mu m$. The concentration of nitrate in the filtered solution from each tube was measured.

Nitrate adsorption isotherm experiments of MCB were designed as above.

2-3. Effect of pH and Competitive Anions

First, 0.2 g of MRB was weighed into a series of centrifuge tubes. Then, 10 mL of $20\,mg\cdot L^{-1}$ KNO_3 solution with different initial pH values (3.0, 5.0, 7.0, 9.0, and 11.0) was added into different centrifuge tubes. Three duplicates were arranged for each pH. Centrifuge tubes were vibrated for 2 h on the shaking table under the conditions of $(10\pm0.5)\,°C$ and 150 rpm. The tubes were taken out and the solution in the tubes was filtered through the membrane with the pore size of $0.45\,\mu m$. The concentration of nitrate in the filtered solution from each tube was measured.

Nitrate adsorption experiments of MCB for different pH values

were designed as above.

Moreover, 0.2 g of MRB was weighed into a series of centrifuge tubes. Then, 10 mL of $20\,mg\cdot L^{-1}$ KNO_3 solution was added into centrifuge tubes and 10 mL of $20\,mg\cdot L^{-1}$ NaCl, KH_2PO_4 and $NaHCO_3$ solution was added into centrifuge tubes, which were vibrated for 2 h on the shaking table under the conditions of $(10\pm0.5)\,°C$ and 150 rpm. The tubes were taken out and the solution in the tubes was filtered through the membrane with the pore size of $0.45\,\mu m$. The concentration of nitrate in the filtered solution from each tube was measured.

Nitrate adsorption experiments of MCB under the existence of competitive anions were designed as above.

2-4. Removal Efficiency of High Concentration of Nitrate from Wastewater

Wastewater was acquired in November 2014 from Mantanghe constructed wetland, Shenyang City, Liaoning Province, China. First, 0.2 g of MRB was weighed into a series of centrifuge tubes. Then, 20 mL of wastewater (nitrate: $12.5\,mg\cdot L^{-1}$, COD: $175\,mg\cdot L^{-1}$, ammonia nitrogen: $24\,mg\cdot L^{-1}$, TP: $4.2\,mg\cdot L^{-1}$) was added into each centrifuge tube, which was put on the shaking table under the conditions of $(10\pm0.5)\,°C$ and 150 rpm. The tubes were taken out after 5, 10, 20, 40, 80, 160, and 320 min. Then wastewater in the tubes was filtered through the membrane with the pore size of $0.45\,\mu m$ and the concentration of nitrate in the filtered solution from each tube was measured in three replicates. The measurement results were averaged.

2-5. Analysis

The concentration of nitrate was determined with with UV spectrophotometry. Zeta potential analyzer (ZEN360, Brookhaven Corporation) was used to determine surface potentials of MRB and MCB. The surface morphology of biochars (JSM-6360LA, JEOL Corporation) was characterized by a microscope.

2-6. Data Processing

Experimental data were processed with SPSS 19.0 and Excel software and the curves were plotted with Origin 8.0 software.

## RESULTS AND DISCUSSION

1. Surface Zeta Points

Hydroxyl, phenolic hydroxyl group, cyclic lactone peroxide, and other oxygen-containing groups were present on the surface of modified biochars [22,23]. Due to the presence of these surface groups, biochars had different surface hydrophilicities and surface acidities, thus resulting in different surface charges (positive or negative) [15]. It was determined that MRB and MCB were negatively charged with the Zeta potentials of $-28.81\,mV$ and $-12.23\,mV$. HCl-modified biochars (MRB and MCB) were positively charged with Zeta potentials of $+2.31\,mV$ and $+5.46\,mV$. Modification with hydrochloric acid reduced negative charges on biochar surface and increased positive charges. The modification of the biochars was conducive to the adsorption of negatively charged nitrate ions.

2. Surface Morphology

The average particle size of the modified biochar was between 0.1 mm and 0.2 mm. The specific surface area of the modified biochar was $312\,m^2\cdot g^{-1}$. In the SEM images (Figs. 1(a) and 1(b)), MRB and MCB show smooth surfaces containing many irregular cavi-
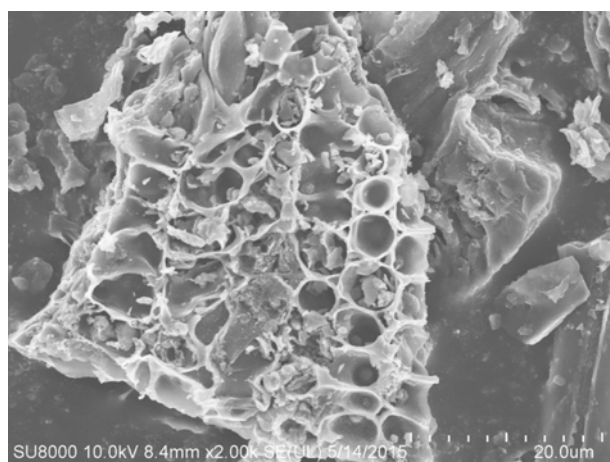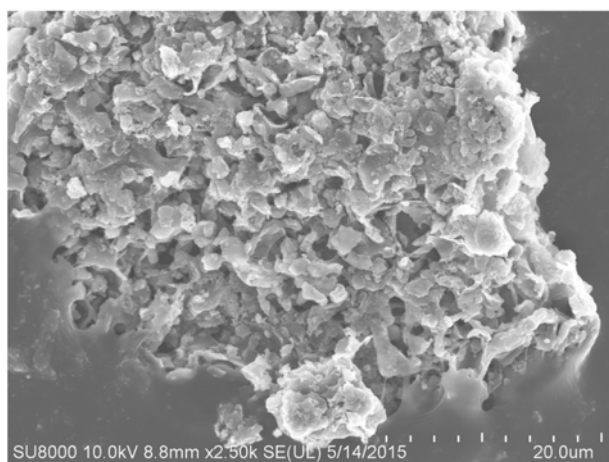
Fig. 1. (a) SEM of MRB. (b) SEM of MCB.
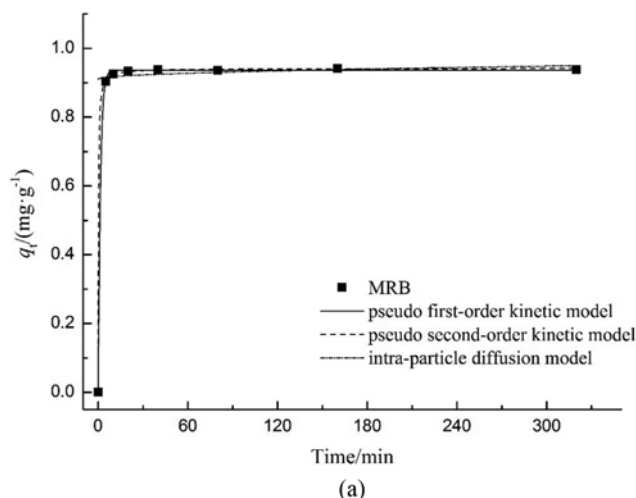

Fig. 2. (a) Kinetics of nitrate adsorption onto MRB. (b) Kinetics of nitrate adsorption onto MCB.

ties. Due to the decomposition of large amounts of cellulose during the pyrolysis at 700 °C, the surface sediments were decreased and micropores were formed on the surfaces of the biochars. High temperature and acid activation greatly increased the surface area of all biochars, which is more conducive to provide more adsorption sites for modified biochars [24,25].
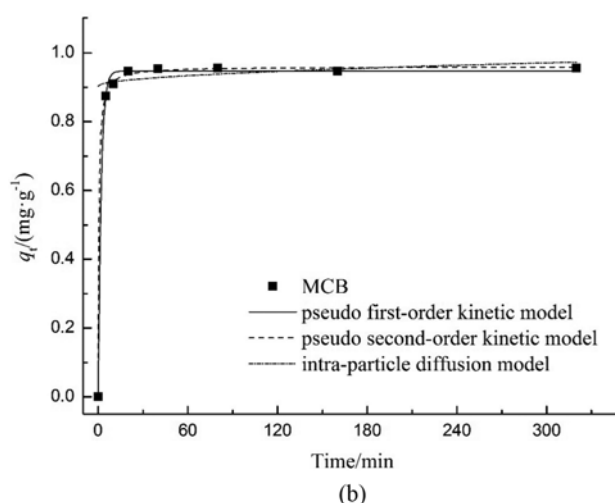
3. Sorption Kinetics

As shown in Figs. 2(a) and 2(b), the sorption effects of nitrate by MRB and MCB were significant. The sorption of nitrate by MRB and MCB was fast in the initial 5 min. After 40 min, the sorption capacity slowly increased and tended to be stable after sorption. The high sorption rate is of great significance to practical applications because a rapid sorption rate can ensure the high removal efficiency. The first phase could be ascribed to rapid occupation of easily accessible external surface sorption sites such as outer sphere complexation. The slow phase could be related to the formation of inner layer complexes [26,27].

The study of sorption kinetics can enhance the understanding of the sorption mechanism. Sorption kinetics mainly involves the sorption rate of solute by adsorbents from the solution. To study the control mechanism of the sorption process, we adopted a pseudo first-order equation, pseudo-second-order equation, and intra-par-

ticle diffusion equation to fit the experimental results.

Pseudo-first-order equation:
$$q_t = q_e(1 - e^{-k_1 t}) \tag{1}$$

Pseudo-second-order equation:
$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \tag{2}$$

Intra-diffusion equation:
$$q_t = q_i t^{1/2} + C \tag{3}$$

where q_t and q_e are, respectively, nitrate sorption at the moment t and after reaching sorption equilibrium, mg·g^{-1}; t is sorption time, min; k_1, k_2, and q_i are the rate constants of pseudo first-order equation, pseudo-second-order equation, and intra-particle diffusion equation and the units were respectively min^{-1}, g·mg^{-1}·min^{-1}, and mg·g^{-1}·min$^{-0.5}$.

The fitting results are shown in Table 1, and fitting curves of three equations are plotted in Figs. 2(a) and 2(b). In Table 1, Fig. 2(a) and Fig. 2(b), the fitting correlation coefficient for the nitrate sorption experimental results of MRB and MCB with pseudo-sec-

Table 1. Kinetic parameters for nitrate adsorption on biochars

Kinetic model	Parameter	MRB	MCB
Pseudo-first-order	k_1/min^{-1}	0.6688	0.5025
	$q_e/mg \cdot L^{-1}$	0.9361	0.9471
	R^2	0.9791	0.9882
Pseudo-second-order	$k_2/g \cdot mg^{-1} \cdot min^{-1}$	5.3415	2.1677
	$q_e/mg \cdot g^{-1}$	0.9415	0.9599
	R^2	0.9999	0.9996
Intra-particle	$q_i/mg \cdot g^{-1} \cdot min^{-0.5}$	0.0021	0.0039
diffusion model	R^2	0.0706	0.1468

ond-order equation is higher than that of pseudo-first-order equation. In addition, the theoretical values of sorption of nitrate onto MRB and MCB calculated with pseudo-second-order equation (q_e) are closer to the measured values, indicating that the pseudo-second kinetic model can better describe the sorption process of nitrate by MRB and MCB.

In intra-diffusion equation, if the fitted curve passed through the origin of coordinates, the intra-diffusion would be the control step of the sorption rate [11]. However, the fitted curve for nitrate sorption experimental did not pass through the origin of coordinates in the experiment, indicating that the intra-diffusion was not the only control step in the sorption process for nitrate sorption experimental [28].

4. Sorption Isotherms

The sorption capacity of nitrate by biochars itself was very limited [15]. As shown in Figs. 3(a) and 3(b), with the increase in the initial concentration of nitrate, the sorption amounts of MRB and MCB also increase.

The sorption isotherms were fitted with Langmuir Equation and Freundlich Equation, which are often used to describe the sorption process of ions onto the adsorbent as follows:

Langmuir Equation:

$$q_e = \frac{bQ_mc_e}{1+bc_e} \qquad (4)$$

Freundlich Equation:

$$q_e = K_f c_e^{1/n} \qquad (5)$$

where q_e is the equilibrium sorption capacity, $mg \cdot g^{-1}$; c_e is the equilibrium concentration, $mg \cdot L^{-1}$; b is the Langmuir equilibrium constant, $L \cdot mg^{-1}$; Q_m is maximum theoretical sorption capacity, $mg \cdot g^{-1}$; K_f is the Freundlich constant, $mg^{-1/n} \cdot g^{-1} \cdot L^{-1/n}$; $1/n$ is the Freundlich exponent. Data fitting results are provided in Table 2 and fitting curves of two models are plotted in Figs. 3(a) and 3(b). Freundlich Equation showed the better fitting results for nitrate
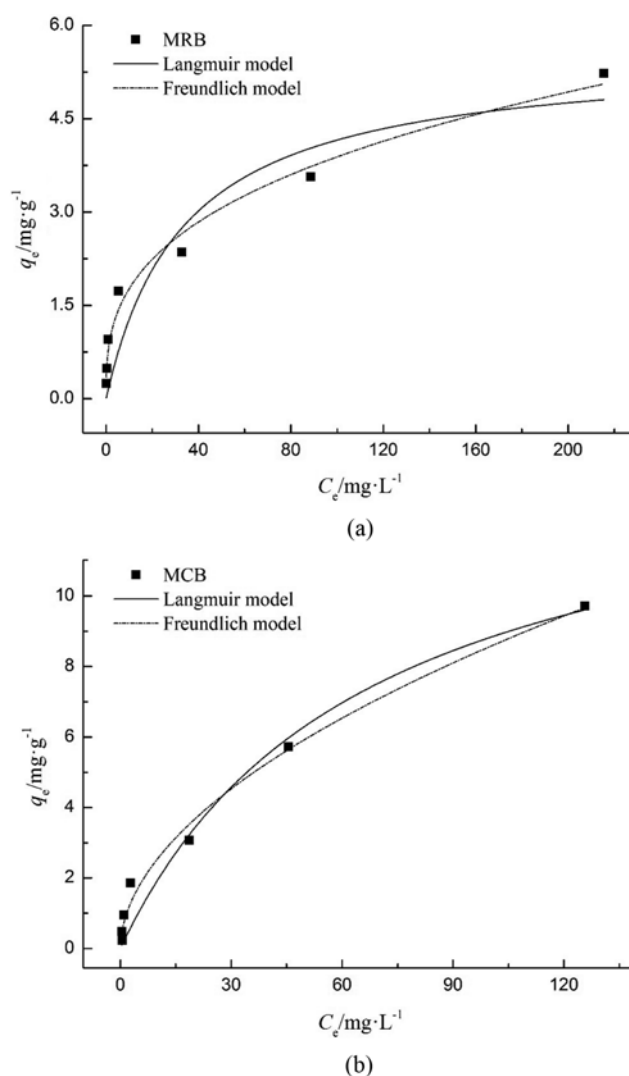
Fig. 3. (a) Adsorption isotherm of nitrate onto MRB. (b) Adsorption isotherm of nitrate onto MCB.

sorption isotherms of MRB and MCB with the correlation coefficient (R^2) larger than 0.98.

Freundlich equation belongs to multilayer adsorption theory, which is more close to practical experience. It showed that the adsorption of MRB and MCB on nitrate was mainly based on multi molecular layer and heterogeneous adsorption model [29]. According to the Freundlich exponent of $1/n$, if $0.1 < 1/n < 1$, the absorption process is easy; the smaller $1/n$ indicates the better absorption effect [30]. MRB and MCB showed better sorption effects of nitrate.

According to the maximum sorption capacity of Q_m, nitrate sorption capacity of Q_m for MRB and MCB were 14.6661 $mg \cdot g^{-1}$

Table 2. Constants and correlation coefficients of Langmuir and Freundlich models for nitrate adsorption onto MRB and MCB

Biochars	Langmuir model			Freundlich model		
	$Q_m/mg \cdot g^{-1}$	$b/L \cdot mg^{-1}$	R^2	$K_f/mg^{1-1/n} \cdot g^{-1} \cdot L^{-1/n}$	$1/n$	R^2
MRB	5.5559	0.0297	0.8531	0.8038	0.2343	0.9826
MCB	14.6661	0.0151	0.9596	0.7493	0.5291	0.9884

and 5.5559 mg·g^{-1}. Zhang et al. adopted Mg-modified peanut shell biochars to adsorb nitrate, and the Q_m was only 1.17 mg·g^{-1} [31]. Rajesh et al. realized the Q_m of 2.47 mg·g^{-1} with Fe-modified crop straw biochars [32]. In the paper, the maximum adsorption capacity realized with hydrochloric acid-modified biochars obtained was higher than the above results of these studies. Therefore, we significantly improved the adsorption capability of nitrate with hydrochloric acid-modified biochars.

The sorption of nitrate onto MRB and MCB could be controlled by multiple processes associated with carbonaceous surfaces [24]. The sorption of nitrate onto a solid surface is most likely controlled by the positive charge of the sorbent surface. They are also predominantly positively charged under the tested experimental conditions. Thus, nitrate sorption at MRB and MCB surfaces may be mainly due to electrostatic interaction (outer-sphere complexation mechanism) and to a lesser extent ionic exchange mechanism, which explains why modified biochar greatly enhanced biochar's

(a)

(b)

Fig. 4. (a) Effects of pH on nitrate adsorption onto MRB and MCB.
(b) Effect of coexisting anions on nitrate adsorption onto MRB and MCB.

sorption ability to nitrate.

5. Effect of pH and Coexisting Anions

In the nitrate solution with the initial concentration of 20 mg·L^{-1}, the variations of nitrate removal rates of MRB and MCB with the initial pH value are shown in Fig. 4(a). When the initial pH value was increased from 3 to 7 in the nitrate solution with the initial concentration of 20 mg·L^{-1}, nitrate removal rates of MRB and MCB were not significantly changed; when the pH value was increased from 7 to 11, nitrate removal rates of MRB and MCB were, respectively, decreased by 59.09% and 55.82%.

Under the lower pH conditions, a large number of H$^+$ ions led to a decrease in the negatively charged groups on biochar surfaces, thereby increasing positively charged groups [32]. Therefore, nitrate nitrogen was more easily absorbed on biochar surfaces. The lower pH of the solution indicated larger adsorption capacity. With the pH rise, negative charges on the surface of modified biochars were increased and electrostatic repulsion force was enhanced. Therefore, the adsorption capacity was decreased [33,34]. The concentration of OH$^-$ was also increased with the pH rise, and OH$^-$ competed adsorption sites with nitrate anions. In this way, effective adsorption sites on the surfaces of modified biochars were decreased. The results were consistent with previous reports.

The presence of competitive anions such as H$_2$PO$_4^-$, HCO$_3^-$ and Cl$^-$ in solution significantly decreased nitrate sorption on MRB and MCB (Fig. 4(b)). The decrease in nitrate sorption may be due to the preference of sorption sites towards more highly negatively charged potential anions such as H$_2$PO$_4^-$, HCO$_3^-$ and Cl$^-$ [33]. This phenomenon was observed to be more predominant with MRB and MCB, which may be due to their higher surface area and greater sorption capacity. Moreover, the effects of the competing anions on nitrate follow this order: H$_2$PO$_4^-$>HCO$_3^-$>Cl$^-$. The binding attraction of Cl$^-$ for MRB and MCB was found to be weaker than that of H$_2$PO$_4^-$ and HCO$_3^-$. The interference study showed the probable effect of higher H$_2$PO$_4^-$ concentration on the removal of nitrate. Thus, designing an effective nitrate treatment system must consider the competitive effect of dissolved anions in water bodies.

6. Removal Efficiency of High Concentration of Nitrate from Wastewater

The content of nitrate in wastewater was 12.5 mg·L^{-1}. The nitrate content decreased rapidly. After 5 min, the removal rate reached 46.22%. After 40 min, the removal efficiency slowly increased and tended to be stable after sorption. After 320 min, the removal rate was the highest and reached 74.35%. Modified hydrophyte biochars prepared with aquatic plant litters collected from constructed wetlands could efficiently remove nitrate from wastewater, improve the performance of constructed wetlands in winter, and promote the utilization of aquatic plants.

CONCLUSIONS

Findings from this study provide a fundamental understanding for effective synthesis method of modified hydrophyte biochars and also give insights for the dynamic utilization of modified hydrophyte biochars for different environmental applications including wastewater treatments. Modified hydrophyte biochars from
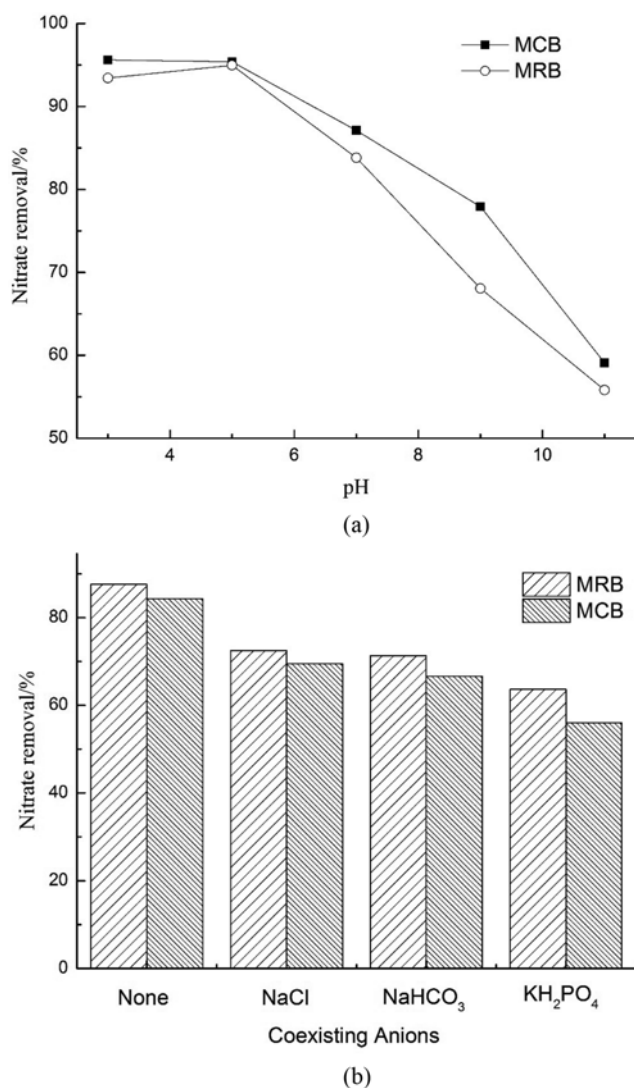
reed and cattail demonstrated superior ability to remove nitrate from wastewater under the condition of winter temperature. The nitrate sorption capacity of modified hydrophyte biochars was observed to depend on surface properties of biochar (surface area and surface charge), solution pH, and presence of competitive ions. Experimental results suggest that electrostatic attraction was the dominant mechanism for enhanced nitrate adsorption on modified hydrophyte biochars. Because both the litter of reed and cattail from constructed wetland are waste materials, the cost to make litter should be very low, thus promoting the utilization of aquatic plants. Moreover, modified hydrophyte biochars should be considered a promising alternative wastewater treatment or environmental remediation technology for nitrate removal from constructed wetland in winter in high-latitude areas.

ACKNOWLEDGEMENTS

REFERENCES

1. Z. Wang, H. Guo, F. Shen, G. Yang, Y. Zhang, Y. Zeng, L. Wang, H. Xiao and S. Deng, *Chemosphere*, **119**, 646 (2015).
2. R. S. Quilliam, M. A. van Niekerk, D. R. Chadwick, P. Cross, N. Hanley, D. L. Jones, A. J. Vinten, N. Willby and D. M. Oliver, *J. Environ. Manage.*, **152**, 210 (2015).
3. O. Coban, P. Kuschk, U. Kappelmeyer, O. Spott, M. Martienssen, M. S. Jetten and K. Knoeller, *Water Res.*, **74**, 203 (2015).
4. A. Iribar, S. Hallin, J. M. S. Pérez, K. Enwall, N. Poulet and F. Garabétian, *Ecol. Eng.*, **80**, 191 (2015).
5. X. Xu, B. Gao, Y. Zhao, S. Chen, X. Tan, Q. Yue, J. Lin and Y. Wang, *J. Hazard. Mater.*, **203**, 86 (2012).
6. A. Canion, W. A. Overholt, J. E. Kostka, M. Huettel, G. Lavik and M. M. Kuypers, *Environ. Microbiol.*, **16**, 3331 (2014).
7. O. R. Stein and P. B. Hook, *J. Environ. Sci. Health*, **40**, 1331 (2005).
8. A. Krevš, J. Darginavičienė, B. Gylytė, R. Grigutytė, S. Jurkonienė, R. Karitonas, A. Kučinskienė, R. Pakalnis, K. Sadauskas and R. Vitkus, *Environ. Pollut*, **173**, 75 (2013).
9. W. Zhang, Q. Li, X. Wang, Y. Ding and J. Sun, *Biogeochemistry*, **94**, 1 (2009).
10. M. Ahmad, A. U. Rajapaksha, J. E. Lim, M. Zhang, N. Bolan, D. Mohan, M. Vithanage, S. S. Lee and Y. S. Ok, *Chemosphere*, **99**, 19 (2014).
11. Y. Zhou, B. Gao, A. R. Zimmerman, J. Fang, Y. Sun and X. Cao, *Chem. Eng. J.*, **231**, 512 (2013).
12. J. W. Gaskin, C. Steiner, K. Harris, K. C. Das and B. Bibens, *Transactions of the ASABE*, **51**, 2061 (2008).
13. O. Mašek, P. Brownsort, A. Cross and S. Sohi, *Fuel*, **103**, 151 (2013).
14. S. Wang, B. Gao, A. R. Zimmerman, Y. Li, L. Ma, W. G. Harris and K. W. Migliaccio, *Bioresour. Technol.*, **175**, 391 (2015).
15. A. Mukherjee, A. R. Zimmerman and W. Harris, *Geoderma*, **163**, 247 (2011).
16. Y. Yao, B. Gao, M. Zhang, M. Inyang and A. R. Zimmerman, *Chemosphere*, **89**, 1467 (2012).
17. K. Ramirez-Muñiz, F. Jia and S. Song, *Environ. Chem.*, **9**, 512 (2012).
18. A. R. Zimmerman, B. Gao and M. Ahn, *Soil Biol. Biochem.*, **43**, 1169 (2011).
19. M. I. Al-Wabel, A. Al-Omran, A. H. El-Naggar, M. Nadeem and A. R. Usman, *Bioresour. Technol.*, **131**, 374 (2013).
20. B. Chen, Z. Chen and S. Lv, *Bioresour. Technol.*, **102**, 716 (2011).
21. M. Zhang and B. Gao, *Chem. Eng. J.*, **226**, 286 (2013).
22. Y. Yao, B. Gao, J. Chen, M. Zhang, M. Inyang, Y. Li, A. Alva and L. Yang, *Bioresour. Technol.*, **138**, 8 (2013).
23. S. P. Sohi, E. Krull, E. Lopez-Capel and R. Bol, *Adv. Agron.*, **105**, 47 (2010).
24. R. Chintala, J. Mollinedo, T. E. Schumacher, S. K. Papiernik, D. D. Malo, D. E. Clay, S. Kumar and D. W. Gulbrandson, *Micropor. Mesopor. Mater.*, **179**, 250 (2013).
25. S. E. Hale, V. Alling, V. Martinsen, J. Mulder, G. D. Breedveld and G. Cornelissen, *Chemosphere*, **91**, 1612 (2013).
26. M. E. Essington, Boca Raton, London, New York, Washington, DC (2004).
27. C. C. Hollister, J. J. Bisogni and J. Lehmann, *J. Environ. Qual.*, **42**, 137 (2013).
28. Y. Ho and G. McKay, *Process. Biochem.*, **34**, 451 (1999).
29. G. Sposito, *Soil Sci. Soc. Am. J.*, **44**, 652 (1980).
30. A. Breeuwsma and J. Lyklema, *J. Colloid Interf. Sci.*, **43**, 437 (1973).
31. M. Zhang, B. Gao, Y. Yao, Y. Xue and M. Inyang, *Chem. Eng. J.*, **210**, 26 (2012).
32. E. Bock, N. Smith, M. Rogers, B. Coleman, M. Reiter, B. Benham and Z. M. Easton, *J. Environ. Qual.*, **44**, 605 (2015).
33. R. Chintala, J. Mollinedo, T. E. Schumacher, S. K. Papiernik, D. D. Malo, D. E. Clay, S. Kumar and D. W. Gulbrandson, *Micropor. Mesopor. Mater.*, **179**, 250 (2013).
34. X. Gai, H. Wang, J. Liu, L. Zhai, S. Liu, T. Ren and H. Liu, *PloS one*, **9**, e113888 (2014).