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Removal of Ammonium and Phosphate from Water by Mg-modified Biochar: Influence of Mg pretreatment and Pyrolysis Temperature

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Poplar chips before and after a magnesium (Mg) pretreatment were pyrolyzed under different temperatures to obtain pristine and Mg-modified biochar samples (i.e., 300/BC, 450/BC, 600/BC, 300Mg/BC, 450Mg/BC, and 600Mg/BC). The biochars were used to evaluate how pyrolysis temperature and Mg modification influenced their capacity to adsorb ammonium and phosphate from eutrophic waters. An increased temperature caused an increase in carbonization degree, a more developed porous structure, and a decrease in the functional groups on biochar. The Mg modification was helpful for the development of a porous structure and the preservation of functional groups. The optimal ammonium adsorption was obtained by 300Mg/BC. This was attributed to the enriched functional groups. The maximum adsorption capacity was 58.6 mg/g. The 600Mg/BC sample exhibited optimal adsorption for phosphate with a maximum adsorption capacity of 89.0 mg/g, which was ascribed to the large surface area, the positively charged surface, and the metal oxides effect. A pseudo-second-order kinetic model and Langmuir-Freundlich isothermal model well described the adsorption of ammonium and phosphate on the modified biochar.

Keywords: Biochar; Pyrolysis temperature; Modification; Adsorption; Ammonium; Phosphate

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INTRODUCTION

Eutrophication is a typical phenomenon of water pollution that severely impacts a water system and the entire ecological environment (Zhu et al. 2018). In addition to external conditions (e.g., sunlight, temperature, water depth, and water velocity), the enrichment of nitrogen (N) and phosphorus (P) in water is an essential and decisive reason for water eutrophication (Jarvie et al. 2018; Ortiz-Reyes and Anex 2018). Therefore, preventing water eutrophication by removing N and P from water is an effective method because the nutrients for algae and plankton are reduced (Tekile *et al.* 2015). Currently, the main approaches to water eutrophication remediation in engineering practice include adding chemicals to induce the deposition and precipitation of nutrients, taking advantage of the metabolism of aquatic plants by assimilating N and P, and aerating and diluting the water (Harris et al. 2015; Copetti et al. 2016; Xu et al. 2018). However, the application of these approaches may cause a secondary pollution of water, require harsh water conditions, or entail a high cost (Yin et al. 2017). Recently, the removal of N and P from water via adsorption has attracted attention because of its easy operation and minimal environmental side effects. Therefore, the development of an efficient and cost-effective adsorbent is imperative.

Biochar is a solid product of biomass pyrolysis, and its functionality presents many advantages in various environmental applications. It can be used as an adsorbent for environmental remediation, particularly the remediation of water pollution (Sumalinog *et al.* 2018; Zhang *et al.* 2018; Van *et al.* 2019; Nguyen *et al.* 2019a; Van *et al.* 2018b). Biomass type, pyrolysis conditions, and pretreatment methods are the main influential factors for biochar properties. The biomass pyrolysis temperature exerts considerable effects on the porous structure and surface properties of biochar, and the biochar properties in turn influence the adsorption capacity for contaminants (Yin *et al.* 2018c). Jung *et al.* (2016) found that macroalgae biochar derived using a high pyrolysis temperature possesses a highly developed porous structure and decreased surface polarity. The oxygen functional groups of sugarcane bagasse biochar are beneficial for the adsorption of lead (Ding *et al.* 2014). Therefore, modifying biochar can change the physicochemical properties of biochar and consequently influence its adsorption property.

Biochar is modified mainly through activation, grafting of oxygen- or N-containing functional groups onto the biochar surface, and the addition of metal oxide to biochar (Rajapaksha et al. 2016; Wang et al. 2018; Vu et al. 2017; Nguyen et al. 2019b). Magnesium (Mg) modified biochar was effectively used in the removal of contaminants from water (Van et al. 2018a). The precursor of Mg oxides acts as the activator during biomass pyrolysis, resulting in a highly developed porous structure of biochar. The Mg modified biochar preserves more surface functional groups than the pristine biochar. Furthermore, Mg in biochar would react with contaminants in water. These factors contribute to the utilization of Mg-modified biochar as a good adsorbent. Biochar can be used as a soil conditioner to improve the fertility and water-holding capacity of soil. Plant growth requires the necessary elements N and P (De Sausa Lima et al. 2018). Thus, biochar after N/P adsorption can act as slow-release fertilizer to improve plant growth (Hale et al. 2013). Mg is a beneficial element for synthesizing chlorophyll (Rittmann et al. 2011; Yao et al. 2013). Therefore, Mg modified biochar can be used as a potential adsorbent for N and P from water, and the post-adsorption biochar modified by Mg can supply additional advantages through its use in soil improvement. Poplar is a widely planted tree that is used in many aspects as raw material. The wastes of poplar after deep processing could be used as raw material for biochar production.

Thus far, the simultaneous study of the effects of pyrolysis temperature and Mg modification on the biochar properties and its adsorption properties has not been extensively explored. In this study, the influences of pyrolysis temperature and Mg modification on the adsorption capacity of poplar biochar for ammonium (NH_4^+) and phosphate (PO_4^{3-}) from eutrophic water were investigated. The results will provide an essential basis for the utilization of biochar in eutrophic water remediation, and a win-win effect will be achieved using the biomass waste derived biochar to treat the polluted water. Moreover, the post-adsorption biochar could be reused as a fertilizer, making effective usage of biomass waste.

EXPERIMENTAL

Materials

Biochar preparation and characterization

Poplar chips were locally obtained, washed to remove impurities, dried, and cut into 0.5-mm pieces. The poplar pieces were placed in a tubular furnace and heated to

 $300 \,^{\circ}$ C, $450 \,^{\circ}$ C, and $600 \,^{\circ}$ C at a heating rate of 5 $^{\circ}$ C/min under a N₂ atmosphere. The peak temperature was maintained for 2 h and then naturally cooled down. The biochar was obtained when room temperature was reached, and the pristine biochar samples were marked as 300/BC, 450/BC, and 600/BC according to their pyrolysis temperatures. The Mg-modified biochar was obtained by immersing the poplar pieces into MgCl₂ × $6H_2O$ solutions for 3 h. The concentration of MgCl₂ solution was $40 \,\text{g/L}$. The solid-to-liquid ratio of poplar chips and MgCl₂ solution was $1:8 \,\text{g/mL}$. Then, the pretreated poplar chips were dried in a water bath and oven under $80 \,^{\circ}$ C. The treated poplar pieces were pyrolyzed under the same procedure as that for the untreated poplar. The corresponding modified biochar samples are represented in this article as 300Mg/BC, 450Mg/BC, and 600Mg/BC.

The elemental content of biochar was conducted using an elemental analyzer (Vario MACRO cube; Elementar, Langenselbold, Hesse, Germany) and an X-ray fluorescence spectrometer (Spectro iQ II; Ametek, Berwyn, PA, USA). The pore structure was analyzed *via* the N₂ adsorption-desorption method with an ASAP 2020Plus (Micromeritics, Norcross, GA, USA). The surface area was calculated based on the Brunauer–Emmett–Teller (BET) method. The surface properties and the crystalline phases of biochar were characterized using a Fourier transform infrared (FTIR) spectrometer (Tensor 27; Bruker, Billerica, MA, USA) and an X-ray diffractometer (Empyrean; Malvern Panalytical, Malvern, UK) for the X-ray diffraction (XRD), respectively. Biochar surface morphology was examined using a scanning electron microscopy (SEM) system equipped with an energy dispersive X-ray spectroscope (EDS) (JSM-7001F; JOEL Ltd., Akishima, Tokyo, Japan).

Methods

Adsorption

The NH₄⁺–N and PO₄³⁻–P aqueous solutions were prepared with ammonium chloride (NH₄Cl) and potassium phosphate monobasic (KH₂PO₄), respectively. In the batch experiment, the adsorption solution concentration (NH₄⁺–N and PO₄³⁻–P) was fixed at 50 mg/L. Aqueous solutions of hydrochloric acid and sodium hydroxide were used to adjust the initial pH of the adsorption solutions (pH = 6.0). The mixture of 0.1 g biochar and 50 mL adsorption solutions was shaken in a mechanical oscillator at 25 °C and 120 rpm for 40 h. Subsequently, a syringe filter was used to separate the biochar from the solutions. The concentrations of NH₄⁺–N and PO₄³⁻–P were determined by Nessler's reagent colorimetric method and the ammonium molybdate spectrophotometric method, respectively. All the experiments for each sample were run in triplicate. The amount of NH $_{4}^{+}$ –N or PO₄³⁻–P adsorbed by biochar was determined using Eq. 1,

$$q_{\rm t} = \frac{V}{m} (C_0 - C_{\rm t}) \tag{1}$$

where q_t is the nutrients amount that is adsorbed on every gram of biochar (mg/g), C_0 and C_t represent the concentrations of nutrients in the initial and residual adsorption solutions, respectively (mg/L), V represents the volume of adsorption solutions (mL), and m is the biochar weight (g).

In the kinetic and isothermal experiments, 300/BC and 300Mg/BC were chosen to study the adsorption properties of NH_4^+ –N, and 600/BC and 600Mg/BC were chosen to study those of PO_4^{3-} –P. The procedure of the adsorption kinetic experiment was the same as that in the batch experiment. The supernatant was filtered and analyzed at different time intervals to obtain the amount of N and P adsorption on biochar with time. The adsorption process was described by the following kinetic models,

Pseudo-first-order
$$q_t = q_e (1 - e^{-k_1 t})$$
 (2)

Pseudo-second-order
$$q_{t} = \frac{k_2 q_e^2 t}{(1 + k_2 q_e t)}$$
 (3)

Intraparticle diffusion $q_t = k_3 t^{0.5} + C$ (4)

where q_e and q_t denote the adsorbed amount of nutrients for every gram of biochar at the equilibrium time and at time *t*, respectively (mg/g), k_1 (h⁻¹), k_2 (g × mg⁻¹ × h⁻¹), and k_3 (mg × g⁻¹ × h^{-0.5}) are the rate constants in the corresponding models, and *C* is a constant.

The adsorption solutions with different nutrient concentrations were prepared and used to study the adsorption isotherms, following the same procedure as that in the batch experiment. The isotherm results were analyzed by three typical models,

Langmuir
$$q_e = \frac{k_l q_m C_e}{(1 + kC_e)}$$
 (5)

Freundlich
$$q_{\rm e} = k_{\rm f} C_{\rm e}^{\frac{1}{\rm n}}$$
 (6)

Langmuir–Freundlich
$$q_{\rm e} = \frac{kq_{\rm m}C_{\rm e}^{\frac{1}{{\rm n}}}}{\left(1 + kC_{\rm e}^{\frac{1}{{\rm n}}}\right)}$$
 (7)

where C_e denotes the equilibrium concentration of nutrients (mg/L), q_m is the maximum amount of nutrient adsorption for every gram of biochar (mg/g), k_1 (L/mg), k_f (mg^{1-1/n} × L^{1/n} × g⁻¹), and k (L/mg) are the constants in the corresponding models, and n is an indicator of heterogeneity.

RESULTS AND DISCUSSION

Biochar Characterization

The data on the biochar yield and elemental composition, which were highly influenced by pyrolysis temperature, are listed in Table 1. The biochar yields from different temperatures ranged from 22.4% to 34.3% for the pristine biochar samples and from 32.9% to 51.2% for the Mg-modified biochar samples. High temperature was beneficial for the decomposition of biomass and explained the low biochar yield. The carbon content increased with the temperature, whereas the content of hydrogen and oxygen decreased with temperature. The breakage of long-chain organics and the release of short-chain chemicals from biomass intensifies with the temperature, thus increasing the carbonization degree of biochar (Liu and Han 2015). An increase in temperature resulted in H/C and O/C decreasing, indicating that the organic functional groups on the biochar were lost at high pyrolysis temperatures (Ahmad et al. 2012). At the same pyrolysis temperature, the carbon content in the Mg-modified biochar was lower than that in the corresponding pristine biochar. This outcome can be ascribed to the introduction of $MgCl_2 \times 6H_2O$, which served as an activator that improved the biomass pyrolysis (Yin et al. 2018b). In addition, O/C and H/C in the Mg-modified biochar samples were higher than those in the corresponding pristine biochar samples, implying that biochar modification was favorable for the preservation of functional groups.

Sample	Yield	С	Н	0	Ν		H/C	Mg	Cu	Ca	Р
	(%)	(%)	(%)	(%)	(%)	0/0		(%)	(%)	(%)	(%)
300/BC	34.30	70.28	3.57	7.00	0.39	0.10	0.05	0.66	12.2	1.53	0.90
450/BC	25.56	84.72	2.08	3.47	0.58	0.04	0.02	0.40	5.19	0.97	0.52
600/BC	22.44	90.36	0.80	2.16	0.73	0.02	0.01	0.27	3.34	0.69	0.28
300Mg/BC	51.18	61.68	3.47	12.17	0.22	0.20	0.06	13.83	5.78	0.66	0.59
450Mg/BC	35.87	74.76	2.01	7.94	0.47	0.11	0.03	9.84	1.88	0.34	0.37
600Mg/BC	32.92	77.46	0.75	7.60	0.58	0.10	0.01	9.26	1.85	0.41	0.31

Table 1. Yields and Elemental Compositions of the Biochar Samples

Table 2 shows the porous structure parameters of the biochar samples. The BET surface areas of 300/BC and 300Mg/BC were small (< 5 m²/g), indicating that a low pyrolysis temperature was unfavorable for the development of pores. Small molecules, *e.g.*, H₂O, CO, CO₂, and CH₄, are released rapidly from the biomass matrix at high temperatures, resulting in a large generation of pores on the biochar (Yin *et al.* 2018b). The percentage of micropores in the total BET surface area increased with the temperature; this increase in the micropore percentage is important for biochar adsorbents to adsorb pollutants from water (Hollister *et al.* 2013). Biochar modification *via* Mg considerably influenced the porous structure. The developed porous structure of the Mg-modified biochar was likely caused by the effect of MgCl₂ × 6H₂O. The MgCl₂ × 6H₂O dehydrated and decomposed during the biomass pyrolysis to release water or other chemical compounds, leaving porous structures in the biochar matrix.

Sample	S _{BET} (m²/g)	S _{micro} (m²/g)	S _{external} (m²/g)	V _{pore} (cm³/g)	V _{micro} (cm³/g)
300BC	1.80	0.49	1.32	0.0058	0.0001
450/BC	15.21	3.65	11.56	0.0155	0.0008
600/BC	84.41	81.37	3.03	0.0415	0.0353
300Mg/BC	4.82	2.15	2.66	0.0103	0.0005
450Mg/BC	250.44	152.89	97.55	0.1259	0.0608
600Mg/BC	254.08	203.42	50.65	0.1302	0.0801

 Table 2. Pore Structure Parameters of the Biochar Samples

As shown in the XRD patterns in Fig. 1, two wide peaks, located at 20° to 30° and 40° to 50°, appeared on each biochar sample due to graphite diffraction (Yin *et al.* 2018a). The peaks at 40° to 50° became increasingly distinct and narrow because of the rise in temperature, indicating that the degree of graphitization increased and that the stability of the biochar improved (Wang *et al.* 2013b). Some diffraction peaks assigned to magnesium oxides and hydroxides emerged on the Mg-modified biochar samples, especially on 450Mg/BC and 600Mg/BC. This outcome was caused by the complete dehydration and decomposition of MgCl₂ × 6H₂O at high temperatures; this phenomenon was consistent with the well-developed pore structure of the Mg-modified biochar samples (Jung and Ahn 2016). No such peaks were found on the pristine biochar samples because of the minute content and amorphous state of the metallic compounds (Wang *et al.* 2013a). There was no significant difference between the 300Mg/BC and 300Mg/BC+N. The peaks for Mg compounds on 600Mg/BC weakened after the adsorption of phosphate, which might be caused by the reactions of Mg and phosphate.



Fig. 1. XRD patterns of the biochar samples (300Mg/BC+N and 600Mg/BC+P denoted the biochars after ammonium and phosphate adsorption, respectively)

Surface functional groups are important to carbonaceous adsorbents because electrostatic interaction, complexation, or a chemical reaction occurs between the functional groups and the adsorbate. Many adsorption peaks could be found in the FTIR spectra for biochar samples, as shown in Fig. 2.



Fig. 2. FTIR spectra of the biochar samples (300Mg/BC+N and 600Mg/BC+P denoted the biochars after ammonium and phosphate adsorption, respectively)

The peaks located at 3400 cm⁻¹ and 1630 cm⁻¹ were ascribed to the stretching vibration of the hydroxyl groups in the hydrogen-bonded groups and water, the adsorption peaks at 1400 cm⁻¹ to 1600 cm⁻¹ were associated with the stretching vibrations of C=O and C=C, and the peak at 2900 cm⁻¹ was attributed to C–H or –CH bonds (Keiluweit *et al.* 2010; Liu *et al.* 2010; Jung *et al.* 2015). The number of functional groups decreased with the temperature because of the cleavage of the chemical bonds of C–H, C–O, C–N, *etc.* This result agrees with the decreased H/C and O/C at the high temperatures. Furthermore, Mg modification is favorable for the preservation of the functional groups on biochar (Wang *et al.* 2015). The adsorption peaks at 600 cm⁻¹ to 900 cm⁻¹ on the Mg-modified biochar samples belong to the chemical bonds of Mg–O or Mg–O–Mg, thereby confirming the introduction of Mg into the biochar matrix (Frost and Kloprogge 1999). The adsorption

peaks located at 2900 cm⁻¹ disappeared after the adsorption of ammonium on 300Mg/BC, indicating that a reaction had occurred between ammonium and alkyl groups (Yin *et al.* 2018c). The peaks of hydroxyl groups at 3400 cm⁻¹ and 1630 cm⁻¹ weakened on 600Mg/BC after the adsorption of phosphate, while the peaks of Mg-O-P at 1048 cm⁻¹ became intense and broad (Liu *et al.* 2015). These findings indicated that ammonium and phosphate were adsorbed by the biochars.

The SEM images of the pristine and modified biochar samples, as well as the images for the post-adsorption biochars, are shown in Fig. 3. The pristine biochar showed a relatively smooth morphology, maintaining the natural structure of the raw biomass to a large extent. The morphology of the Mg-modified biochar was considerably changed, with some flakes emerging. These flakes were caused by Mg oxides, which contributed to the well-developed pore structure. The morphology of the biochars before and after ammonium and phosphate adsorption exhibited no significant difference.



Fig. 3. SEM images and the corresponding EDS spectra of the biochar samples (The images of 300Mg/BC and 600Mg/BC after ammonium and phosphate adsorption were inserted in their bottom-left corners, respectively.)

Ammonium and Phosphate Adsorption

The adsorption capacities of the biochar samples for ammonium and phosphate are presented in Fig. 4. As shown in Fig. 4a, the adsorption capacities of both pristine and Mg-modified biochar for ammonium decreased with the temperature, decreasing from 1.52 mg/g for 300/BC to 0.35 mg/g for 600/BC and from 2.45 mg/g for 300Mg/BC to 0.72 mg/g for 600Mg/BC. These results implied that the biochar derived from high temperatures that possessed a developed pore structure, deep carbonization degree, and a small number of functional groups was not suitable for ammonium adsorption. Therefore, a developed pore structure and large surface area were not the main influential factors for ammonium adsorption on biochar, implying that physical adsorption was not the main adsorption mechanism between the biochar and NH_4^+ . The high ammonium adsorption capacity in this work was obtained on the biochar derived from a relatively low temperature, especially for

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the Mg-modified biochar derived from a low temperature, which had rich functional groups. This result indicated that the surface functional groups are the crucial factor in ammonium adsorption on biochar (Yin *et al.* 2018b). Zeng *et al.* (2013) found that the functional groups C=O, C–C, –CH₂, and –COO could react with NH₄⁺; therefore the presence of these groups can improve the adsorption for NH₄⁺. Additionally, electrostatic attraction occurs between the negatively charged functional groups and NH₄⁺ and consequently contributes to NH₄⁺ to form struvite (MgNH₄PO₄·6H₂O), which improve the adsorption of NH₄⁺ (Yin *et al.* 2018b).

The pristine and Mg-modified biochar samples exhibited different adsorption capacities for phosphate, as shown in Fig. 4b. The pristine biochar showed poor phosphate adsorption capacity. The adsorption amount of phosphate on 300/BC was negative, indicating that the P released from the biochar into the solution was greater than that adsorbed by the biochar. On the one hand, the high content of P in 300/BC increased the possibility of P release from biochar. Additionally, the small surface area of 300/BC could not supply sufficient adsorption sites for PO_4^{3-} . The same phenomenon has been reported for the pristine biochar derived from different types of biomass in previous studies (Zeng et al. 2013; Takaya et al. 2016). In this study, the adsorption of phosphate on the pristine biochar became positive due to an increase in the pyrolysis temperature, although the adsorption capacity remained low. The adsorption capacity for PO_4^{3-} on biochar was remarkably improved after the Mg modification, especially for the Mg-modified biochar derived from a high temperature. The adsorption amounts of PO_4^{3-} on 450Mg/BC and 600Mg/BC reached 31.3 mg/g and 44.4 mg/g, respectively. The developed pore structure and large surface area of the Mg-modified biochar from a high pyrolysis temperature can supply sufficient adsorption sites and support the mass transfer of adsorbates (Jung et al. 2016). The existence of Mg in the modified biochar was crucial for PO_4^{3-} adsorption. The Mg oxides in the biochar would form mono-, bi-, and trinuclear complexes with PO_4^{3-} through weak chemical bonds (Yin et al. 2018b). Additionally, Mg²⁺ was released from the biochar into the solution when PO_4^{3-} was present, and insoluble compounds (e.g., magnesium phosphate and magnesium hydrogen phosphate) formed between the Mg²⁺ and PO_4^{3-} (Yao *et al.* 2013). In addition, Bolan *et al.* (1999) reported that the surface of an adsorbent will have positive charges when the pH_{pzc} (point of zero charge) of the adsorbent is higher than the pH of the solution; otherwise, the surface of adsorbent will have negative charges. The pH_{pzc} value of MgO is 12, and the pH value of the PO_4^{3-} solution was 6.0 in this study. Thus, the surface of the Mg-modified biochar had positive charges, which could improve the adsorption of negatively charged PO_4^{3-} . In addition, the pH value of the PO_4^{3-} solution increased from 6.0 to 9.0 for 600Mg/BC after 40 h. Therefore, the exchange of surface hydroxyl groups with PO_4^{3-} may be a possible adsorption mechanism for phosphate.

Kinetic studies can reflect the adsorption equilibrium time and the adsorption nature of an adsorbent for an adsorbate. The pseudo-first-order and pseudo-second-order models described the physical and chemical adsorption of the nutrients on biochar, respectively. The intraparticle diffusion model showed the detailed procedure of the adsorption of nutrients. Figure 5 shows the kinetic curves whose best-fit parameters for each model are presented in Table 3. The intraparticle diffusion model depicted the ammonium adsorption on 300/BC well as indicated by the high R² and the small intercept value. This result implied that the diffusion of NH⁴₄ in biochar was the main rate-controlling process. The fitted curve did not pass the origin (C = 0.359), suggesting that both external and internal diffusion simultaneously occurred.



Fig. 4. Adsorption of ammonium (a) and phosphate (b) on the different biochar samples

The adsorption equilibrium of ammonium on 300Mg/BC was achieved at approximately 30 h. The adsorption was well-described by the pseudo-second-order model, with $R^2 = 0.956$. The predicted adsorption amount of NH_4^+ on 300Mg/BC (2.68 mg/g) from the pseudo-second-order model was close to the result of the batch experiments. The enriched functional groups on the Mg-modified biochar were beneficial for the chemisorption of NH_4^+ . Additionally, the adsorption of PO_4^{3-} on the pristine and modified biochar samples was described by the pseudo-second-order model. The adsorption equilibrium of PO_4^{3-} on 600/BC and 600Mg/BC was reached at approximately 12 h. The intraparticle diffusion model was not suitable to describe PO_4^{3-} adsorption on 600/BC and 600Mg/BC because both samples possessed developed pore structures and sufficient adsorption sites on the internal and external surfaces. Therefore, the diffusion of PO_4^{3-} in the biochar was not the controlling factor in adsorption.

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Fig. 5. Adsorption kinetic curves of ammonium on 300/BC (a), ammonium on 300Mg/BC (b), phosphate on 600/BC (c), and phosphate on 600Mg/BC (d)

Table 3	. Kinetic F	varameters of	of Ammor	nium and	Phosphate A	Adsorption on the	
Biochar	Samples				-		

Sample	Adsor-	Pseudo-first-order			Pseudo	o-secon	d-order	Intraparticle Diffusion		
	bate	k 1	$q_{ m e}$	R ²	k 2	$q_{ m e}$	R ²	k	С	R ²
300/BC	NH_4^+	0.228	1.69	0.798	0.168	1.89	0.886	0.251	0.359	0.933
300Mg/BC	NH_4^+	0.207	2.43	0.900	0.114	2.68	0.956	0.364	0.446	0.887
600/BC	PO ₄ ³⁻	0.270	2.19	0.916	0.145	2.44	0.971	0.317	0.514	0.887
600Mg/BC	PO ₄ ³⁻	0.247	44.53	0.935	0.006	49.76	0.982	6.147	10.300	0.870

Adsorption isothermal studies of ammonium and phosphate on biochar were conducted to evaluate the distribution of the adsorbates on the adsorbent and the maximum adsorption capacity of nutrients for each biochar. The Langmuir isothermal model describes the monolayer adsorption onto a uniform surface with no interactions between the adsorbed molecules (Swenson and Stadie 2019). The Freundlich model describes the adsorption on a heterogeneous surface. In addition, the Langmuir–Freundlich model is an empirical model describing multiple adsorption processes. The isothermal curves for the ammonium and phosphate adsorption on biochar are presented in Fig. 6, and the corresponding best-fit parameters for each model are shown in Table 4. Both ammonium and phosphate adsorption on the pristine and Mg-modified biochar was well-described by the Langmuir model, with high R² values, implying that the adsorption capacity derived

from the Langmuir model for NH_4^+ on 300/BC and 300Mg/BC was 57.25 mg/g and 58.60 mg/g, respectively, whereas the values for PO_4^{3-} on 600/BC and 600Mg/BC were 24.67 mg/g and 88.97 mg/g, respectively. The value of *n* in the Langmuir–Freundlich model is an indicator of the degree of interaction between the adsorbent and the adsorbate. A high *n* value means a strong interaction (Tseng and Wu 2008). Therefore, Mg modification is beneficial for the interaction between biochar and N and P nutrients for high *n* values. Therefore, the Mg-modified biochar samples exhibited great potential to remove ammonium and phosphate from eutrophic waters.



Fig. 6. Adsorption isothermal curves of ammonium on 300/BC (a), ammonium on 300Mg/BC (b), phosphate on 600/BC (c), and phosphate on 600Mg/BC (d)

Table 4	. Isothermal	Parameters of	f Ammonium	and Phosphate	Adsorption	on the
Biochar	Samples					

Sample	Adsor-	Langmuir			Freundlich			Langmuir-Freundlich			
	bate	<i>k</i> ı	q m	R ²	<i>K</i> f	n	R ²	k	n	q m	R ²
300/BC	NH_4^+	0.002	57.25	0.994	0.255	1.332	0.989	0.001	0.881	44.23	0.994
300Mg/BC	NH_4^+	0.002	58.60	0.993	0.360	1.383	0.989	0.002	0.992	57.62	0.994
600/BC	PO ₄ ³⁻	0.007	24.67	0.979	0.809	1.910	0.929	0.001	0.677	19.96	0.987
600Mg/BC	PO ₄ ³⁻	0.029	88.97	0.987	11.543	2.936	0.957	0.049	1.308	101.50	0.993

Adsorption mechanisms of NH_4^+ and $PO_4^{3^-}$ on biochar could be presented from the results of the experiments and the characterizations of biochar samples. The adsorption capacities for NH_4^+ and $PO_4^{3^-}$ on Mg modified biochars were improved compared with those of the pristine biochars. 300Mg/BC, derived from relatively low temperature, showed high adsorption capacity for NH_4^+ . The adsorption of NH_4^+ was mainly through the reaction between the functional groups on biochar and NH_4^+ , as well as the formation of struvite *via* chemical reaction of Mg, P and NH_4^+ . Furthermore, the electrostatic attraction and the exchange with cationic species on biochar also contributed to NH_4^+ adsorption. The adsorption of $PO_4^{3^-}$ on biochar was fast. The biochar from high temperature possessed high surface area and provided sufficient adsorption sites for $PO_4^{3^-}$ adsorption. Complexes and insoluble phosphate would form between Mg and $PO_4^{3^-}$ through chemical bonds, and then deposited on the biochar surface. Furthermore, the electrostatic attraction between $PO_4^{3^-}$ and the positively charged biochar surface also contributed a lot to $PO_4^{3^-}$ adsorption on the Mg modified biochar.

CONCLUSIONS

- 1. Biochar is a green adsorbent for environmental remediation. The influences of pyrolysis temperature and Mg modification of biochar on the adsorption capacity of biochar for NH_4^+ and PO_4^{3-} from eutrophic waters were examined.
- 2. High pyrolysis temperatures and Mg modification were beneficial for developing a porous structure, whereas low pyrolysis temperatures and Mg modification were beneficial for the preservation of surface functional groups.
- 3. The adsorption of NH_4^+ was relevant to the surface functional groups, whereas PO_4^{3-} adsorption was mainly determined by the pore structure, surface charges, and metal oxides.
- 4. The sample 300Mg/BC allowed for good NH⁺₄ adsorption and showed a high adsorption capacity of 58.6 mg/g. The sample 600Mg/BC allowed for good PO³⁻₄ adsorption and showed a high adsorption capacity of 89.0 mg/g. Therefore, Mg-modified biochar can be utilized as an efficient adsorbent for the eutrophic water remediation.

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