Adsorption of phosphorus onto Fe-modified *Thalia dealbata*-derived biochar

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Abstract. How to remove P effectively in eutrophic water is an urgent problem to be solved. In this study, a Fe-modified biochar was prepared by pyrolyzed wetland plant *Thalia dealbata*. The adsorption of P was investigated by using the prepared biochar (TBC-Fe) as an adsorbent. The effects of contact time, initial P concentration, temperature and initial solution pH on adsorption behavior of P on TBC-Fe were studied. The results showed that P adsorption process on TBC-Fe was controlled by internal and external diffusion of particles, due to the adsorption kinetic was better fitted by Intra-particle diffusion model. The adsorption isotherm on TBC-Fe was well performed by Langmuir model, with a maximum P adsorption capacity of 15.86 mg/g. The best adsorption performance was exhibited at 25°C with the initial pH of 10. Overall, the results indicate a promising option of utilizing Fe-modified biochar derived from wetland plants as an efficient remediation adsorbent for phosphorus in water.

1 Introduction

Phosphorus is a limiting factor of water contamination, growth of algae and macrophytes. Massive studies have reviewed on using different methods for removing phosphorus concentration in water efficiently. Among these treatments for phosphorus-rich water, adsorption is widely recognized as the most effectively method to remove phosphorus from water environment ^[1,2].

Biochar is an amorphous, stable, heterogeneous material by pyrolyzed biomass under oxygen deficient condition, to be used as an eco-friendly adsorbent like activated carbon ^[3,4]. Some researchers have illustrated that biochar showed well performance on adsorption of cations or organic matters, but limited adsorption capacity of anionic (like phosphate) ^[5,6]. As results obtained of Jeong et al., biochar had a small adsorption capacity for phosphorus as a adsorbent, due to the repulsion between PO_4^{3-} in the water and anionic forms on the surface of biochar ^[6]. After modification, the adsorption capacity of biochar on anions increased significantly, in view of the drastic changes in physicochemical properties of biochar ^[1,3,7,8]. Fe impregnation improved adsorption capacity of biochar for phosphates effectively and stably ^[9], which related to the electronegativity of cations on the surface of biochar ^[10]. At the same time, pore characteristics, surface active sites, functional group density varied when biochar modified with iron ^[1]. It was a complicated reaction process of phosphorus adsorption on biochar, which influenced by the environmental conditions, such as temperature, pH, ion contents and so on ^[11]. Once the property of solutions changed (e.g. solution pH increased),

adsorption properties changed and the sorption mechanism may gradually diverse from electrostatic interaction to adsorption onto biochar surface.

Herein, in this study, biochar was obtained from wetland plant *Thalia dealbata* though pyrolysis at 200°C with ferrous sulfate modified based on previous studies ^[9]. The objectives of this study were to (1) investigate the phosphorus adsorption behaviour of the biochar, and (2) analyze the influence of environmental conditions on adsorption performance of phosphorus.

2 Material and methods

2.1 Biochar preparation

Thalia dealbata was collected from wetland in Yanting, Sichuan Province, China. After be cleaned with running water and air-dried, *T. dealbata* was cut into small pieces of 0.5 cm with scissors and then made it into powder with a grinder. Filled up into a lidded crucible under 200°C for 6 hours, and grinded through a 100 mesh sieve. Then 50.0 g was weighed into 500 mL solution with 1.0 mol/L ferrous sulfate for 2h and oven-dried at 60°C. After washed by deionized water several times until pH of the overlying water was neutral. This modified biochar gathering under drying environment was referred as TBC-Fe.

2.2 Phosphorus adsorption experiment

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All the adsorption experiments were conducted in 50mL brown glass bottle with 0.5g TBC-Fe and 40mL phosphate solutions. Phosphate solutions with certain concentration (computed in P) was prepared by dissolving certain calculated quantities of K_2HPO_4 in deionized water.

Adsorption kinetic experiment was conducted at 10 mg/L P concentration at 25°C. At the shaking time of 0, 0.5, 1, 2, 4, 6, 8, 12, 18, 24, 36 and 48 h (150 rpm), samples were taken out and solution were filtered through a 0.45 μ m microfiltration membrane. Batch isotherm experiment was performed at P concentration of 0, 1, 2, 5, 10, 15, 25, and 40 mg/L at 25°C for 24 h shaking.

The effect of temperature on P adsorption was conducted at 10 mg/L P concentration for 24 h at 25°C, 15°C, and 5°C, respectively. And the effect of pH was investigated by adjusting the pH of initial P solution to 2, 4, 6, 8, 10, and 12 using 0.05M $H_2SO_4/NaOH$ at 25°C shaking for 24 h.

All the phosphate sorption experiments in this study were carried out in batches with three duplicate and one blank control.

2.3 Data analysis

The concentration of P was analyzed using Mo-Sb-Vc spectrophotometer method. The amount of phosphorus retained in the adsorbent was calculated using following equation:

$$Q_{eq} = \frac{(C_0 - C_{eq}) \times V}{m} \quad (1)$$

where, Q_{eq} is the P amount absorbed on biochar (mg/g), C_0 and C_{eq} is the initial and equilibrium phosphorus concentration in solution (mg/L), V is the solution volume (L) and m is the biochar mass (g).

2.3.1 Sorption kinetic model

Pseudo-first-order model, pseudo-second-order model, Intra-particle diffusion model and Elovich model were used to explain the adsorption process of P on TBC-Fe. The equations of the four models were as follows:

Pseudo-first-order:

$$\frac{dQ_t}{dt} = K_1 \times (Q_{eq} - Q_t) \quad (2)$$

Pseudo-first-order:

$$\frac{dQ_t}{dt} = K_2 \times (Q_{eq} - Q_t)^2 \quad (3)$$

Intra-particle diffusion

$$Q_t = K_p \times t^{0.5} + C \quad (4)$$

Elovich

$$\frac{dQ_t}{dt} = a \times e^{-b \times Q_t} \quad (5)$$

where, Q_t is the P amount absorbed on biochar at time t (mg/g), K_1 , K_2 and K_p are adsorption rate constants of the first-order, second-order and intra-particle diffusion (/h, g/mg/h and mg/g/h). C is the constant of the Intra-particle diffusion model. And a is the initial adsorption rate (mg/g/h), b is the desorption rate (g/mg).

2.3.2 Sorption isotherm model

In order to investigate the adsorption mechanism, Langmuir isotherm was used. The model is expressed by the following equation:

$$Q_{eq} = \frac{K_L \times Q_{max} \times C_{eq}}{1 + K_L \times C_{eq}} \quad (6)$$

where, K_L is the Langmuir bonding term related to interaction energies (/mg), Q_{max} is the Langmuir maximum adsorption capacity (mg/g).

All models fitting and parameters obtained were analyzing by custom nonlinear curve in Origin 8.1. And figures were also completed by Origin 8.1.

3 Results and discussion

3.1 Effect of sorption time

In Fig. 1, it can be seen that P adsorption on TBC-Fe occurred rapidly at first. With the increase of adsorption time, the P concentration in solution decreased [8,12] and then be stay stable after 24 h. In general, the process of P adsorption on biochar was divided into two stages [4]. In the first stage, P can diffuse rapidly to the surface of biochar by occupied of accessible external surface sorption sites [13], leading to a quick increase in P adsorption capacity of biochar. In the second stage, with the saturation of the surface sites and be hardly occupied [14], P entered into inner pore of biochar slowly, making the P concentration in solution gradually decrease. And then adsorption rate decreased slowly to the final equilibrium.

Kinetic data of TBC-Fe was fitted by pseudo-first order model, pseudo-second order model, Elovich, and intra-particle diffusion model. The fitting parameters were listed in Table 1. Calculated R^2 values from non-linear regression indicate that the best fit was obtained with Intra-particle diffusion model. That was in line with the result of P adsorption on iron modified corn straw derived biochar [8], which revealed that the P adsorption process on biochar was controlled by internal and external diffusion of particles.

Fig. 1. Kinetics of P adsorption on TBC-Fe

Table 1. Fitting parameters for phosphorus adsorption on TBC-Fe

Models	Parameters		R^2
Pseudo-first order	K_1	Q_e (mg/g)	0.769
	0.15	1.06	
	K_2	Q_e (mg/g)	0.855

Pseudo-second order	0.19	1.18	
Intra-particle diffusion	K_p	C	0.973
	0.15	0.23	
Elovich	a (mg/(g·h))	b (g/mg)	0.920
	0.34	0.45	
Langmuir	K_L	Q_{max} (mg/g)	0.981
	0.01	15.86	

3.2 Effect of solution phosphorus concentration

Fig. 2 showed the sorption isotherm of P on TBC-Fe at 25°C. It was found that the P adsorption amount on TBC-Fe increased dramatically with the P concentration in solution [3]. When the initial P concentration raised from 1 to 40 mg/L, the P removal efficiency decreased from 85.71% to 37.91% and no significant change observed at initial P concentration of 6–40 mg/L (seen in Fig. 3). While the amount of P absorbed on TBC-Fe increased from 0.17 mg/g to 3.08 mg/g with increased initial P concentration in solution. Higher the initial P concentration, higher the adsorption capacity for P, due to significant driving force was provided to overcome the mass transfer resistance between solutions and adsorbents [15].

The isotherm data (in Fig. 2) was well fitted with Langmuir model ($R^2=0.981$, Table 1). Similar observations were reported previously [9,10], which illustrated that the monolayer adsorption happened on the surface of TBC-Fe for P adsorption. The maximum adsorption capacity for P of TBC-Fe was 15.86 mg/g, similar to previous studies of modified biochars [8,9,15].

Fig. 2. Isotherm of P adsorption on TBC-Fe fitted with Langmuir Model

Fig. 3. Removal efficiency and P adsorption amount on TBC-Fe at equilibrium with different initial P concentration

3.3 Effect of solution temperature

After 24h with 10 mg/L initial P concentration, the P removal efficiency by TBC-Fe absorbed from solution and P adsorption amount on TBC-Fe with respect to temperature was presented in Fig. 4. At temperature of 25°C, 15°C and 5°C, the removal efficiency were 40.78%, 16.61%, 37.04% and P adsorption amount were 0.81 mg/g, 0.07 mg/g, 0.15 mg/g, respectively.

At 25°C, the P adsorption capacity of TBC-Fe was obviously higher than that at 15°C and 5°C. This was because the P adsorption process of biochar was spontaneous and endothermic [15,16], so the high temperature benefited the P adsorption on biochar [9,10,17]. Many studies had shown that in the range of 10 to 60°C with the temperature increased, the kinetic energy and active of ions in solution enhanced, which may make contribute to the adsorption capacity of biochar by accelerating the reaction between the surface of biochar and ion [18,19]. However, the adsorption capacity and removal efficiency of P at 15°C were not greater than those at 5°C. This might because the characterizations of biochar changed at lower temperature which could boost the random thermal motion of ions on biochar surface [15].

Fig. 4. Removal efficiency and P adsorption amount with different temperature

3.4 Effect of initial solution pH

Initial solution pH value affected the morphology of phosphorus in water and the active components on the surface of the adsorbent, which attributed to adsorption of P on biochar [1,2]. It was detected that P adsorption capacity of TBC-Fe increased with the escalating initial pH value ranging from 2 to 10 (seen in Fig. 5.). When the pH was 10, the Q_{eq} reached its maximum of 0.26 mg/g, and the decreased with pH raised. This was in accordance with previous studies [10,18].

Under different solution pH, the phosphorus presented in different forms. When pH was 2.13–7.2, the phosphorus form presented in solution was $H_2PO_4^-$, when pH was 7.20–12.33, it was mainly HPO_4^{2-} , and when pH was greater than 12.33, it was PO_4^{3-} [20]. Meanwhile, Liu et al. demonstrated that the P adsorption activity on modified biochar was in the order of PO_4^{3-} , HPO_4^{2-} , and $H_2PO_4^-$ [17]. This was consistent with our findings that the presence of H^+ will prevent phosphorus from forming complexes with other metal ions [1].

It was shown in Fig. 5 that pH of solution were draw close to 2.22~2.46 regardless of the different initial pH value of phosphate solution (ranging from 2.0 to 12.0). However, when P adsorbed on Mg/Al LDH biochar (the pH_{zpc} was about 9), it was found that the final pH tended to 9.3 with the initial pH ranging from 3 to 11 [3]. Since the surface property of biochar was sensitive to pH, the pH_{zpc} will be reduced after Fe modified (about 3.8) [1], which was a significant factor for affecting biochar adsorption capacity [21]. If the pH of solution was less than pH_{zpc} , electrostatic attraction between P and the adsorbent played dominant role in P adsorption on biochar. And if not, the P adsorption turned to be controlled by chemical interaction [3,17].

Fig. 5. P adsorption amount and the final pH value with different initial pH

4 Conclusions

In this work, a Fe-modified biochar was prepared by pyrolysis of wetland plant *Thalia dealbata*. TBC-Fe was used to investigate the P sorption capacity in water and exhibited remarkable adsorption performance with a maximum capacity of 15.86 mg/g. Contact time, initial concentration, temperature and initial solution pH were important factors that affected the P adsorption on TBC-Fe. This Fe-modified biochar could be used as an efficient remediation adsorbent for phosphorus and would reduce the secondary pollution caused by unharvested wetland plants, due to its low cost and fast preparation.

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