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Synthesis of MgO-Coated Canna Biochar and Its Application in the Treatment of Wastewater Containing Phosphorus

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Abstract: In order to treat phosphorus-containing wastewater and realize the resource utilization of wetland plant residues, biochar was prepared by the pyrolysis of canna aquatic plant waste at 700 °C, and the adsorption characteristics of phosphorus by MgO-modified biochar (MBC) were explored. The main results are as follows: the adsorption capacity of the MBC was eight times that of unmodified biochar (BC), and the adsorption capacity was up to 244 mg/g. The isothermal adsorption data were consistent with the Langmuir equation, which indicates monolayer adsorption. The functional groups changed little before and after the modification, but a new diffraction peak appeared after the modification. Compared with the standard card, it was suggested that there were MgO crystals with a higher purity. SEM images showed that the BC had a smooth surface, an obvious pore structure, and a thin pore wall, while the MBC had a rough surface and a layered structure, which can provide more adsorption sites for phosphate adsorption. In addition, an XPS analysis showed that Mg₃(PO₄)₂ crystals appeared on the surface of the MBC after adsorption. The mechanism analysis showed that MgO is an important substance for MBC to adsorb phosphorus, and electrostatic adsorption and complex precipitation play key roles. In the test to verify the removal of actual phosphorus-containing wastewater by MBC, it was found that the removal rates for wastewater with 2.06 mg/L and 199.8 mg/L of phosphorus by MBC were as high as 93.4–93.9% and 99.2–99.3%, respectively. MBC can be used as an efficient adsorbent for phosphorus removal.

Keywords: canna plant residues; MgO-modified biochar; adsorption; phosphorus



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1. Introduction

Phosphorus (P) is an essential element in life processes and a non-renewable resource [1]. However, the loss of P from the environment not only causes a waste of resources, but it also leads to an increasingly serious problem for groundwater and surface water bodies [2] that can endanger human health. Therefore, research on efficient and low-cost P removal technology has become a research hotspot in recent years. The main methods for treating P in eutrophic water include biological treatment technology, chemical precipitation, and adsorption [3]. However, traditional technologies such as chemical precipitation and biological treatment technology still face problems, such as high operating costs, complex treatment processes, and secondary pollution [4,5]. For example, biological treatment technology involves complex processes and high quality requirements for operators, and this technology is easily affected by processing conditions, resulting in unstable system operations and a difficulty in guaranteeing the dephosphorization effect. Chemical precipitation methods require the addition of a large number of flocculants, resulting in lots of chemical sludge; meanwhile, sludge disposal causes an increase in the operating costs and the release of a large amount of phosphate during the sludge concentration process, resulting in secondary pollution problems. Among these phosphorus-removal technologies,

adsorbents for phosphorus removal show inherent advantages. Biosorbent technology is an economical and environmentally friendly technology [6] that has the advantages of a simple operation and low secondary pollution [7,8], but it still faces the problems of a high adsorbent cost and a low removal rate. Therefore, it is of practical significance to find low-cost and high-efficiency adsorbents. Biochar is a kind of new and cheap adsorbent material with a large specific surface area, abundant pores, and a stable structure that is produced by biological residues under hypoxia and high-temperature conditions [9]. However, the surface of traditional biochar is negatively charged, and there are some limitations to its adsorption of P [10]. Therefore, some scholars have modified biochar by loading it with the metal ions Fe [11,12], Al [13], Mg [14,15], Ca [16], Bi [17], La [18], etc., so as to improve the adsorption capacity of biochar for P. Compared with other elements, magnesium (Mg) is a medium element required by plants; it is inexpensive and environmentally safe, and phosphorus-adsorbed biochar that contains more magnesium can be used as a soil amendment to reduce soil toxicity and provide the nutrients needed for crops. In some studies, MBC was prepared by the pyrolysis of magnesium salt and straw biochar, and modified with amino and hydroxyl functional groups. MBC has a good adsorption capacity for P, with a maximum adsorption capacity of up to 52.53 mg/g [19]. Some researchers have prepared a highly efficient P adsorbent using lotus seed shells and magnesium citrate as raw materials, with a P adsorption capacity of 452.752 mg/g [20]. Fang et al. [21] prepared a new type of composite biochar (MFBC) rich in magnesium oxide for the adsorption of P in wastewater by the pyrolysis of magnesite and food waste. Compared with the original food waste biochar, MFBC was a uniformly mixed MgO–biochar composite with a P capture capacity of 523.91 mg/g. This Mg-rich biochar with adsorbed P can be used as fertilizer to provide the necessary nutrients for soil. These findings provide a good solution for controlling water eutrophication and improving polluted soil by using biochar.

In the past five years, China has added more than 2000 km² of wetland area, and the wetland protection rate has reached more than 50%. The number of wetland plant residues will increase accordingly, and the waste accumulation and incineration of wetland plants will cause resource waste and environmental pollution at the same time [22]. Wetland plant residues are rich in carbon sources and mineral elements, and are good materials for preparing biochar. If the plant residues are not treated in time, it will affect not only the ecological environment, but also waste resources. In our previous studies, we used four kinds of wetland plants (canna, umbrella palm, bamboo reed, and thalia dealbata) as raw materials to prepare biochar at different temperatures, and found that the biochar obtained at 700 °C was more conducive to P adsorption and that the maximum theoretical adsorption capacity of canna biochar was up to 39.24 mg/g [23]. In addition, canna is widely distributed in wetlands, its biomass is large, and the number of canna wetland plant residues has increased; therefore, canna biochar sources are widespread, their cost is low, and the use of canna biochar to remove P can not only solve the problem of water eutrophication, but also solve the problem of wetland plant solid waste residues. However, unmodified canna biochar has certain limitations in P removal, and there is a risk of P release in the treatment of wastewater containing P below 50 mg/L [23], because it is generally negatively charged and has a repulsive effect with phosphate. It has been reported that the adsorption capacity of the original oak BC produced at 550 °C is only 2.5 µmol/g, while the original corn BC cannot even adsorb any P [24,25]. Biochar produced by the pyrolysis of biogas residue and thorn grass showed P release [26], and the P desorption of the biogas residue biochar occurred in a short period of time [27]. These results are similar to those in this paper. Therefore, it is of practical significance to improve the P removal capacity of biochar by modification. In this paper, canna biochar was modified by MgO, and the adsorption effect, adsorption behavior, and adsorption mechanism of the MBC on P are discussed.

2. Materials and Methods

2.1. Materials

The cannas were obtained from the moon lake wetland park in Guiyang, Guizhou Province, China. The cannas were washed off with distilled water and dried in a drying oven at 80 °C. Later, the dried cannas were crushed and passed through a 100-mesh sieve. Analytically pure chemicals, including KH_2PO_4 , NaHCO_3 , MgO , ammonium molybdate tetrahydrate, ascorbic acid, and antimony potassium tartrate, were provided by Guangdong Guanghua Tech. The pH of the solutions in the study was adjusted using a 1.0 mol/L NaOH solution and a 1.0 mol/L HCl solution.

2.2. Biochar Preparation

The sieved canna powder mixed with 0.5 mol/L of MgO at a solid-to-liquid ratio of 1:10 (g:mL) was first subjected to an ultrasound for 30 min and then stirred for 12 h at 160 r/min and 25 °C. The mixture was oven dried at 105 °C and was then placed in a muffle furnace. The pyrolysis temperature was increased to 700 °C at a heating rate of 5 °C/min and held for 2 h. The biochar obtained was MgO -modified biochar (MBC); thus, the unmodified biochar was BC.

2.3. Adsorption Performance Tests

2.3.1. Adsorption Kinetics Experiments

Potassium dihydrogen phosphate was dissolved in deionized water to make a P stock solution (50 mg/L). The initial pH for each sorption solution was adjusted to 7.0. An amount of 0.050 g of biochar was added to a triangle flask with 30 mL of the P solution. Subsamples were taken after 1 min, 5 min, 10 min, 15 min, 30 min, 1 h, 1.5 h, 2 h, 3 h, 4 h, 8 h, 13 h, 24 h, 36 h, 48 h, 60 h, and 72 h and shaken at 160 r/min in an air bath oscillator at room temperature (25 °C). The P content of the subsamples was measured at a wavelength of 700 nm with a spectrophotometer according to the molybdenum antimony resistance spectrophotometry method. The amount of phosphorus adsorbed by the biochar was calculated by the following equation (Equation (1)):

$$Q_t = (C_0 - C_t)V/m \quad (1)$$

where Q_t (mg/g) is the amount of phosphorus adsorbed by the biochar at the given time; C_0 is the initial phosphorus concentration; C_t (mg/L) is the phosphorus concentration after adsorption at time t ; V (L) is the volume of the adsorption solution; and m (g) is the weight of the biochar. The pseudo-first-order, pseudo-second-order, intra-particle diffusion, and Elovich dynamic models, as expressed in Equations (2)–(5), were used to fit the adsorption kinetics experiment data.

Pseudo-first-order:

$$q_t = q_e \left(1 - e^{-k_1 t}\right) \quad (2)$$

Pseudo-second-order:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (3)$$

Intra-particle diffusion:

$$q_e = k_d \sqrt{t} + C \quad (4)$$

Elovich dynamic model equations:

$$q_e = a_1 + k_3 \ln t \quad (5)$$

where q_t is the adsorption capacity of the adsorbent at t (mg/g); q_e is the adsorption capacity of the adsorbent at the equilibrium time (mg/g); k_1 is the adsorption rate constant of the pseudo-first-order model in $\text{mg}/(\text{L} \cdot \text{min})$; k_2 is the adsorption rate constant of the pseudo-second-order model in $\text{mg}/(\text{g} \cdot \text{min})$; C is the kinetic constant in mg/L ; k_d is the diffusion

rate constant in mg/(g·min); a_1 is the kinetic constant in mg/L; and k_3 is the rate constant of the Elovich model in mg/(g·min).

2.3.2. Adsorption Isotherm Experiment

An amount of 0.050 g of the sample was accurately weighed and placed in a triangle flask, and 30 mL of the P solution with an initial concentration of 0, 1, 2, 5, 8, 10, 30, 50, 100, or 200 mg/L was added. The sample was placed in a thermostatic oscillator at a speed of 160 r/min and oscillated at 25 °C for 24 h. After balancing, the filtrate was filtered and the concentration of P was determined by molybdenum antimony anti-spectrophotometry:

$$Q_e = (C_0 - C_t)V/m \quad (6)$$

where Q_e is the adsorption capacity of the biochar to be measured at equilibrium in mg/g; C_0 is the initial concentration of P in mg/L; C_t is the concentration of the filtrate P at the adsorption equilibrium in mg/L; V (L) is the volume of the adsorption solution; and m (g) is the weight of the biochar. The Langmuir and Freundlich isothermal adsorption equations, which are shown in Equations (6) and (7), were used to simulate the experimental data.

Langmuir model:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (7)$$

Freundlich model:

$$q_e = K_F C_e^n \quad (8)$$

where q_e is the adsorption quantity at the adsorption equilibrium in mg/g; q_m is the saturated adsorption capacity in mg/g; C_e is the solution concentration at equilibrium in mg/L; K_L is the adsorption equilibrium constant in mg/L; K_F is the adsorption strength constant; and n is a constant that is related to the adsorption system.

2.4. Adsorption of Real Wastewater Experiment

In the actual wastewater treatment experiment, 2 mg/L and 200 mg/L phosphorus-containing wastewater solutions were prepared from domestic sewage in Anshun University. A total of 0.050 g of the BC or MBC was added to a triangle flask with 30 mL of the P solution (triple repetition), and the solutions were oscillated in an air bath oscillator at 160 r/min for 12 h. The phosphorus content was determined by molybdenum antimony resistance spectrophotometry.

2.5. Characterization of Biochar

The specific surface area of the samples was measured using an automatic surface and porosity analyzer (BET, Micromeritics ASAP 2460, USA). The crystalline structure of the MBC was identified using X-ray diffraction (XRD, Rigaku D/MAX-2600, Tokyo, Japan). The surface morphology was examined through scanning electron microscopy (SEM, ZEISS Sigma 300, Oberkochen, Germany). The surface functional groups of the MBC, both pre- and post-phosphate adsorption, were analyzed using Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific Nicolet iS20, Waltham, MA, USA). The surface chemical composition and elemental valence states were determined through X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Waltham, MA, USA). Analyses of the carbon (C), hydrogen (H), and nitrogen (N) content were conducted using an Elemental Analyzer (EA, Elementar Vario EL cube, Langensfeld, Germany).

2.6. Statistical Analysis

All samples were repeated in triplicate. SPSS22.0 was used for the data analysis and data processing. Origin 9.0 was used for graph drawing and model fitting.

3. Results and Discussion

3.1. Yields, Ash, and pH of Modified Biochar (MBC) and Unmodified Biochar (BC)

In this study, the raw materials for preparing biochar were all from canna plant waste. The yield, ash, and pH varied greatly between the BC and MBC, as presented in Table 1. The yield of biochar was affected by many variables, such as the feedstock and the operating factors. The modification of biochar with MgO significantly improved the yield, resulting in an MBC yield of up to 40.11%, which was higher than that of the BC. The reason for this result was the loading of MgO on the biochar. This was also confirmed by an elemental analysis (Table 2) and XRD (Figure 1a).

Table 1. Yields, ash, and pH of BC and MBC.

Biochar	Yield (%)	Ash (%)	pH
BC	27.23	41.00	10.95
MBC	40.11	49.12	11.18

Table 2. The main elements in the BC and MBC.

	C (%)	H (%)	N (%)	O (%)	H/C	O/C	(O + N)/C	Mg (%)	P (%)
BC	39.24	1.343	1.39	17.02	0.034	0.433	0.469	0.06	1.43
MBC	26.50	0.900	0.55	22.93	0.033	0.486	0.507	0.39	0.72

Note: O% = 100% − (C% + N% + H% + Ash%).

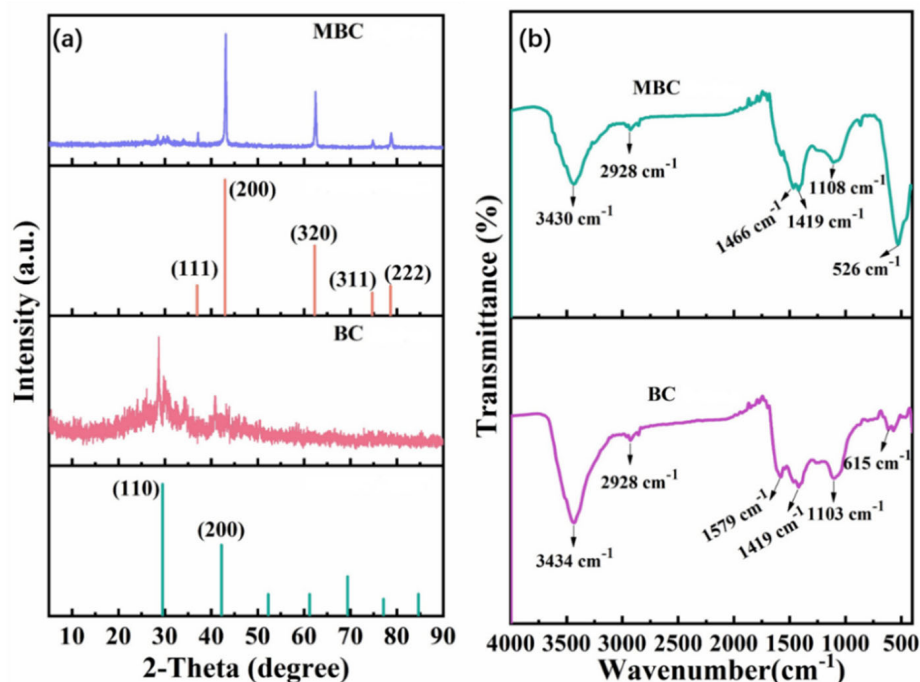


Figure 1. XRD patterns (a) and FT-IR spectra (b) of MBC and BC.

3.2. Composition and Structure of the BC and MBC

3.2.1. Element Composition and Pore Structure Analysis

After the canna biochar was modified by MgO, the C, H, and N content decreased. However, the oxygen content increased, and the Mg content increased significantly, indicating that the biochar was loaded with MgO. This result was also verified by an XRD analysis (Figure 1). The low values of H/C in the BC and MBC (0.034–0.035) indicated that the biochar was highly carbonized [28], and high carbonization contributes to the formation of aromatic structures [29]. Simultaneously, the difference between the H/C values of the

BC and MBC was small, indicating that the modification had little effect on the aromatic functional groups in the biochar. This was also verified by FT-IR. O/C-reactive biochar indicates hydrophilicity, and the higher the value, the stronger the hydrophilicity [30]. The hydrophilicity of the biochar was increased by the magnesium oxide modification. (O + N)/C represents the number of polar functional groups, and the greater the value, the greater the polarity of the biochar [31]. It can be seen from Table 2 that the modification with MgO improved the hydrophilicity and polarity of the biochar, which is more conducive to the adsorption of phosphorus by biochar. As can be seen from Table 3, the specific surface area of the MBC improved due to the MgO modification. The increase in the specific surface area was due to the increase in the total pores of the biochar, but the average pore diameter and volume proportion of the micropores decreased, probably because MgO damaged the micropore structure and caused the pores to be blocked by modifiers. The scanning electron microscope image also confirmed this hypothesis (Figure 2).

Table 3. The mesopores in the BC and MBC.

	BET (m ² /g)	Average Pore Diameter (nm)	S _{micro} (m ² /g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)	V _{micro} /V _{total} (%)
BC	5.759	11.141	4.027	0.0160	0.00138	0.0863
MBC	8.147	8.325	3.472	0.0169	0.00106	0.0631

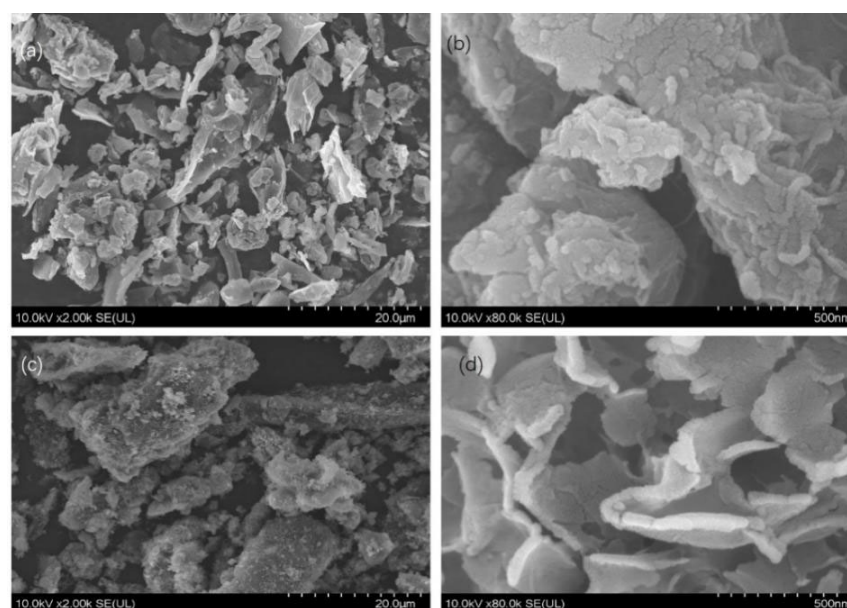


Figure 2. SEM image of MBC (a,b) and BC (c,d).

3.2.2. Biochar Microstructures

The XRD patterns of the BC and MCB are shown in Figure 1a. According to the standard spectrum of MgO, the MBC had strong diffraction peaks at $2\theta = 37^\circ, 42.8^\circ, 62.2^\circ, 74.6^\circ$, and 78.5° . These five peaks corresponded to the five crystal faces of MgO crystals: (111), (200), (320), (311), and (222), respectively [32], indicating that there were MgO crystals on the surface of the MBC. The BC had strong diffraction peaks at $2\theta = 29^\circ$ and 42° , and these two peaks are typically observed for biochar and carbon-based materials [33]. The FT-IR spectra were used to determine the structure and functional groups of the substances. The values of 3434 cm^{-1} for the BC and 3430 cm^{-1} for the MBC, as shown in Figure 1b, indicated that the molecules contained hydroxyl [34]. In both the BC and the MBC, the wavelengths of 2928 cm^{-1} and 1419 cm^{-1} were, respectively, C-H [35] stretching vibrations and C=N [36]; 1103 in the BC and 1108 in the MBC were non-carboxyl C-O stretching vibrations [37,38]. In the BC, 615 cm^{-1} was the -C-H bending vibration, and 1579 cm^{-1}

was the aromatic stretching C=C bond [38,39]. In the MBC, the peaks of 526 were caused by Mg-O vibrations, and the intensity of the peaks representing aromatic C-H and C=C at 615 and 1579 cm^{-1} were significantly reduced or even disappeared after the MgO modification, suggesting that the MgO was coated on the aromatic structure.

The surface morphologies of the MBC and BC are shown in Figure 2. It can be seen that the MBC exhibited a porous and twisted structure with a much coarser surface than the BC, while the BC had a smooth, shallow, and concave surface with a certain number of pores scattered on the surface. The layered structure of the MBC was developed, the volume of micropores was large, and the loaded MgO nanoparticles provided an active site for phosphate adsorption. This hypothesis was also confirmed by XRD (Figure 1a), FT-IR (Figure 1b), and the elemental analysis (Table 2).

3.3. Adsorption Isotherms and Kinetics

3.3.1. Adsorption Isotherm

In order to investigate the influence of the BC and MBC on the P adsorption reaction (Figure 3), the isothermal adsorption results were fitted using the Langmuir and Freundlich equations. The results are shown in Table 4. By comparing the fitting coefficients, it was found that the Langmuir equation had a better fitting effect on the BC and MBC, and the R^2 fitting coefficients were 0.995 and 0.988, respectively. Langmuir had the best fit for the MBC adsorption of phosphorus, and the theoretical adsorption capacity of 291.2 mg/g (25 °C) was close to the actual adsorption capacity of 244 mg/g. Compared with the previous findings for other sorbents, the MBC was able to achieve a higher P adsorption capacity with a smaller dosage; this highlights its P removal advantage (as shown in Table 5).

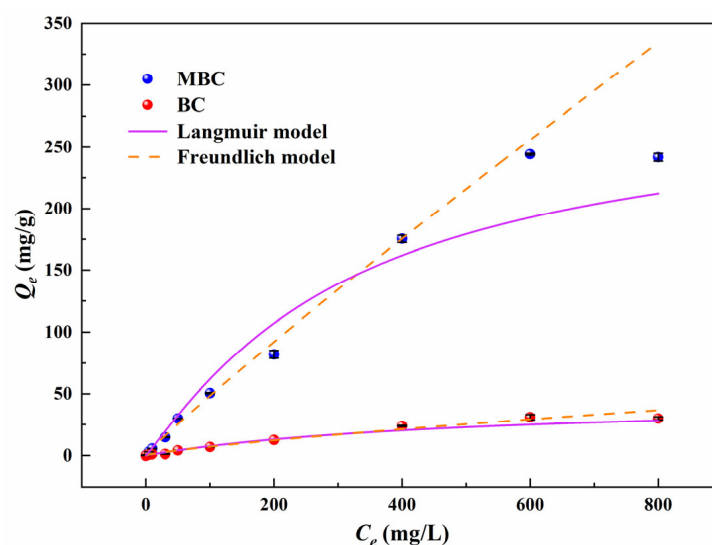


Figure 3. The adsorption amount of the MBC and BC changed with a change in the phosphorus concentration.

Table 4. Parameters of isothermal adsorption equation for phosphorus adsorption by biochar.

	Langmuir			Freundlich		
	K_L	q_m	R^2	n	K_F	R^2
BC	0.002	46.34	0.995	0.692	0.32	0.974
MBC	−0.602	291.2	0.988	0.749	1.78	0.979

Table 5. Performance comparison of biochar-based adsorbents.

Adsorbents	Adsorption Conditions	Dosage (g/L)	Qmax (mg/g)	References
MgCl ₂ -modified sugarcane	$C_0 = 3\text{--}5800 \text{ mg/L}$; pH = 1.9	10	129.79	[40]
Calcium-doped biochar	$C_0 = 100\text{--}1500 \text{ mg/L}$; pH = 4.5	10	147	[41]
La(OH) ₃ -supported corn straw magnetic biochar	$C_0 = 2\text{--}100 \text{ mg/L}$; pH = 7	0.5	116.08	[42]
MgO-doped biochar	$C_0 = 0.5\text{--}2000 \text{ mg/L}$; pH = 7	2	129.4	[43]
Lanthanum carbonate/biochar	$C_0 = 30\text{--}100 \text{ mg/L}$; pH = 7	0.4	71.9	[6]
Pig manure, Brazil -N ₂ -Mg	$C_0 = 10\text{--}10,000 \text{ mg/L}$; pH = –	25	226.9	[44]
MgO-modified canna	$C_0 = 10\text{--}1000 \text{ mg/L}$; pH = 7	1.67	244	[this work]

3.3.2. Adsorption Kinetics

The quasi-first-order kinetic, quasi-second-order kinetic, and Elovich equations were used to fit the BC and MBC (see Figure 4a and Table 6), which had a good adsorption effect on P, and the optimal adsorption model was determined by the R^2 correlation coefficients and the gap between the actual saturation adsorption capacity and the theoretical maximum adsorption capacity. The theoretical adsorption capacity of the BC of the quasi-second-order model was 6.81 mg/g, which was less different from the actual saturated adsorption capacity of 7.61 mg/g. The quasi-first-order kinetic fitting adsorption capacity of the MBC was 29.33 mg/g, which was very close to the actual maximum adsorption capacity of 29.98 mg/g. Simultaneously, the quasi-second-order kinetic fitting adsorption capacity of the MBC was 31.6, which was also very close to the true value. In addition, in the MBC, the quasi-first-order kinetic, quasi-second-order kinetic, and Elovich equations demonstrated a good fit, and the R^2 correlation coefficients were 0.98, 0.96, and 0.83, respectively, indicating that the internal chemical bonds and the physical adsorption of biochar are the factors affecting adsorption. This hypothesis was also verified by the XRD and XPS results. In order to gain insight into the adsorption processes of BC and MBC, the data were fitted using intra-particle diffusion, which is often used to study rate-limiting steps in the adsorption process. In Figure 4b, the adsorption process of the BC and MBC for P was divided into three stages, corresponding to the rapid adsorption stage on the outer surface, the internal diffusion stage, and the adsorption equilibrium stage [45]. As shown in Figure 4b, in the first stage, there were a large number of active sites on the surface of the BC and MBC, and the P adsorption rate of the BC and MBC was very fast. In the second stage, due to the gradual saturation of active sites on the outer surface of the BC and MBC, P in the solution was further transferred to the inner surface of the BC and MBC. In the process of P diffusion, the resistance increased and the adsorption rate slowed down. In the third stage, with the continuous reduction in the P concentration in solution, the adsorption and desorption rates of the BC and MBC reached the dynamic equilibrium stage. As can be seen from Table 6, the order of adsorption rate constants of the BC and MBC was $k_{d1} > k_{d2} > k_{d3}$, indicating that the highest adsorption rate occurred in the first stage, where P was adsorbed on the surface of the BC and MBC through external diffusion [46]. However, the C values for both the BC and MBC were far from zero, suggesting that intra-particle diffusion is not the only control step [47,48]. At the same initial P concentration, K_{d2} was much smaller than K_{d1} , indicating that the rapid adsorption of the outer surface plays a key role in the entire adsorption process, while the internal diffusion has limited influence on the adsorption process.

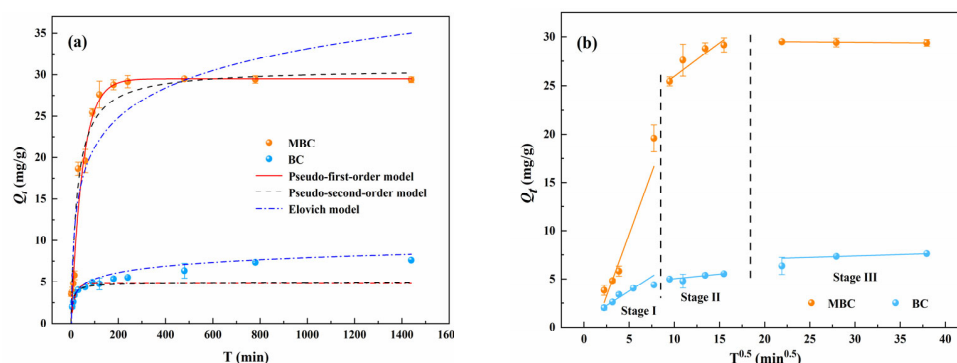


Figure 4. The adsorption kinetics (a) and intra-particle diffusion model (b) fitting curves of the MBC and BC for phosphate.

Table 6. Comparison of fitting results of adsorption kinetics model.

Biochar	Quasi-First-Order Kinetic			Quasi-Second-Order Kinetic			Elovich Equation		
	K_1	Q_e	R^2	K_2	Q_e	R^2	a_1	K_3	R^2
BC	0.04	6.14	0.69	0.006	6.81	0.85	0.943	0.584	0.98
MBC	0.0226	29.33	0.98	0.001	31.6	0.96	4.496	0.485	0.83
Diffusion equation in particles	Stage I			Stage II			Stage III		
	C_1	K_{d1}	R^2	C_2	K_{d2}	R^2	C_3	K_{d3}	R^2
BC	0.750	0.598	0.975	4.069	0.095	0.986	6.504	0.029	0.869
MBC	−3.169	2.561	0.881	19.128	0.683	0.940	29.669	−0.008	0.961

3.4. Effect of pH

As shown in Figure 5, the initial concentration of P in the solution was 50 mg/L, and when the pH ranged from 3 to 11, the adsorption capacity of the MBC for P experienced little change. The adsorption range was 18.6 to 22.0 mg/g, but the overall adsorption capacity showed a trend of decreasing with an increase in the pH. When the pH was >10, the adsorption capacity of phosphorus decreased significantly. This was mainly because, with an increase in the pH, the negative surface charge of the MBC increased, and the valence state of the oxygen-containing anion of phosphorus also increased, thus increasing the repulsive force between the MBC and phosphorus [49]. Considering the pH range of P-containing wastewater from 7 to 9, MBC has a wide range of applicability as a P removal adsorbent.

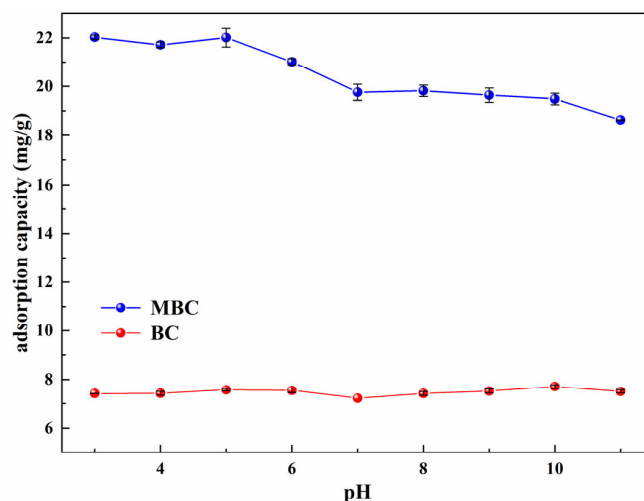


Figure 5. Effect of pH on P adsorption capacity.

3.5. The Removal Effect on Actual Wastewater Treatment

As can be seen from Table 7, MBC showed great advantages in the treatment of wastewater with phosphorus concentrations of 2.06 mg/L or 199.8 mg/L, and the removal efficiencies were higher than 90%, which is significantly better than the phosphorus removal effect of BC. The results indicated that the modified canna biochar with MgO could significantly improve the potential of P removal, and it is an excellent adsorbent that should be popularized.

Table 7. Comparison of the treatment effect of the MBC and BC on actual wastewater.

	BC		MBC	
Initial phosphorus content (mg/L)	2.06	199.8	2.06	199.8
Phosphorus content after treatment (mg/L)	0.69~0.76	54.06~55.10	0.12~0.14	1.45~1.55
Average phosphorus removal rate (%)	63.1~66.6	72.4~72.9	93.4~93.9	99.2~99.3

3.6. Mechanism of Phosphorus Adsorption by MBC

Compared with BC, MBC has a significant advantage for P removal, so this paper focused on the P removal mechanism of MBC. The various functional groups, including C=C, C-O, and Mg-O, contributed together to the effective removal of P from aqueous solutions [1]. However, it can be seen from Figure 6 that the FT-IR spectrum after P adsorption changes very little, which proves the dominant role of electrostatic force. In addition, the XRD diffraction peak of the MBC after adsorption showed little change compared with that before adsorption, and the main crystal was MgO, indicating that the structure of the MBC was relatively stable. In the meantime, the formed MgO served as the active site for phosphate adsorption. Jung [50] considered that MgO undergoes a hydroxylation reaction when it meets water, and the zero charge point of MgO is 12. When the pH of the aqueous solution is less than 12, MgO has a positive charge and can electrostatically adsorb negatively charged phosphate and form an amorphous precipitate. The SEM and XRD tests in this experiment also showed that the MBC contained a large number of MgO particles, which is the dominant factor for P adsorption.

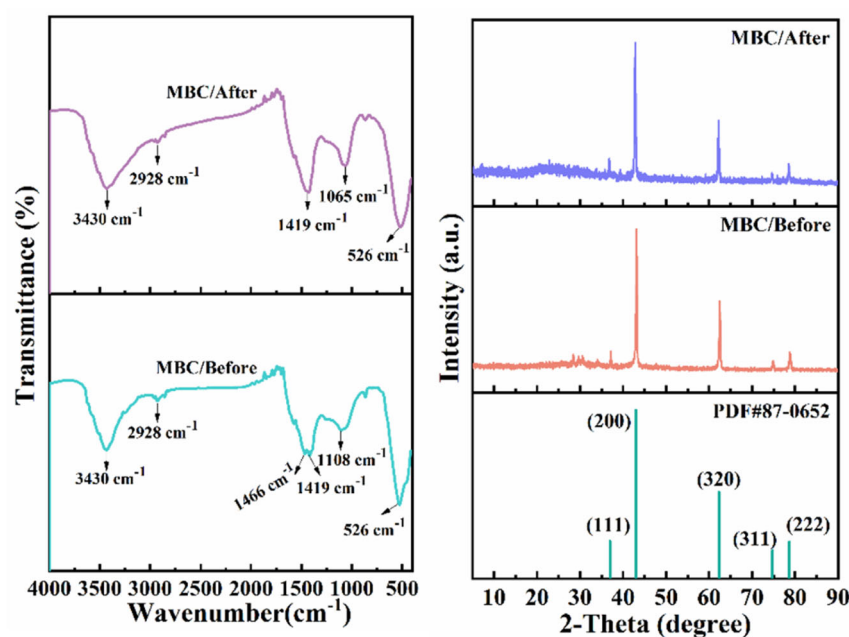


Figure 6. FT-IR and XRD spectra of modified biochar (MBC) before and after adsorption.

The P 2p map of the MBC has only one peak, PO_4^{3-} (133.9 eV). The binding mode of P and Mg on the surface of the MBC was mainly $\text{Mg}_3(\text{PO}_4)_2$, and the binding energy was 1306.1 eV [51]. The peak at 1304.5 eV corresponded to the MgO (see Figure 7). At the initial stage of the MBC reaction, more MgO was carried, resulting in the rapid protonation of the surface and a positive charge on the surface, which was quickly adsorbed by the electrostatic interaction with PO_4^{3-} and HPO_4^{2-} . According to the results of the XPS, the precipitation of P with Mg is also an important adsorption mechanism on the biochar surface.

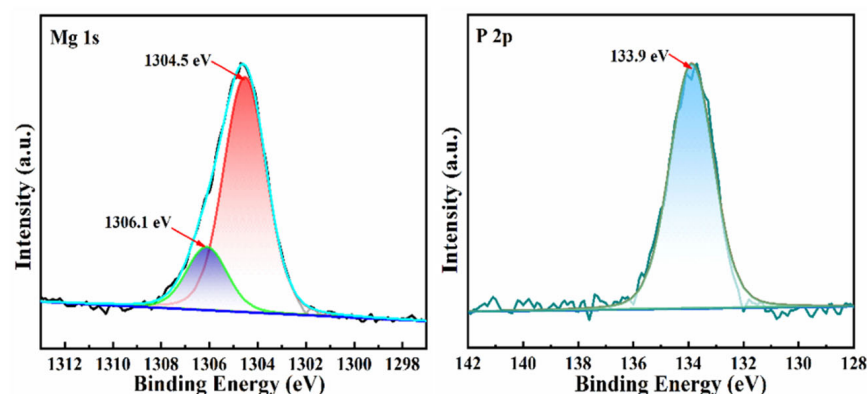


Figure 7. XPS spectra of modified biochar (MBC).

4. Conclusions

The P adsorption capacity of BC in water was 29.98 mg/g, and the capacity of the MBC was 244 mg/g. The removal rates of BC for wastewater containing 2.06 mg/L or 199.8 mg/L of P were 63.1~66.6% and 72.4~72.9%, respectively, while the removal rates of the MBC were 93.4–93.9% and 99.2–99.3%, respectively. It can be seen that MgO-modified canna biochar has great application potential for the removal of P-containing wastewater. In addition, the preparation of MBC is simple and low-cost, and it can realize the reuse of aquatic plant resources. SEM showed that a good deal of MgO crystals were loaded onto the MBC. The MgO modification improved the hydrophilicity and polarity of the biochar, and increased the specific surface area and pore volume. MgO with a positive charge ($\text{pH} < 12$) can electrostatically adsorb negatively charged phosphate and form an amorphous precipitate. In addition, according to the results of the XPS, the precipitation of $\text{Mg}_3(\text{PO}_4)_2$ was the main component on the surface of the MBC. Therefore, the main mechanisms of MBC are electrostatic adsorption and complex precipitation.

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