Magnetic biochar particles prepared by ion cross-linking to remove phosphate from water

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Abstract

In this study, the ionic cross-linking method was used to synchronize the granulation and magnetization of biochar powder. A precursor of Ca/Mg modified, tobacco stalk biochar combined with sodium alginate as the functional monomer, CaCl\(_2\) solution as the cross-linking agent, and a Fe\(_3\)O\(_4\) magnetic fluid dopant were used to prepare magnetic biochar particles (EMCSB3), which were easy to separate and recover. The adsorption performance of phosphate by these EMCSB3 was explored. The Langmuir model fitted adsorption capacity of phosphate on the EMCSB3 was 8.93 mgP g\(^{-1}\), which was comparable to other materials at the same concentration. The process of phosphate adsorption by magnetic particles followed a pseudo-second-order model, and the adsorption mechanism was chemisorption. EMCSB3 was suitable for use in environments with pH \(\leq 8\), the best dosage was 6.67 g l\(^{-1}\), and its removal rate was maintained at about 85\%. Phosphate adsorption was greatly affected by coexisting CO\(_3^{2-}\). This study provides a technical approach for the granulation and magnetization of powdered biochar and improves its feasibility of use.

Biochar is a stable, C-rich, by-product synthesized by the carbonization of biomass in an environment with limited oxygen [1]. With an abundant pore structure, large specific surface area, and more oxygen-containing active groups on the surface, biochar is a multi-functional material with a wide range of raw materials and low cost [2–6]. Biochar can be used to remove inorganic anions such as PO\(_4^{3-}\) in water, but the removal ability of conventional biochar is usually low [7]. Therefore, metal loading, such as Mg, Al, Fe, La, and Ca, is often used to improve the ability of biochar to remove inorganic anions in water [8–16]. Currently, biochar is mostly prepared by pyrolysis and usually exists in the form of powder or small particles [17], but these are easily lost in applications and are difficult to separate [18]. Granulating the biochar or increasing the particle size of the biochar can effectively solve the problem of loss. The addition of magnetic materials, such as Fe\(_3\)O\(_4\), enables the adsorbent to be separated by a magnet [19]. The current granulation technologies mainly include rolling granulation with polytetrafluoroethylene as the binder [20], wet granulation with hydroxypropyl methylcellulose as the binder [21], and cross-linking reactions, such as the interaction of sodium alginate and polyvalent metals [22]. The sponge technology using acrylamide has also been used for the granulation of powdered materials [23]. The combination of granulation and magnetization can address the loss of powdered biochar and facilitates separation and recycling. However, the combination of granulation and magnetization methods remains to be studied.

Biopolymer materials, such as sodium alginate, are used in phosphate removal-related research, due to their non-toxic and biodegradable properties [22]. It also shows good phosphate fixation performance and application prospects in phosphate adsorption [24]. Based on this, the purpose of this study is to achieve solid and magnetic separation of powdered biochar using magnetic materials and granulation. Therefore, this study...
uses the ion cross-linking reaction of sodium alginate and divalent calcium to immobilize powdered biochar along with a magnetic fluid to prepare magnetic biochar particles for phosphate adsorption. The adsorption performance and mechanism of these magnetic biochar particles were explored through batch adsorption experiments and characterization techniques.

1. Materials and methods

1.1. Experiment materials
The powdered biochar selected was Mg/Ca modified, tobacco stalk biochar (EM-C24), and the preparation method of He et al [25] was followed. Fe₃O₄ magnetic fluid was prepared by a co-precipitation method [26]. Potassium dihydrogen phosphate (KH₂PO₄, Analytical Reagent) purchased from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). Anhydrous calcium chloride (CaCl₂, AR), magnesium chloride hexahydrate (MgCl₂·6H₂O, AR), potassium persulfate (K₂S₂O₈, AR), and sodium alginate were purchased from Shanghai Macleans Biochemical Co., Ltd. (Shanghai, China). The test water used deionized water with a resistivity of 18.2 MΩ·cm.

1.2. Preparation of magnetic biochar particles
200 ml of 2% sodium alginate viscous solution was placed in a beaker, and biochar was added to get solutions with concentrations of 5 g l⁻¹, 10 g l⁻¹, and 20 g l⁻¹. Magnetic fluid was added, according to the ratios of 1 g biochar: 1 ml magnetic fluid (1 g: 1 ml) and 1 g biochar: 2 ml magnetic fluid (1 g: 2 ml). After stirring and mixing, ultrasonic treatment was performed for 15 min, and mechanical stirring was performed at 400 rpm for 1 h to fully mix.

The mixed solution was dropped into 2% or 4% CaCl₂ solution using a 50 ml acid burette at a slow and uniform rate. After ion cross-linking for 12 h, the gel balls were taken out, washed with ultra-pure water 3 times, and dried at 45 °C to obtain the magnetic biochar particles, denoted as EMCSB1—EMCSB7.

1.3. Magnetic particle characterization
Fourier infrared spectrometer (FTIR, Thermo Fisher Nicolet IS10, Waltham, Massachusetts, USA) was used to measure the transmission curves of magnetic particles before and after adsorption in the wavenumber range of 4000–4000 cm⁻¹, and analyze changes in functional groups. The surface morphology of the magnetic particles was observed by field emission scanning electron microscopy (SEM, Geminisem 300, Zeiss, Oberkochen, Baden-Württemberg, Germany), and the surface element content of the magnetic particles was analyzed by x-ray energy spectroscopy (EDS, Merlin Compact, Zeiss, Oberkochen, Baden-Württemberg, Germany). The specific surface area of the material was analyzed using an automated physical adsorption meter (BET, ASAP2460, Norcross, Georgia, USA). The saturation magnetization of the magnetic particles was measured at 25 °C with a vibrating magnetometer (Lake Shore, VSM 7404, Columbus, Ohio, USA) in the external magnetic field range of -2–2 T. x-ray diffraction (XRD) patterns in the range of 5°–85° were obtained by Bruker D8 Advance made of Germany, and Jade 6.5 was used to analyze the spectra.

1.4. Phosphate adsorption test
1.4.1. Adsortion kinetics test
30 ml of 2 mg P l⁻¹ phosphate solution was absorbed by 0.2 g of the EMCSB3 at 25 °C and oscillated at 180 rpm for 5 min, 10 min, 20 min, 30 min, 1 h, 2 h, 3 h, 4 h, 8 h, 12 h, and 24 h to evaluate the adsorption kinetics. The sample solution was determined by a double beam UV-Vis spectrophotometer (TU-1901, Beijing General Analysis General Instrument Co. Ltd., Beijing, China) at 700 nm using the molybdate color method. The control steps of adsorption rate and the adsorption effect were explained by fitting pseudo-first-order, pseudo-second-order, and Weber-Morris intra-particle diffusion models (pseudo-first-order (1), pseudo-second-order (2), and Weber-Morris intra-particle diffusion models (3)).

\[ q_t = q_e \left(1 - \frac{1}{e^{kt}}\right) \]  \hspace{1cm} (1)

\[ \frac{t}{q_t} = \frac{1}{k_1} \left(1 + \frac{1}{q_e}\right) + t \]  \hspace{1cm} (2)

\[ q_t = k_2 \sqrt{t} + C_i \]  \hspace{1cm} (3)

where, \( q_e, q_t (\text{mg} \cdot \text{g}^{-1}) \) were the adsorption capacities of biochar for phosphate at equilibrium and at time \( t \), respectively; \( k_1 \) (h⁻¹), \( k_2 \) (mg·g⁻¹·h⁻¹) were the adsorption rate constants of the corresponding model.
respectively; \( k_{p} \) (mg·g\(^{-1}\)·h\(^{-1/2}\)) was the internal diffusivity constant; \( C_{i} \) (mg·g\(^{-1}\)) was a constant representing the thickness of the boundary layer, and \( i \) is the adsorption stage.

### 1.4.2. Isotherm adsorption test
Phosphate solutions with initial concentrations of 0.5, 1, 2, 5, 10, 15, and 20 mg P l\(^{-1}\) were adsorbed by 0.2 g of EMCSB3 at 15, 25, 35 \( ^\circ \)C and oscillated at 180 rpm for 24 h to study the isotherm adsorption. The adsorption mechanism of phosphate by magnetic particles and its adsorption effect were explained by fitting Langmuir and Freundlich model (Langmuir (4) and Freundlich (5)).

\[
Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (4)
\]
\[
Q_e = K_F C_e^{1/n} \quad (5)
\]

where \( K_L \) (L·mg\(^{-1}\)), \( K_F \) (mg\((1-1/n)\)·L\(^{1/n}\)/g) were the Langmuir and Freundlich adsorption equilibrium constant, respectively; \( n \) was a constant index indicating the strength of adsorption, the larger the value, the stronger the adsorption; \( Q_e \) (mg/g), \( Q_m \) (mg/g) were the adsorption capacity of phosphate at equilibrium and the maximum, respectively; \( C_e \) (mg/L) was the concentration of phosphate at adsorption equilibrium.

### 1.4.3. Influencing factor test
To explore the effect of the addition amount on phosphate adsorption by the EMCSB3, 30 ml of 2 mg P l\(^{-1}\) solution was adsorbed by EMCSB3 (0.05, 0.1, 0.15, 0.2, 0.25 g) at 25 \( ^\circ \)C oscillating at 180 rpm for 24 h.

To explore the effect of solution pH on phosphate adsorption by the EMCSB3, 0.2 g of the magnetic particles were used to adsorb 30 ml of 2 mg P l\(^{-1}\) solution with pH of 2, 4, 6, 8, 10, and 12 at 25 \( ^\circ \)C oscillating at 180 rpm for 24 h.

To explore the effect of coexisting ions on the adsorption of phosphate by the EMCSB3, 0.2 g of the EMCSB3 and 30 ml of a coexisting ion solution containing the number of plasmas (0.0016 mol l\(^{-1}\) P mixed with Cl\(^-\), SO\(_4\)\(^2-\), NO\(_3\)\(^-\), CO\(_3\)\(^2-\), and NH\(_4\)\(^+\) respectively) in a 100 ml conical flask, and then adsorbed at 25 \( ^\circ \)C and 180 rpm for 24 h.

## 2. Results and discussion

### 2.1. Optimization of preparation conditions
Sodium alginate has unique spheroidizing properties. It forms a gel network through ion exchange in the CaCl\(_2\) solution. Other components can be added to give the gel sphere different properties. Figure 1 shows the effects of CaCl\(_2\) mass concentration, EM-C24 addition, and the magnetic fluid addition ratio on the adsorption performance of magnetic biochar particles. As shown in figure 1(a), when the addition ratio and mass concentration of CaCl\(_2\) remained unchanged, the phosphate removal rate of magnetic biochar particles showed an increasing and then decreasing trend with the addition of EM-C24. When the amount of EM-C24 added was 10 g l\(^{-1}\), the maximum removal rate was 82.8%. Controlling the amount of EM-C24 and the addition ratio of
magnetic fluid, the magnetic particles prepared with the 2% CaCl₂ solution had a higher adsorption removal rate than the particles made with the 4% CaCl₂ solution. This was because too large of a CaCl₂ mass concentration resulted in a compact internal structure of the particles, which is not conducive to solution penetration and reduces the adsorption effect [27]. Figure 1(b) shows that the adsorption removal rate of phosphate by magnetic particles prepared with a magnetic fluid addition ratio of 1 g: 2 ml was higher than that of magnetic particles with the addition ratio of 1 g: 1 ml. Based on this analysis and test results, the optimal preparation conditions of magnetic particles were obtained as follows: 2% of CaCl₂ (mass concentration), 2% of sodium alginate viscous liquid (mass concentration), 10 g l⁻¹ EM-C24, and the 1 g biochar : 1 ml magnetic fluid addition ratio, denoted as EMCSB3.

2.2. Characterization of magnetic particles

2.2.1. BET and magnetic intensity analysis

The BET analysis result of EMCSB3 are shown in table 1. The BET surface area, external specific surface area, and micropore area of the EMCSB3 after adsorption dropped sharply. Also, the average pore size increased following adsorption, which was related to the adsorption of phosphate by the magnetic biochar particle. The adsorption process of phosphate on the magnetic particles included both surface and internal pore adsorption [24]. The pore structure before adsorption consisted of micropores and mesopores. The specific surface area of the EMCSB3 was 14.42 m²/g, the proportion of micropores was 21.22%, and the average adsorption pore size was 8.06 nm. Compared with the magnetic particles prepared by Ren et al [20], EMCSB3 had a smaller specific surface area, a smaller proportion of micropores, a larger external specific surface area, a larger adsorption pore size, and a stronger adsorption capacity. This indicated that the adsorption capacity of the EMCSB3 had no noticeable correlation with the specific surface area. However, there is no doubt that a large external specific surface area and adsorption pore size were conducive to adsorption, which was also shown by Xu et al [14]. After adsorption, the specific surface area of the EMCSB3 decreased to 6.38 m² g⁻¹, and the micropore area and external specific surface area decreased to 0.77 m² g⁻¹ and 5.61 m² g⁻¹, respectively. This indicated that the internal pore adsorption process included both mesoporous and microporous adsorption, but mainly mesoporous adsorption. The pore structure of the EMCSB3 was blocked by adsorption, which resulted in a decrease in the specific surface area and an increase of the average pore size to 12.35 nm.

The magnetic intensity analysis result of EMCSB3 is shown in figure 2. Figure 2(a) shows that the saturation magnetic intensity of the EMCSB3 was 3.35 emu g⁻¹ before adsorption and decreased to 1.92 emu g⁻¹ after adsorption. Figure 2(b) shows the magnetic separation effect of EMCSB3. This indicates that magnetic separation can still be achieved even though the saturated magnetic intensity of the adsorbed material was
reduced. At the same time, the residual magnetization and coercivity of the magnetic particles are both 0, showing superparamagnetism, which indicates that the magnetic particles can actively respond to the external magnetic field. Once the external magnetic field is removed, the particles can quickly redisperse without any agglomeration between the particles.

2.2.2. SEM-EDS
The SEM-EDS images of the EMCSB3 surface and the cross-section before and after adsorption are shown in figure 3. Before adsorption, the surface and cross-section of the biochar magnetic particles had an observable pore structure, the surface was smooth and without particles, indicating that the biochar powder and magnetic fluid were evenly dispersed in the sodium alginate. The alginate prevents the accumulation of powder and magnetic fluid. Subsequent granulation finally caused the biochar powder and magnetic fluid to be dispersed and fixed inside the calcium alginate particles while forming a pore structure. The powdered biochar was successfully coated and fixed in the grid structure [26]. EMCSB3 has a layered structure and unperforated pores, which was due to the presence of alginic acid which gave the material a dense, layered structure [28]. After the adsorption of phosphate, there was no observable pore structure on the surface, and the granularity and roughness were increased. The cross-section had many paper-like folds. There are lumps and flakes, and the pore structure was reduced. EDS energy spectrum scanning found that six elements, C, Mg, Ca, O, Fe, and P, existed on the surface of the material. Before adsorption, EMCSB3 contained a very small amount of phosphorus, which came from the original tobacco stalk and had been fixed during the material preparation.

Figure 3. SEM of the surface (a) and cross-section (b) of EMCSB3 before phosphate adsorption, surface EDS of ECMSB3 (c) before phosphate adsorption. SEM of the surface (d) and cross-section (e) of EMCSB3 after phosphate adsorption, and surface EDS of ECMSB3 (f) after phosphate adsorption.

Figure 4. FITR spectra (a) and XRD (b) spectra of EMCSB3 before and after phosphate adsorption.
The adsorption kinetics of EMCSB3 are shown in figure 5(a). The pseudo-first-order and pseudo-second-order models, as shown in figure 5(b), were used to fit the experimental data. The correlation coefficient was used to evaluate the relationship between the fitted parameters and the experimental values of qe. This indicates that the adsorption rate of EMCSB3 was faster in the first 4 h, and then the adsorption rate gradually slowed down, and the adsorption became saturated after 12 h. The adsorption process was accompanied by a change in the pH of the solution, and the trend was the same as the adsorption rate. The final solution was weakly alkaline with a pH of about 9.0. Model fitting was performed on the test results, and the fitted parameters are shown in table 2. The results showed that the pseudo-second-order kinetic model fitting led to a higher $R^2$ value and was closer to the experimental values of $q_e$. This indicated that the adsorption rate of phosphate by EMCSB3 was determined by the unoccupied adsorption sites of the adsorbent, and the adsorption process was mainly influenced by chemisorption, which involved electron sharing or electron transfer and the formation of new compounds [24, 25]. The mechanism of phosphate adsorption by EMCSB3 includes electrostatic attraction and chemisorption. Chemical adsorption is mainly chemical precipitation and ion exchange in EMCSB3, there are MgO and CaCO$_3$, which may mainly have the following reactions [25]:

\[
\text{Mg}^{2+} + 2\text{HPO}_4^{2-} \rightarrow \text{Mg(H}_2\text{PO}_4)_2, \quad \text{Mg(H}_3\text{PO}_4)_2 \rightarrow \text{MgHPO}_4 + \text{H}_2\text{PO}_4, \\
\text{Mg}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{MgHPO}_4, \quad \text{CaCO}_3 + \text{HPO}_4^{2-} \rightarrow \text{CaHPO}_4 + \text{CO}_3^{2-}, \\
\text{CaCO}_3 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Ca(H}_2\text{PO}_4)_2 + \text{CO}_2, \quad \text{CaCO}_3 + \text{PO}_3^{2-} \rightarrow \text{Ca}_3(\text{PO}_4)_2 + \text{CO}_3^{2-}.
\]

### 2.2.3. FTIR and XRD analysis

The FTIR spectra of EMCSB3 before and after phosphate adsorption are shown in figure 4(a). The broad absorption peak at 3398 cm$^{-1}$ was the absorption band of –NH$_2$ and hydrogen bonds [29, 30]. The absorption peak at 1600 cm$^{-1}$ was due to –OH vibrations [31]. The broad absorption peak at 1037 cm$^{-1}$ indicated the presence of PO$_4^{2-}$ [32]. The absorption peak of 819 cm$^{-1}$ was from CO$_3^{2-}$ out-of-plane bending vibrations [33]. The absorption peak at 3697 cm$^{-1}$ was the absorption band of MgCO$_3$ in BC [35]. The 875 cm$^{-1}$ absorption band corresponded to the out-of-plane bending vibration of a benzene ring hydrogen atom [36]. Comparing the FTIR spectra before and after adsorption the existing forms of Mg was not changed, indicating that the Mg contained in the granular carbon was not chemically adsorbed to the phosphate. After adsorption, the absorption peak at 819 cm$^{-1}$ disappeared, indicating that CO$_3^{2-}$ was removed and the phosphate ion was exchanged to achieve adsorption [37]. According to Jade 6.5, the wide-angle diffraction analysis results of EMCSB3 before and after phosphate adsorption are shown in figure 4(b). It can be seen from figure 4(b) that the main phases in EMCSB3 before and after phosphate adsorption are CaCO$_3$ (104, PDF # 72-1214) and MgO (111, PDF # 75-0447). At the same time, the diffraction peak of Ca$_3$(PO$_4$)$_2$ (208, PDF # 09-0348) appeared in the XRD analysis of EMCSB3 after adsorption.

### 2.3. Study on adsorption properties

#### 2.3.1. Adsorption kinetics

The adsorption kinetics of EMCSB3 is shown in figure 5. To study the relationship between adsorption process and time, test results were analyzed using pseudo-first-order and pseudo-second-order models, as shown in figure 5(a). The adsorption efficiency of EMCSB3 was faster in the first 4 h and then the adsorption rate gradually slowed down, and the adsorption became saturated after 12 h. The adsorption process was accompanied by a change in the pH of the solution, and the trend was the same as the adsorption rate. The final solution was weakly alkaline with a pH of about 9.0. Model fitting was performed on the test results, and the fitted parameters are shown in table 2. The results showed that the pseudo-second-order kinetic model fitting led to a higher $R^2$ value and was closer to the experimental values of $q_e$. This indicated that the adsorption rate of phosphate by EMCSB3 was determined by the unoccupied adsorption sites of the adsorbent, and the adsorption process was mainly influenced by chemisorption, which involved electron sharing or electron transfer and the formation of new compounds [24, 25]. The mechanism of phosphate adsorption by EMCSB3 includes electrostatic attraction and chemisorption. Chemical adsorption is mainly chemical precipitation and ion exchange in EMCSB3, there are MgO and CaCO$_3$, which may mainly have the following reactions [25]:

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\text{Mg}^{2+} + 2\text{HPO}_4^{2-} \rightarrow \text{Mg(H}_2\text{PO}_4)_2, \quad \text{Mg(H}_3\text{PO}_4)_2 \rightarrow \text{MgHPO}_4 + \text{H}_2\text{PO}_4, \\
\text{Mg}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{MgHPO}_4, \quad \text{CaCO}_3 + \text{HPO}_4^{2-} \rightarrow \text{CaHPO}_4 + \text{CO}_3^{2-}, \\
\text{CaCO}_3 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Ca(H}_2\text{PO}_4)_2 + \text{CO}_2, \quad \text{CaCO}_3 + \text{PO}_3^{2-} \rightarrow \text{Ca}_3(\text{PO}_4)_2 + \text{CO}_3^{2-}.
\]
The Weber-Morris diffusion model was used to analyze the diffusion to further explain the adsorption mechanism and control steps of adsorption rate. The results are shown in figure 5(b) and table 2. The adsorption process can be divided into three stages, namely the initial adsorption stage with faster adsorption, the

![Figure 6. Isothermal adsorption results (squares) compared to the best fit Langmuir (solid) and Freundlich (dotted) adsorption models.](image)

![Figure 7. Influence of different dosages of particulate biochar on phosphate adsorption capacity (gray circles) and removal rate (black squares).](image)

| Material | Pseudo-first-order | Pseudo-second-order |
|----------|-------------------|---------------------|
| EMCSB3   |                   |                     |
|          | $K_1 \ (h^{-1})$  | $q_e \ (mg \cdot \ g^{-1})$ | $R^2$ | $K_2 \ (g \cdot mg^{-1} \cdot h^{-1})$ | $q_e \ (mg \cdot g^{-1})$ | $R^2$ |
|          | 0.45              | 1.48                | 0.983 | 0.51                   | 1.60                | 0.993 |

| W-M model |
|-----------|
| EMCSB3    |                   |                     |
|          | $k_{p1}$          | $C_1$               | $R^2$ | $k_{p2}$          | $C_2$               | $R^2$ | $k_{p3}$ | $C_3$ | $R^2$ |
|          | 0.98              | -0.08               | 0.971 | 0.3                   | 0.58                | 0.984 | 0.03     | 1.37  | 0.979 |

The Weber-Morris diffusion model was used to analyze the diffusion to further explain the adsorption mechanism and control steps of adsorption rate. The results are shown in figure 5(b) and table 2. The adsorption process can be divided into three stages, namely the initial adsorption stage with faster adsorption, the
intermediate adsorption stage with slow adsorption, and the equilibrium stage with adsorption saturation. The first stage of adsorption (0–1 h) mainly occurs on the outer surface or large pores, and the main limiting step is external diffusion [38]. Meanwhile, due to the large concentration difference, the diffusion rate was fast and the adsorption rate was fast. The C1 value was $-0.08$, indicating that the boundary layer has no effect on adsorption. The second stage (1–12 h), the adsorbate entered the inner pores of the adsorbent, the adsorption rate decreased, and internal diffusion becomes the control step of adsorption rate [39]. Meanwhile, due to the decrease in concentration, the mass transfer force was weakened and the adsorption rate slowed down. In the first stage of adsorption, the thickness of the boundary layer increased, the influence of the boundary layer on the adsorption increased, and the C value increased. After that, the adsorption process reached an equilibrium state, the adsorption rate tended to zero, the adsorption amount slowly increased, and the boundary layer limited the adsorption process.

2.3.2. Adsorption isotherms

The adsorption isotherm of phosphate on EMCSB3 was used to explain the relationship between the concentration of phosphate and the adsorption effect, and to evaluate its potential to remove phosphate from bodies of water, as shown in figure 6 and table 3. As can be seen from figure 6, under the same initial concentration condition, the adsorption capacity gradually increases with the increase of temperature. This shows that the adsorption of phosphate by EMCSB3 is an endothermic reaction. When the temperature increased from 15 °C to 25 °C, the adsorption capacity increased significantly, but when the temperature increased from 25 °C to 35 °C, the adsorption capacity did not change significantly with the temperature. The goodness of fits between the Freundlich model and the Langmuir model were $R^2 > 0.9$, which indicated that the adsorption process may include both single-layer adsorption on a uniform surface and multilayer adsorption on a non-uniform surface [40, 41]. $0 < 1/n < 1$, which means that there is easy adsorption of phosphate on the granular biochar [25]. Langmuir model fitting showed that the maximum adsorption capacity was 8.93 mg g$^{-1}$. Compared with the adsorption capacity of some other granular and powdered materials, such as carbon fiber, and sodium alginate gels, in a similar range of phosphate concentration, the adsorption capacity of EMCSB3 was similar or better, as shown in table 4.

2.3.3. Effect of adsorbent dosage

The effect of the dosage of biochar magnetic particles on the removal of phosphate in water is shown in figure 7. With the increase of the dosage of magnetic particles added, the removal rate of phosphate by magnetic particles increased at first and then stabilized. When the dosage of magnetic particles added to 30 ml of 2 mgP l$^{-1}$ phosphate solution increased from 1.67 g l$^{-1}$ to 6.67 g l$^{-1}$, the phosphate removal rate rose from 41.91% to

$$\text{Table 4. Comparison of adsorption capacity at low phosphate concentrations.}$$

| Adsorbent                  | $Q_m$ (mg P/g) | Phosphate concentration | References |
|----------------------------|----------------|-------------------------|------------|
| EMCSB3                     | 8.93           | 0.5–20 mg P l$^{-1}$    | this study |
| Commercial granular ferric hydroxide | 8.99           | 5 mg P l$^{-1}$         | [41]       |
| Calcium Alginate Column    | 0.74           | 20 mg P l$^{-1}$        | [42]       |
| Al-NaBT (Modification of bentonite, powder) | 9.16           | 20 mg P l$^{-1}$        | [42]       |
| Ca-alginite entrapped Al-NaBT beads | 6.61           | 20 mg P l$^{-1}$        | [42]       |
| Ferrihydrite-impregnated granular activated biochar | 5.73           | 3.33 g l$^{-1}$        | [43]       |
| Fe-loaded granular activated biochar | $\approx$ 0.94 | 3–65 mg l$^{-1}$        | [44]       |
| Fe-coated granular activated biochar (pre-oxidized) | 10.8           | 1–100 mg l$^{-1}$      | [45]       |
| Fe-and Zr-loaded activated biochar nanofiber | $\approx$ 8.6  | 1.5–20 mg l$^{-1}$      | [46]       |
| La-doped activated biochar fiber | 7.92           | 5–30 mg l$^{-1}$        | [47]       |
| Lanthanum hydroxide-doped activated biochar fiber | $\approx$ 5.0  | $\approx$ 3.3–22.8 mg l$^{-1}$ | [48] |
| Clinoptilolite              | 6.6            | up to $\approx$ 36 mg l$^{-1}$ | [49]       |
| Mg-alginate modified T. dealbata biochar | $\approx$ 15.2 | 0–36 mg l$^{-1}$        | [50]       |
80.36% and stabilized. Therefore, increasing the dosage of adsorbent was beneficial for the removal of phosphate from water. However, the adsorption capacity per unit of adsorbent showed a gradual decrease, which was because the adsorbent reduced the concentration of phosphate in the water by adsorption. When the phosphate concentration dropped below a certain level, the mass transfer force between the solid and liquid phases was insufficient, and the adsorption behavior gradually decreased [51]. Meanwhile, as the concentration of the phosphate solution remained constant, the P available to each unit adsorption site on the surface of the EMCSB3 decreased, which also decreased the amount adsorbed by EMCSB3.

2.3.4. Effect of pH on adsorption
Figure 8 shows the effect of the initial pH of the solution on the adsorption of phosphate by EMCSB3 and the Zeta potential of EMCSB3. As shown in figure 8(a), the phosphate adsorption removal rate of 6.67 g l\(^{-1}\) EMCSB3 in the pH range of 2–8 was about 85%, but when pH > 8, the adsorption removal rate gradually decreased with the increase in pH. When the pH was 12, the removal rate dropped to 64.52%. Comparing the pH of the solution before and after adsorption, the pH of the final solution after adsorption equilibrium fluctuated in the range of 9.3–9.7, which may be because the biochar and phosphate constitute a buffer solution and maintained a relatively stable pH. The pH value of the solution affected the charge of the adsorbent and the existence of the adsorbate through the mechanism of protonation and deprotonation, which in turn led to changes in the adsorption effect [52]. When the initial pH was less than 9.3, the EMCSB3 adjusted the pH of the solution to 9.3 by absorbing H\(^+\) while adsorbing phosphate. The absorption of H\(^+\) leads to the protonation of the metal oxide and –OH contained in the magnetic particles, which causes the magnetic particles to be positively charged and promotes the adsorption of phosphate. When the initial pH > 9.7, the addition of EMCSB3 absorbed OH\(^-\) in the solution, reduced the pH of the solution, and caused its own deprotonation. At the same time, OH\(^-\) competed with the phosphate ions for the active adsorption sites, resulting in a decrease in the adsorption removal rate. The pH of the solution also changed the form of phosphate present. When pH > 9.7, the forms of phosphate included PO\(_4^{3-}\) and HPO\(_4^{2-}\). When pH < 9.3, the forms of phosphate in solution were H\(_2\)PO\(_4\), H\(_2\)PO\(_4\), and HPO\(_4^{2-}\), and the adsorption energies required by the different forms of phosphate were different, so the adsorption also changed [46, 53]. At the same time, the influence of pH is also related to the Zeta potential of the material. As shown in figure 8(b), the Zeta potential of EMCSB3 was 7.83. When the pH of the solution is lower than 7.83, the material is positively charged, which is conducive to adsorption; when the pH of the solution is higher than 7.83, the material is negatively charged, which is not conducive to the adsorption of phosphate. Therefore, the adsorption effect is good in the solution with pH lower than 8. When the pH is greater than 8, the adsorption effect decreases with the increase of pH, which is consistent with the result of figure 8(a).

2.3.5. Effect of coexisting ions on adsorption
Figure 9 shows the effect of the presence of coexisting ions on the adsorption of phosphate by the EMCSB3. The results of significant difference analysis showed that the presence of Cl\(^-\) and SO\(_4^{2-}\) did not affect the adsorption of phosphate by EMCSB3 compared with the presence of only P. This indicated that EMCSB3 may adsorb phosphate in the form of inner ring complexes with functional group coordination [34]. The existence of NO\(_3^-\), NH\(_4^+\) and CO\(_3^{2-}\) led to significant differences in the removal rate. When NO\(_3^-\), NH\(_4^+\) and phosphate coexist separately, they respectively promoted and inhibited the adsorption by EMCSB3. However, from the point of
view of the removal rate, the promotion and suppression effects have little effect. EMCSB3 can still effectively remove phosphate while coexisting with nitrogen and phosphate. The presence of CO$_3^{2−}$ significantly reduced the phosphate removal rate of EMCSB3. When only CO$_3^{2−}$ and P were together at the same time, the phosphate removal rate dropped to 57%. This may be caused by CO$_3^{2−}$ increasing the pH of the solution before the phosphate can interact with the system [55], leading to the decrease of the adsorption removal rate. Jia et al [56] also had similar results in their studies. But the co-existence of Cl$^{−}$, SO$_4^{2−}$, NO$_3^{−}$, and NH$_4^{+}$ can weakened the influence of CO$_3^{2−}$ on adsorption. Compared with the absence of coexisting ions, the phosphate removal rate only decreased by 5%. This may be because the coexistence of Cl$^{−}$, SO$_4^{2−}$, NO$_3^{−}$, and NH$_4^{+}$ increased the electrostatic repulsion between ions, impeded CO$_3^{2−}$ from competing for adsorption sites, and thus weakened the influence of CO$_3^{2−}$ on adsorption.

3. Conclusions

The ion cross-linking method was used to successfully prepare magnetic particles with certain adsorption performance for phosphate and easy separation performance. The EMCSB3 were prepared by adding biochar and magnetic fluid to 2% sodium alginate solution in the proportion of 1 g biochar : 1 ml magnetic fluid and 10 g l$^{-1}$ biochar to make a viscous liquid, and then adding the viscous liquid droplets to 2% mass fraction CaCl$_2$ solution. After ion cross-linking for 12 h, the gel was taken out, washed with ultra-pure water 3 times, and dried at 45 $^\circ$C. The Langmuir fitted adsorption capacity was 8.93 mgP/g, which was better than calcium alginate gel, and better than some granular materials prepared by non-granulation technologies, such as zeolites, granular activated carbon, and other precursor granular materials fixed by the same method, including bentonite and carbon fiber. The adsorption rate of phosphate by EMCSB3 was determined by the unoccupied adsorption sites of the adsorbent, and the adsorption process includes external diffusion and internal diffusion. The adsorption mechanism may include both monolayer chemisorption on a homogeneous surface and multilayer chemisorption on a non-homogeneous surface. EMCSB3 was suitable for use in an environment with pH $\leq$ 8, the optimal dosage was 6.67 g l$^{-1}$, and its removal rate was maintained at about 85%. The adsorption was greatly affected by environmental CO$_3^{2−}$, but the composite effect of multiple coexisting ions in the integrated water remains to be explored.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of interest statement

The work has not been previously published in a peer-reviewed publication in any format, including in languages other than English but excluding theses; that it is not under consideration for publication anywhere else; that its publication has been approved by all co-authors. Authors have no conflict of interest to declare.

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