Biochar produced from tobacco stalks, eggshells, and Mg for phosphate adsorption from a wide range of pH aqueous solutions

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Abstract
Preparing biochar from tobacco stalks modified with Mg is a feasible way to utilize tobacco stalks as a resource. However, the capacity of phosphate removal of Mg-biochar is affected greatly with increasing pH. In the present work, biochar produced from the tobacco stalks was modified via Mg addition and eggshells during the preparation for improving the phosphate adsorption performance at higher pH. The results revealed that the theoretical maximum adsorption capacity of phosphate for the biochar increased from 110.62 to 272.37 mg P g\textsuperscript{-1} when the mass ratio of Mg to tobacco stalk increased from 0.12:1 to 0.48:1 (M-C). The adsorption capacity of the biochar with a mass ratio of 0.3:1 (M-C2) was more than 200 mg P g\textsuperscript{-1} in the pH range of 3 to 7 but with further increase of pH from 7 to 12 the capacity decreased from 205 to 135.2 mg P g\textsuperscript{-1}. Addition of eggshells with the magnesium solution during the dipping process can effectively improve the capacity of the modified biochar for phosphate in the alkaline condition. When the mass ratio of eggshell to tobacco stalk was ≥0.25:1, the phosphate adsorption capacities of the biochar can reach above 200 mg P g\textsuperscript{-1} within a wide pH range of 3 to 12, and the maximum adsorption capacity can reach more than 270 mg P g\textsuperscript{-1} for the mass ratio of 1:1 (EM–C24). The characterization results demonstrated that Ca and Mg were loaded on the biochar. The high adsorption performance provides reference values for the utilization of tobacco stalks and eggshells.

1. Introduction

Phosphorus is a key element for the growth of plants and animals but if excessive phosphorus is discharged into the water supply, it will cause eutrophication and serious damage to the water ecosystem [1–3]. Phosphate is considered to be one of the main factors affecting the quality of water environment [4, 5]. There will be a risk of eutrophication when the concentration exceeds 0.02 mg l\textsuperscript{-1} [6–9]. In addition, phosphorus concentration exceeding 0.5 mg l\textsuperscript{-1} in the surface water will be harmful to human health [10]. Removal of phosphate from wastewater is of great significance scientifically and economically. At present, the methods of phosphorus removal in water include membrane separation, chemical precipitation, biological method and adsorption method etc [10]. Adsorption method has been widely used in water treatment research as adsorption is considered to be one of the most promising methods due to low cost and high efficiency [11] and has proved to be an effective and feasible method for controlling the water eutrophication [12]. The development of inexpensive adsorption materials with high adsorption capacities and strong environmental adaptabilities has become an active research area.

Biochar is the residue of the thermochemical transformation of biomass under anaerobic or hypoxia conditions [13]. It has high specific surface area, large porosity and functional groups [14, 15] and has been recognized as a multifunctional environmental material that can be applied to different applications, including
soil fertilization [16], carbon sequestration [17], greenhouse-gas emission reduction [18] and environmental pollution control [19]. Generally, the biochar prepared by pyrolysis at high temperatures (600 °C–700 °C) has a stable layered carbon structure, high aromaticity and low polarity, and good adsorption properties [20, 21]. Pure biochar is generally able to remove cations but the removal capacity for anionic pollutants (such as phosphate) is rather limited [6, 22]. This is due to the negative surface potential of the pure biochar material and shows certain negative electrical properties [23] and so it produces electrostatic repulsion for the negatively charged pollutants. Therefore, Mg, Al, Fe, La, and other metals are often loaded on biochar to improve its ability of phosphate adsorption from the wastewater [24–27]. Mg has abundant reserves in the Earth’s crust, with a high equipotential point of MgO (PZC MgO = 10.8 [28]), and Mg has been proven to be an excellent metal for the modification of biochar [29]. Mg-loaded biochar has shown excellent adsorption performance in the related studies for phosphate removal from water. Kyung-won Jung et al [30] prepared MgCl₂ modified seaweed biochar having phosphorus adsorption capacity of 157.7 mgP g⁻¹. Zhang Ming, et al [31] prepared nanocomposite materials from the beet tailings having the best performance with the Langmuir adsorption capacity of phosphate reaching 835 mgP g⁻¹. Research on the mechanism of phosphate removal by Mg-loaded biochar has also improved and the influencing factors have gradually changed from the single-factor analysis to the currently used, multi-factor analysis. Chen et al [32] used a response surface methodology to study the optimal conditions for removal of phosphate by the Mg-loaded cattle manure biochar in presence of multiple influencing factors. Meanwhile, many studies have found that the solution pH is one of the key factors affecting the adsorption [24]. The adsorption capacity of Mg-loaded biochar was high under low pH conditions but weakened under high pH conditions [33–37]. pH is one of the basic conditions that affect the morphology, migration and transformation of phosphorus in water [38], and the eutrophication water, aquaculture wastewater and surface water are usually alkaline in properties. Improving the adsorption capacity of magnesium-loaded biochar at higher pH has important theoretical significance and application value. In accordance with the previous reports, the phosphorus adsorption capacity of the Ca-containing adsorbents was poor at lower pH but better at higher pH [39, 40]. Therefore, it is proposed to use Mg modification to prepare biochar for improving the phosphorus adsorption capacity, and doping with Ca to prepare Mg/Ca biochar composite materials for maintaining high phosphorus adsorption capacity over a wide range of pH values. However, the traditional calcium modification method of loading Ca²⁺ onto the biochar in the form of chemical reagents can be costly [39]. Considering the production cost of the metal biochar composite materials, there are a large number of waste items in the environment which are good sources of Ca, such as eggshells, oyster shells, scallop shells, crab shells, and lobster shells. In this work eggshells were chosen to be the Ca source for the preparation of low-cost, metal modified biochar.

Flue-cured tobacco is the major economic crop of China, and its planting area and output rank first in the world. The tobacco leaves are harvested leaving behind large amounts of tobacco stalks. According to the reports, the annual output of tobacco stalks in China reach up to 2.43 million tons [41]. The direct burning of tobacco stalks not only wastes resources but also causes adverse effects on the environment. Based on the above analysis, this manuscript starts from the co-pyrolysis of tobacco stem load magnesium and eggshells. The goals of this article are as follows: (1) preparation of Mg-biochar by MgCl₂ solution pretreatments to realize the resource utilization of tobacco stalk; (2) doping with eggshells during MgCl₂ solution pretreatments to improve the adsorption phosphorous capacity of magnesium-loaded biochar at higher pH.

2. Experimental

2.1. Materials
The tobacco stalks were obtained from a tobacco growing area of Dali, Yunnan Province, China. The tobacco variety was K26. The tobacco stalks were washed with deionized water (DI water) to remove the soil from the surface, then the stalks were dried, pulverized and sieved through 60–100 mesh sieve (0.25–0.15 mm). Eggshells were collected from the local food market and washed three times with DI water, dried at 105 °C, and then passed through 100 mesh sieve (0.15 mm) prior to use. Potassium dihydrogen phosphate (KH₂PO₄) was purchased from Fu Chen Chemical Reagent Factory in Tianjin. Magnesium chloride hexahydrate (MgCl₂·6H₂O) was purchased from Sinopharm Chemical Reagent Co., Ltd in Shanghai. The experiments used DI water with a resistivity of 18.2 MΩ·cm.

2.2. Preparation of biochar
2.2.1. Preparation of Mg-loaded biochar
MgCl₂ solutions with different mass concentrations were prepared. The mass ratios of Mg to the tobacco stalk for different solutions were 0:1, 0.12:1, 0.3:1, 0.48:1, respectively. 20 g of the tobacco stalk powder was added to each of the MgCl₂ solutions (180 ml) with different mass concentrations. The solution was stirred (800 rpm) by
magnetic stirrers (IT-09-5, Shanghai Yiheng Scientific Instrument Co., Ltd) at room temperature for 1 h and then dried at 105 °C for 8 h. After drying, the samples were transferred to a porcelain crucible and placed in a programmable muffle furnace (SX2F-2.5-10, Hangzhou Lantian Instrument Co., Ltd) and heated to 700 °C at a rate of 5 °C min⁻¹ and kept at 700 °C for 2 h. After the furnace temperature dropped to a safe temperature, the product was removed and cleaned three times with DI water, filtered through a vacuum filter, dried at 105 °C for 6 h, and then lightly ground through a 60 mesh sieve (0.25 mm) to obtain Mg-loaded tobacco stalk biochar. According to the dosage of Mg, the biochars were denoted as BC, M-C1, M-C2, M-C3.

2.2.2. Preparation of Mg/Ca-loaded metal biochar
Based on the above experimental results, the mass ratio of Mg to tobacco stalk was set as 0.3:1. 20 g of the tobacco stalk powder was added to each of the 180 ml MgCl₂ solutions, and then 5 g, 10 g, 15 g, or 20 g eggshell powders were added to different solutions to create the mixed system. The remaining steps were the same as in section 2.2.1. According to the amount of the doped eggshells, these biochar were denoted as EM-C21, EM-C22, EM-C23, EM-C24.

2.3. Adsorption experiments
0.05 g of the biochar was placed in a 100 ml conical flask containing 30 ml phosphorus solution at different concentrations with KH₂PO₄ and the conical flasks were oscillated (180 rpm) at 25 °C for a given time. Then the suspension was filtered through a 0.45 μm filter and phosphorus was determined by a dual-beam UV-visible spectrophotometer (TU-1901, Beijing General Analysis General Instrument Co. LTD, China) using the molybdenum-antimony anti-spectrophotometric method at 700 nm.

Adsorption kinetics were evaluated by mixing 30 ml of 500 mg P/L solution with different materials in an Erlenmeyer flask and sampling analysis at specified times (5 min, 10 min, 20 min, 30 min, 1 h, 2 h, 3 h, 4 h, 8 h, 12 h, 24 h) for each group. Each group was repeated 3 times. The fitting of the kinetic model was to explain the control steps of the adsorption rate and to evaluate the effect of adsorption. The kinetic data were fitted by pseudo-first-order, pseudo-second-order, and Weber-Morris intra-particle diffusion models (equations (1)–(3)):

\[ q_t = q_e - q_e e^{-k_1 t} \]  \hspace{1cm} (1)

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \]  \hspace{1cm} (2)

\[ q_t = k_{pi} t^{1/2} + C_i \]  \hspace{1cm} (3)

where, \( q_e, q_t (\text{mg} \cdot \text{g}^{-1}) \) are the adsorption capacities of biochar for phosphate at equilibrium and at time \( t \), respectively, \( k_1 (\text{h}^{-1}) \), \( k_2 (\text{mg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}) \) are the adsorption rate constants for the pseudo-first-order and pseudo-second-order, respectively, \( k_{pi} (\text{mg} \cdot \text{g}^{-1} \cdot \text{h}^{-1/2}) \) is the internal diffusivity constant, and \( C_i (\text{mg} \cdot \text{g}^{-1}) \) is a constant of the intra-particle model involving the thickness and the boundary layer, \( i \) is the adsorption stage.

Isothermal adsorption experiments were performed by changing the initial phosphorus concentration (2, 10, 20, 30, 50, 100, 150, 200, 300, 500 mg P/L). The adsorption equilibrium time was 24 h. Each group was repeated for 3 times. The thermodynamic equations of the Langmuir and Freundlich model (equations (4) and (5)) were used to fit the data for further analysis to explain the phosphate adsorption mechanism of biochar and evaluate its adsorption effect.

\[ Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \]  \hspace{1cm} (4)

\[ Q_e = K_F C_e^{1/n} \]  \hspace{1cm} (5)

where, \( K_L (\text{L} \cdot \text{mg}^{-1}) \) is the Langmuir equilibrium constant, \( K_F (\text{mg}^{(1-1/n)} \cdot \text{L}^{1/n} / \text{g}) \) is the Freundlich adsorption equilibrium constant, \( n \) is the constant, \( Q_e \) is the adsorption capacity (mg g⁻¹) at equilibrium, \( Q_m \) is the maximum adsorption capacity (mg g⁻¹), and \( C_e \) is the concentration of phosphate at equilibrium (mg L⁻¹).

The effect of pH on the phosphate adsorption was investigated by placing 30 ml of the 500 mg P/L solution and 0.05 g biochar in a 100 ml Erlenmeyer flask. The solution was adjusted to different pH values (3, 4, 5, 6, 7, 8, 9, 10, 11, 12) by 0.2 M HCl or NaOH solutions. Then the samples were oscillated (180 rpm) at 25 °C for 24 h. Each group was repeated 3 times.

The effect of environmental temperature on phosphate adsorption by EM-C24 was investigated by placing 30 ml of the 2–500 mg P/L solution and 0.05 g EM-C24 in a 100 ml Erlenmeyer flask. Then the samples were oscillated (180 rpm) at 15, 25, and 35 °C for 24 h. Each group was repeated 3 times.

The effect of the amount of EM-C24 addition on phosphate adsorption was investigated by placing 30 ml of the 500 mg P/L solution and 0.025, 0.05, 0.1, 0.15 and 0.2 g EM-C24 in a 100 ml Erlenmeyer flask. Then the samples were oscillated (180 rpm) at 25 °C for 24 h. Each group was repeated 3 times.
The effect of coexisting ions on the phosphate adsorption by EM-C24 was investigated by placing 30 ml solutions containing 0.016 mol l\(^{-1}\) of equal concentrations of the coexisting ions (P was respectively mixed with Cl\(^-\), SO\(_4\)^{2-}, NO\(_3\)^- and CO\(_3\)^{2-}) and 0.05 g EM-C24 in a 100 ml Erlenmeyer flask. Then the samples were oscillated (180 rpm) at 25°C for 24 h. Each group was repeated 3 times.

### 2.4. Characterizations

Thermo Fisher Nicolet IS10, USA was used to record the infrared spectra of the biochar in the 4000–400 cm\(^{-1}\) wave-number range. X-ray diffraction (XRD) patterns in the range of 5°–85° were obtained by Bruker D8 Advance made of Germany. SU8220 produced by Hitachi was used to observe the surface morphology of biochar and analyze the surface element content of biochar. The content of C, H, O, N, and S of the tobacco stalk and the biochar were determined by an elemental analyzer (EA, Elementar Vario EL Cube, Germany). The content of Ca and Mg in the tobacco stalk and biochar were determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Agilent 730, USA). Specific surface area analysis was performed on the material using the automatic physical adsorption apparatus (BET, ASAP2460, USA).

**Table 1. Elemental composition of the main materials used in this study.**

| Material          | C   | H   | O   | Ca  | Mg  | N   |
|-------------------|-----|-----|-----|-----|-----|-----|
| Tobacco stalk     | 38.57 | 6.31 | 42.65 | 0.49  | 0.18  | 2.26 |
| BC                | 72.41 | 1.66 | 18.07 | 4.87  | 1.08  | 1.51 |
| M-C2              | 33.67 | 1.59 | 7.25  | 4.26  | 37.15 | 0.65 |
| EM-C24            | 32.35 | 1.61 | 13.08 | 11.89 | 30.85 | 0.65 |

**Figure 1.** SEM and EDS of BC (a), M-C2 (b), EM-C24 (c).
3. Results and discussion

3.1. Characterization of Biochar, Mg-Biochar, and Ca-Mg-Biochar

3.1.1. Main element composition

As shown in table 1, before pyrolysis, the C content in the tobacco stalk was 38.57%, while the oxygen content was as high as 42.65%. After pyrolysis into biochar, the proportion of O in BC decreased sharply, while the content of C increased. The main reason was that volatilization of water took place during the pyrolysis, hemicellulose was decomposed into CO₂ and CH₄ at 200 °C–250 °C, the pyrolysis of cellulose occurred between 290 and 390 °C and CO₂ was generated, whereas lignin released CO₂ and CH₄ in the temperature range of 200 °C–700 °C [42]. After loading the biochar with Mg, the proportion of Mg in M-C₂ increased significantly along with sharp decrease in the C content of M-C₂ due to the loading of Mg and the increase in the total mass. When the biochar was doped with the eggshell, the C content in EM-C₂ increased slightly and the O content increased because the main component of the eggshell was CaCO₃, which was 12% C and 48% O by mass.

3.1.2. SEM–EDS analysis

The morphologies of BC, M-C₂, and EM-C₂ were analyzed with SEM under different magnification using SU8220, as shown in figure 1. The surface of BC was relatively smooth, and there were some folds on the local
surface which were mainly caused by the morphology of the biomass itself. The surface of the M-C2 was noticeably rough, with enhanced graininess. The porous structure was significantly increased compared to BC while some granular and flake-like substances appeared on the surface, indicating that the active Mg component was successfully loaded onto the surface of the biochar. The surface roughness of EM-C24 was further increased, with even further granulation and obvious macroporous structure appeared. Some substances with lamellar were also seen in the SEM image. Through energy spectrum analysis of the surface, it was found that by adding chemical agents rapid and large loading of Mg can be achieved on the biochar while mixing the tobacco stalk and Mg with eggshells via pyrolysis can achieve Ca loading on the biochar. EDS results show that the addition of eggshells will promote the formation of macropores in biochar, which is more conducive to the loading of Mg, and the relative content of Mg increases.

3.1.3. FTIR and XRD analysis
To investigate the effect of the loaded metal on the functional groups of the materials, Fourier transform infrared spectroscopy analysis was performed on BC, M-C2, and EM-C24. As shown in figure 2, in BC, the absorption peak of 1440 cm\(^{-1}\) was mainly attributed to the aliphatic C-O stretching vibrations [43]. In M-C2, a wide absorption peak appeared at 1583 cm\(^{-1}\), which may be due to the bending vibrations of C=O [44, 45], and the sharp absorption peak at 459 cm\(^{-1}\) mainly was due to the stretching vibrations of Mg-O [34, 46]. In EM-C24, there was absorption peak around 3700 cm\(^{-1}\) assigned to the Mg-OH bond [47]. The absorption bands at 1420 cm\(^{-1}\) and 878 cm\(^{-1}\) were attributed to the vibration of CO\(_3^{2-}\) molecules [48].

An x-ray diffractometer was used to obtain wide-angle diffraction for BC, M-C2, EM-C24 in the range of 5°–85° and analyze the phase composition. As shown in figure 3, the broad diffraction peak of the biochar at about 22° was mainly caused by the graphitization and aromatization of the organic matter in the biomass at high temperature [49]. The diffraction peak at about 29.5° was mainly caused by the diffraction of the (104) crystal plane from the CaCO\(_3\) phase (PDF # 72-1214). In M-C2, the diffraction peaks were mainly originated from MgO (PDF # 75-0447), which also indicated that the MgO on the surface of the biochar was highly crystalline. This was because MgCl\(_2\) [17] would decompose and transform into MgO [31, 34]. In EM-C24, the phases mainly corresponded to MgO and CaCO\(_3\), which may be caused by the incomplete decomposition of CaCO\(_3\) at 700 °C [39].

3.1.4. BET analysis
The BET analysis results are shown in table 2. The BET surface area of biochar decreased by 66.27% and 53.21% after the addition of metal Mg and Mg/Ca. Mg-loaded blocked the microporous structure of biochar, resulting in a decrease in BET surface area.

| Material (m\(^2\) g\(^{-1}\)) | BET surface area | Micropore area | External surface area | Adsorption average pore width (nm) |
|-------------------------------|------------------|----------------|-----------------------|-----------------------------------|
| BC                            | 498.14           | 437.21         | 60.94                 | 5.85                              |
| M-C2                          | 168.81           | 128.29         | 40.52                 | 9.31                              |
| EM-C24                        | 233.69           | 56.16          | 177.53                | 5.64                              |

Figure 4. Pseudo-first-order and pseudo-second-order fitting results for phosphate adsorption on BC, M-C1, M-C2, M-C3 (left), and EM-C24 (right). (Dosage: 0.05 g; Temperature: 25 °C; Time: 24 h; Initial phosphorus concentration: 500 mg P/L).
in decreased micropore area and external surface area. After the addition of egg shells, the micropore area of EM-C24 continued to decrease, while the external surface area increased. It is related to the formation of macroporous structure on the surface, and consistent with SEM result.

3.2. Adsorption experiments

3.2.1. Sorption kinetics

As shown in figure 4, the materials M-C1, M-C2, M-C3, and EMC-24 adsorbed phosphate at a faster rate in the initial phase up to 4 h. Subsequently the adsorption rate gradually slowed down from 4 to 12 h with subsequent equilibrium at around 12 h. In reversal to the other materials, the original biochar (BC) showed release of phosphorus into the aqueous solution which was previously present on the tobacco stalk. Without chemical modification, BC has a very high negative Zeta potential and due to the electrostatic repulsion phosphate cannot

| Material | $K_1$ (h$^{-1}$) | $q_e$ (mg g$^{-1}$) | $R^2$ | $K_2$ (g mg$^{-1}$ h$^{-1}$) | $q_e$ (mg g$^{-1}$) | $R^2$ |
|----------|------------------|---------------------|-------|-----------------------------|---------------------|-------|
| M-C1     | 0.46             | 100.35              | 0.926 | 0.0195                      | 98.19               | 0.934 |
| M-C2     | 0.36             | 196.27              | 0.963 | 0.0039                      | 209.32              | 0.976 |
| M-C3     | 0.72             | 234.99              | 0.95  | 0.0065                      | 245.11              | 0.980 |
| EM-C24   | 0.46             | 239.58              | 0.965 | 0.0019                      | 271.82              | 0.986 |

Figure 5. W-M fitting results for phosphate adsorption on BC, M-C1, M-C2, M-C3 (left), and EM-C24 (right). (Dosage: 0.05 g; Temperature: 25 °C; Time: 24 h; Initial phosphorus concentration: 500 mg P/L).

Figure 6. Adsorption isotherms of phosphate on M-C1, M-C2, M-C3 (left), and EM-C24 (right). (Dosage: 0.05 g; Temperature: 25 °C; Time: 24 h; Initial phosphorus concentration: 500 mg P/L).
be absorbed [50]. Rather, there will be release of phosphorous from BC due to the acidity of the phosphorus solution along with the osmotic pressure of biochar and solution during the adsorption. The fitting parameters in table 3 showed that the R² values of the pseudo-second-order kinetic model were significantly higher than that of the pseudo-first-order kinetic model, indicating that the adsorption rate of phosphate on four kinds of biochar was controlled by a chemical adsorption mechanism, which involved the sharing or exchange of electrons between the biochar and phosphate and the formation of new compounds [51]. Chemical adsorption is mainly the precipitation reaction of Mg and Ca with phosphate on biochar. EM-C24 biochar will undergo the following reaction to immobilize phosphorus [50]: Mg²⁺ + 2H₂PO₄⁻ → Mg(H₂PO₄)₂, Mg(H₂PO₄)₂ → MgHPO₄ + H₃PO₄, Mg²⁺ + HPO₄²⁻ → MgHPO₄, CaCO₃ + H₂PO₄⁻ → CaHPO₄ + CO₃²⁻, CaCO₃ + 2H₂PO₄⁻ → Ca(H₂PO₄)₂ + CO₃²⁻.

It was observed from figure 5 that the rate of increase for qt of M-C1, M-C2, M-C3, and EM-C24 was relatively fast in the first 4 h which slowed down after 4 h. The fitting results were not a straight line across the origin, which indicated that the intra-particle diffusion was not the controlling step of the adsorption process and the adsorption behavior of the intra-particle diffusion gradually decreased with the adsorption process. The fitting parameters of Weber–Morris intra-particle diffusion models are shown in table 4. The kwi is proportional to the adsorption rate. Table 4 showed that with the increasing amount of Mg and the addition of eggshell, kwi tended to increase. The increase in kwi in different materials should be resulted from the amount of active metals in the material increases. Meanwhile, the kwi was greater than kwp, which was due to the reduction of P concentration in the solution by adsorption, resulting in a smaller driving force [52]. Along the adsorption process, the behavior of the intra-particle diffusion gradually decreased. Fast adsorption rate at the initial stage of the process was due to the high P concentration and the abundance of active sites on the biochar. Decreasing number of active sites led to gradual slowing down of the adsorption rate at the second stage and meanwhile, intra-particle diffusion gradually became the adsorption control step [53, 54]. Cn is a constant of the intra-particle model involving the thickness and the boundary layer. The boundary layer is a fluid adsorption retention layer formed on the surface of porous media during adsorption. Boundary layer fluid does not participate easily in the flow and the generation of boundary layer reduces the permeability of solution, which has a great impact on the seepage. If Cn is zero, then the rate of adsorption is controlled by the intra-particle diffusion for the entire adsorption process [55], and larger the Cn, the greater the influence of boundary layer on the diffusion adsorption in the particles. It can be seen from table 4 that the C value increases (C₂ > C₁) with the progress of adsorption, which is due to the gradual saturation of diffusion adsorption within the particles leading to enhanced surface adsorption behavior, increased boundary layer thickness, and hindered internal diffusion at the same time.

3.2.2. Sorption isotherms

The results of the adsorption isotherms for phosphate on M-C1, M-C2, M-C3, and EM-C24 are shown in figure 6 and table 5. As evident from figure 6, there was rapid increase of the adsorption capacity and equilibrium phosphorus adsorption for the four biochar samples with increasing initial concentration. The fitting parameters in table 5 show that the R² values of the Langmuir model were significantly higher than that of the Freundlich model, which indicated that the adsorption process of phosphate was a monolayer chemical binding.
adsorption taking place on the surface of the adsorbent. It indirectly showed that the material was better suited for phosphate concentrations in the medium to high range. Although the R² values from the fitting results of the Freundlich model were low, it showed that the amount of the metal added was proportional to the amount of adsorption per unit concentration of the biochar, and it was easy to adsorb phosphate by the biochar after metal modification. The maximum adsorption capacity obtained by isothermal model fitting is also in the category of higher adsorption capacity compared with similar studies, shown in Table 6. Mg-modified biochar has a large adsorption capacity. In contrast, the adsorption capacity of this study was upstream.

3.2.3. The effect of solution pH on phosphate adsorption

Figure 7 shows the phosphate adsorption capacity of M-C2 and Mg/Ca biochar under different initial pH of the solution. The results indicated that the adsorption of phosphate by Mg-loaded tobacco stalk biochar is limited under environmental pH condition. The results showed that under the acidic conditions, M-C2 had good adsorption capacity for phosphate with its adsorption capacity in the pH range of 3–5 being 235.8–237.8 mg P g⁻¹. For neutral solution (pH 7), the adsorption capacity decreased by 12 %. However, changing the solution from acidic to alkaline led to sharp decrease in the phosphate adsorption capacity of M-C2. The adsorption capacity of M-C2 decreased by 31.69 % at pH = 8 and 43.15 % at pH = 12 in comparison to the maximum value. This phenomenon was mainly caused by two reasons, the first one was the dissociation constants of

| Material                                      | Maximum Adsorption capacity (mg P g⁻¹) | year  |
|-----------------------------------------------|----------------------------------------|-------|
| tobacco stalk (M-C2)                          | 206.68                                 | This study |
| tobacco stalk (EM-C24)                        | 210.66                                 | This study |
| Peanut shells and sugarcane bagasse           | 129.79                                 | [56]  |
| coffee waste                                  | 56                                     | [57]  |
| cypress sawdust                               | 66.7                                   | [58]  |
| carrot residues                               | 138                                    | [50]  |
| Anaerobic digestion residue                   | 149.25                                 | [35]  |
| Thalia dealbata                               | 46.56                                  | [47]  |
| Sugarcane harvest residue (leafy trash)       | 398                                    | [34]  |
| hickory wood chips and bamboo                 | 119.6                                  | [29]  |
H$_3$PO$_4$, H$_2$PO$_4^-$, and HPO$_4^{2-}$, which are 2.12, 7.21, and 12.31, respectively. In the pH range of 2.12–7.21, phosphate is present mainly as H$_2$PO$_4^-$, whereas in the range of 7.21–12.31 the form is mainly HPO$_4^{2-}$. Thus, with increasing solution pH, there will be gradual change of H$_2$PO$_4^-$ to HPO$_4^{2-}$. HPO$_4^{2-}$ has higher adsorption energy compared to H$_2$PO$_4^-$ and is more difficult to be adsorbed. Thus, with increasing pH value, the adsorption capacity will decrease [34, 59]. The second is that the increase of the pH value of the solution will cause changes in the degree of protonation and deprotonation of the material itself, which will affect the electrostatic adsorption. Third, the OH$^-$ in the solution will compete with the phosphate ion for active adsorption sites under high pH conditions.

However, this problem was solved by introducing Ca from the eggshells. The Ca loading of the magnesium-bearing biochar was realized by co-pyrolysis of the tobacco stalk and eggshells with the results being shown in figure 7. After addition of the eggshells, there was significant improvement of the adsorption capacity of the biochar under alkaline conditions. The adsorption capacity under alkaline conditions for the EM-C biochar increased by more than 80% compared to the M-C2. This was due to the capability of the Ca-based adsorbents to adsorb phosphate under high pH conditions. K$_{sp}$ is the solubility product constant, which represents the precipitation dissolution equilibrium of insoluble electrolyte [60]. The K$_{sp}$ of CaCO$_3$, Ca$_3$(PO$_4$)$_2$, and hydroxy calcium phosphate (HAP) are 2.9 $\times$ 10$^{-9}$, 2.0 $\times$ 10$^{-29}$, and 26.8 $\times$ 10$^{-39}$, respectively. Generally, insoluble electrolytes will convert to substances having smaller K$_{sp}$. The addition of eggshells into the biochar introduce CaCO$_3$ which after encountering phosphate is transformed to Ca$_3$(PO$_4$)$_2$ and HAP due to the differences in K$_{sp}$ and thereby achieving phosphorus fixation. Meanwhile, with the increasing pH, K$_{sp}$ of the insoluble electrolyte would also decrease and the decrease of solubility would also increase the adsorption capacity to some extent.

3.2.4. The effect of environment temperature on phosphate adsorption by EM-C24

Figure 8 shows the effect of different temperatures on the adsorption of EM–C24. It can be seen from the figure that the influence trend of temperature is consistent between different initial concentrations. The adsorption capacity and phosphorus removal rate of EM–C24 increase with the increase of initial phosphorus concentration. At different temperatures, this trend has not changed. This trend has not changed at different temperatures. This outcome could be explained by the difference in concentration resulting in insignificant temperature effects. The dynamic gradient between the surface of the biochar and the solution resulted in a large diffusion rate, which promotes continuous phosphorus migrate to the surface of biochar [58], weakening or even offsetting the effect of temperature.

However, the effect of temperature on EM–C24 is different under the same initial phosphorus concentration. The adsorption capacity and removal rate of EM–C24 at the same concentration decreased with increasing temperature for the initial phosphorus concentration was 2–30 mg P/L. The increase in ambient temperature results in an increase and then a decrease in adsorption at 100–500 mg l$^{-1}$. The increase in temperature leads to a decline in the adsorption effect, indicating that the adsorption system is mainly an
exothermic process [61]. The ambient temperature should not be too high or too low at 100–500 mg P/L and 25 °C is the optimal temperature for EM-C24 adsorption. For high concentration, there is a large amount of P, and the increase of temperature intensifies the thermal movement of molecules and increases the probability of collision between phosphate and the active sites of EM-C24, thus improving the adsorption effect. However, temperature changes disrupt thermal and chemical balance, causing dissolution/precipitation reactions to move [62]. Excessive high temperature is not conducive to exothermic adsorption and will cause the precipitation dissolution equilibrium reaction related to chemical adsorption to move towards the dissolution direction and thus reducing the adsorption effect.

3.2.5. The effect of EM-C24 addition amount on phosphate adsorption

Figure 9 shows the effect of addition amount of EM-C24 on the adsorption phosphorus from 30 ml of solution containing 500 mg P/L. When the addition amount was increased from 0.83 g l$^{-1}$ (0.025 g) to 3.33 g l$^{-1}$ (0.1 g),...
the adsorption removal rate increased from 23.05 % to 98.10 %. Continuing increase of the addition amount led to gradual stabilization of the removal rate. At the beginning, the amount of EM-C24 was low, the adsorption sites and the amount of Ca and Mg were low, resulting in a low adsorption removal rate. When the dosage was increased to a certain amount, the adsorption sites provided by the adsorbent along with the amount of Ca and Mg is sufficient to adsorb the phosphorus in the solution and thus increasing and stabilizing the adsorption rate.

3.2.6. The effect of coexisting ions on phosphate adsorption by EM-C24

The presence of co-existing anions would compete with phosphorus for adsorption sites and thus affect the adsorption behavior of phosphorous on biochar. Figure 10 shows the phosphorus removal rate of EM-C24 in presence of co-existing anions Cl\(^-\), SO\(_4^{2-}\), NO\(_3^-\), and CO\(_3^{2-}\). The presence of Cl\(^-\) and CO\(_3^{2-}\) had no effect on the removal efficiency of phosphate for EM-C24. NO\(_3^-\) was found to promote the removal of phosphate by EM-C24. However, the presence of SO\(_4^{2-}\) leads to the reduction of the phosphate removal efficiency of EM-C24. For the co-existence of SO\(_4^{2-}\) and P, the phosphate removal efficiency of EM-C24 decreased from 71.86% to 23.34%. This can be interpreted as due to the similar ionic radius of SO\(_4^{2-}\) (0.230 nm) and H\(_3\)PO\(_4\) (0.238 nm), SO\(_4^{2-}\) could actively compete for the charged position on the surface of the adsorbent, preventing Ca and phosphate from forming amorphous calcium phosphate together [34]. However, in the presence of Cl\(^-\), NO\(_3^-\) and CO\(_3^{2-}\) together, the influence of SO\(_4^{2-}\) was weakened, and the removal rate decreased from 71.86% to only 55.92%. This may be due to the fact that Cl\(^-\), NO\(_3^-\) and CO\(_3^{2-}\) not only compete for the positive sites with SO\(_4^{2-}\), but also lead to the conversion of CaSO\(_4\) to CaCO\(_3\) and Ca\(_3\)(PO\(_4\))\(_2\) due to the difference of \(K_{sp}(K_{spCaSO_4} = 9.1 \times 10^{-7})\).

4. Conclusions

(1) In this study, MgCl\(_2\) pretreated biomass was used to prepare a Mg-loaded tobacco stalk biochar composite material. The adsorption capacity of the material for phosphate increased with the increase of Mg content. The adsorption capacity ranged from 110.62 mg P g\(^{-1}\) to 272.37 mg P g\(^{-1}\) which was significant improvement over pure tobacco stalk biochar with no adsorption capacity.

(2) The Mg/Ca tobacco stalk metal biochar composite material was prepared by MgCl\(_2\) pretreatment and eggshell addition, which successfully realized the metal loading under the condition of co-pyrolysis and solved the problem of declining adsorption capacity of the Mg-modified biochar under high pH conditions. The Mg/Ca biochar composite material exhibited a high adsorption capacity for phosphorus under high pH conditions. The test results provide a reference for the preparation of low-cost, metal biochar composite materials, and also provide new ideas for the disposal and treatment of waste sources with high Ca content. At the same time, it provides a reference for exploring the mixed treatment of biomass.

(3) Biochar has not been used in actual wastewater dephosphorization. Biochar can improve the soil, and Ca, Mg, and P are beneficial to crop growth. However, after phosphate adsorption, this material has not been applied in actual soil which should be discussed in future research.

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