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Rapid Separation and Efficient Removal of Cd Based on Enhancing Surface Precipitation by Carbonate-Modified Biochar

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ABSTRACT: The high buoyancy of biochar makes its application difficult in Cd removal. In this paper, the content of minerals was increased by modifying carbonate on the biochar surface using the vacuum impregnation method. Enhancing surface precipitation between minerals and Cd introduced a correspondingly great number of Cd precipitates on the biochar surface, leading to the rapid precipitation filtration and separation of buoyant biochar. The physical and chemical properties of carbonate-modified biochar and the adsorption mechanism of Cd were comprehensively studied by jar tests, scanning electron microscopy−energy-dispersive X-ray spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. The results showed that the adsorption of Cd by carbonate-modified biochar was controlled by multiple mechanisms, including surface precipitation, surface complexation, and Cd−π interaction. Surface precipitation dominated the removal of Cd. The contributions of Cd removal mechanisms indicated that the contribution proportions of minerals increased from 89.73 to 97.9% when the pyrolysis temperature increased from 300 to 600 °C, while the contribution proportions of Cd−π binding decreased from 9.99 to 2.08%. Meanwhile, oxygen functional groups have only a marginal effect on Cd adsorption. Besides, the results revealed that the higher surface hydrophobicity and the lower polarity were conducive to biochar separation from water. The Cd removal method can provide efficient adsorption and rapid separation, making it possible to use biochar in water treatment.
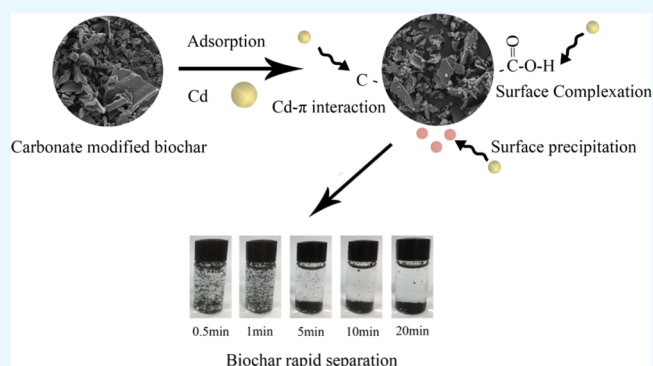
1. INTRODUCTION

Cadmium (Cd) is a kind of common toxic heavy metal element, which is a great threat to environment and human beings.[1−3] Long-term exposure to Cd-polluted water can lead to osteoporosis and softening, with the obvious damage to the kidneys.[4] Therefore, Cd removal from contaminated water is of great concern.[5−7] Many treatment techniques such as membrane filtration and separation, chemical precipitation, ion exchange, and adsorption have been developed for removing Cd in contaminated water.[8] Compared with the other treatment, the adsorption method is regarded as a more effective method for removing Cd because of its low cost, high efficiency, and simplified operation.[9,10]

Biochar as a potential substitute for activated carbon can effectively remove Cd due to its unique characteristics such as low cost, diversified structure, and rich surface functional groups.[11] For instance, biochar prepared from the digested residue of corn straw silage was used to remove Cd from water.[12] Hydrochars and pyrochars derived from animal manure were applied to adsorb Cd in an aqueous solution.[13] Biochar derived from different raw biomass has different adsorption capacities for Cd, but the adsorption effect is

mostly low.[14−17] It has been reported that biochar loaded with metal oxides/hydroxides, involving CaO, MgO/Mg(OH)$_2$, and Al$_2$O$_3$, can significantly improve the adsorption capacity of Cd.[18] Therefore, biochar has attracted wide attention as a potential carrier material. Biochar can overcome adverse effects such as secondary pollution brought by chemical methods.

Therefore, impregnating biomass feedstocks with CaCl$_2$ and Na$_2$CO$_3$ solutions is conducive to form minerals such as CaO and CaCO$_3$ on the biochar surface after pyrolysis.[19] Besides, CaCl$_2$ can form many mesopores to increase the porosity of biochar, thus increasing the specific surface area of biochar.[20] *Phytolacca acinosa* Roxb., as biomass feedstock, has the advantages of large biomass, a fluffy structure, and can be easily obtained in nature. In addition, carbonate ions loaded on the surface of biochar can be released continuously, forming

microprecipitates with Cd on the surface. This method could achieve rapid separation using biochar as an adsorbent without additional operation after adsorbing Cd. At the same time, it avoided the secondary pollution caused by the large use of chemical reagents. This research aims to obtain an efficient and simple adsorbent that is combined with carbonate on the surface of *P. acinosa* Roxb. to remove Cd from aqueous solutions. The objects of this study are: (1) to prepare mineral-loaded biochar for rapid removal of Cd; (2) to characterize biochar by jar tests, scanning electron microscopy−energy-dispersive X-ray spectroscopy (SEM−EDX), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS); and (3) to elucidate the mechanism of Cd removal by modified biochar.

2. RESULTS AND DISCUSSION

2.1. Characterization of Biochars at Different Temperatures.
The physical and chemical properties of biochar at different temperatures are shown in Table S1. With the increase of pyrolysis temperature, the ash content increased significantly, while the specific surface area and total pore volume decreased. This could be because minerals influence biochar characteristics. The molar ratio of (O + N)/C, O/C, and H/C correlates well with biochar polarity and aromaticity.[21,22] The lower H/C ratio illustrates higher carbonization with higher aromaticity.[23] As the pyrolysis temperature increases, the H/C ratio of biochar decreases, manifesting that the aromaticity of biochar increases. Hence, the higher surface hydrophobicity and the lower polarity can be achieved at higher pyrolysis temperatures. To remove impurities on the biomass surface, raw materials were treated using HCl for several days. The amount of minerals on the biochar surface is increased by adding carbonate as minerals to raw materials using the vacuum impregnation method. The dried biomass was treated using $CaCl_2$ before modifying Na_2CO_3, which would be a benefit for biochar formation.[24] Furthermore, the surface of biochar is loaded with carbonate, and the generated $CaCO_3$ makes biochar separation more effective after Cd adsorption.

The morphology and surface properties of biochar were characterized using SEM and SEM-mapping (Figure S1). The SEM-map exhibited that there were Na_2CO_3 crystals on the biochar surface, which are conducive to the precipitation between the metal cation and Na_2CO_3. This was further confirmed that the crystal is Na_2CO_3 by EDX analyses (Figure S2). The X-ray diffraction spectra showed the existence of the crystals NaCl, Na_2CO_3, and $CaCO_3$ on the biochar surface (Figure 1), which proved that the mineral composition was successfully loaded onto the surface of the biochar. In addition, XRD demonstrated that the $CaCO_3$ still existed after adsorption, indicating that calcium may not participate in the chemical adsorption. The result is consistent with SEM-mapping analyses (Figure S1). Minerals such as $CaCO_3$ and Na_2CO_3 can be formed on biochar surfaces.

2.2. Cd Removal Using Biochars.
As shown in Figure S3, BioC400, BioC500, and BioC600 can be flocculated in 1 min. Most of the biochars were separated from the water after 20 min. Due to the increase of surface minerals of biochar, surface precipitation occurred between carbonate and Cd. This phenomenon reflected a large number of Cd precipitates on biochar surfaces, giving rise to biochar rapid precipitation and separation. Meanwhile, biochars at high pyrolysis temperatures have higher carbonization and a lower polarity, which
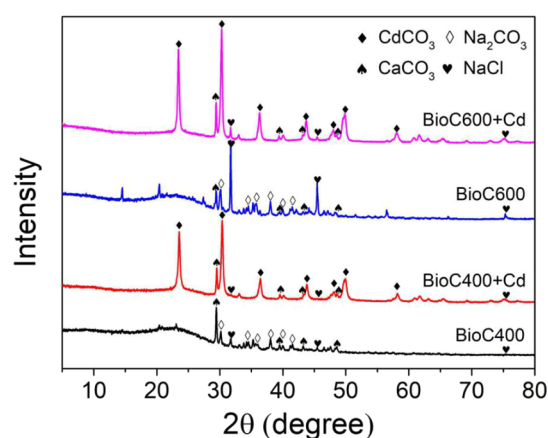

Figure 1. X-ray diffraction spectra of BioC400 and BioC600.

accelerates biochar flocculation and separation from water. However, BioC300 cannot be flocculated quickly within 20 min. The reason can be explained as the prepared biochar at lower pyrolysis temperature has more surface functional groups and higher hydrophilicity, engendering slower separation.

2.3. Mechanisms of Cd Removal Using Biochars.
The adsorption of Cd by carbonate-modified biochar was controlled by multiple mechanisms. The Cd removal efficiency at different adsorbent dosages and various pHs was studied (Figure 2).

The pH of biochars increases from 7.31 to 9.78 when pyrolysis temperature increases from 300 to 600 °C (Table S1). It reflects that the increase of pyrolysis temperature is beneficial to the mineralization of Na_2CO_3, inducing a pH change. The ΔpH method was used to identify pH_{zpc} (Figure S4). pH_{zpc} increases from 8.19 to 9.16 as pyrolysis temperature increases, suggesting that biochars carry the positive charge under acidic conditions. Biochars have lower removal efficiency under lower pHs such as pH 3. The removal efficiencies of BioC600 have no significant differences at different pHs except pH 3. BioC300 has a significantly lower removal efficiency than other biochars. When the solution pH > pH_{zpc}, biochar could absorb metal cations because of the deprotonation of the adsorbent-hydrated surface. Biochar possesses positive charge owing to the characteristic of pH_{zpc} under each pH. Electrostatic repulsion between the positive charge cadmium ion and biochar is unfavorable for heavy metal removal. Furthermore, the protonation of the surface functional groups including −COOH and −OH occurs easily under acidic conditions. A higher dosage of the adsorbent is beneficial for Cd removal. Besides, biochar by preparing at a higher pyrolysis temperature is more conducive to Cd removal. This suggests that the characteristics of biochar decided by pyrolysis temperature, including hydrophobicity and minerals content, have a greater impact on adsorption and separation.

The SEM images (Figure 3) illustrate the different morphological characteristics of biochar before and after adsorption. Compared (a) with (b), a lot of precipitates on the biochar surface after adsorption can be observed. SEM-mapping analyses proved that $CdCO_3$ is attached to the biochar surface (Figure S5). Na element was still observed on the biochar surface after adsorption. Residual Na element mapping is consistent with Cd element mapping, implying that the precipitation between Cd and Na_2CO_3 occurs on the surface of biochar. EDX analyses further exhibited that
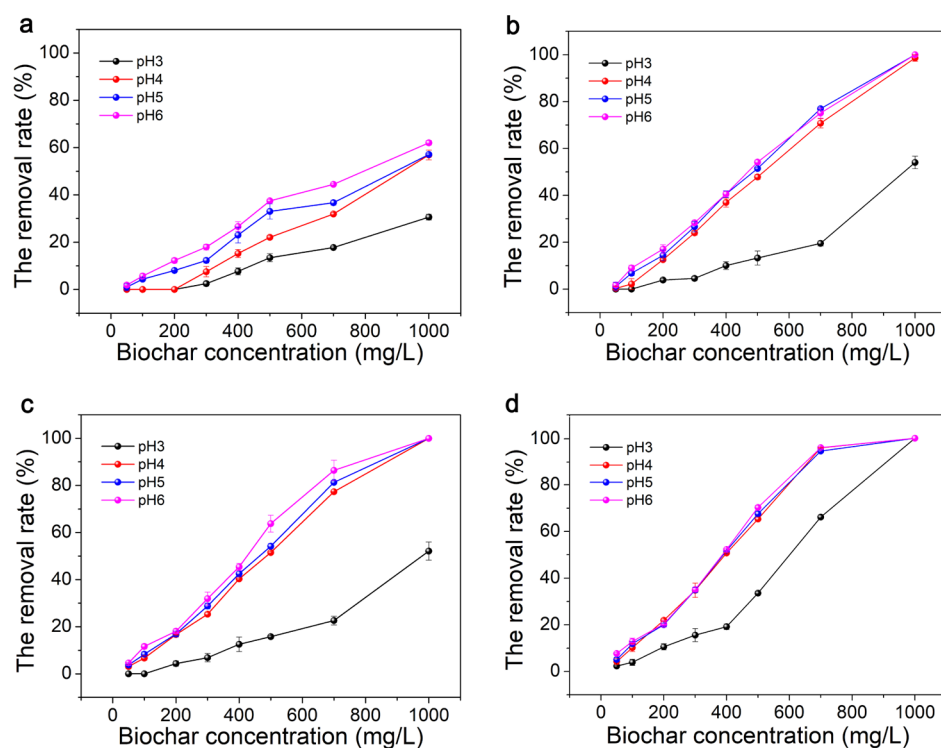
Figure 2. Cd removal efficiency at different dosages and various pHs using BioC300 (a), BioC400 (b), BioC500 (c), and BioC600 (d), (Cd: 100 mg·L^{-1}).
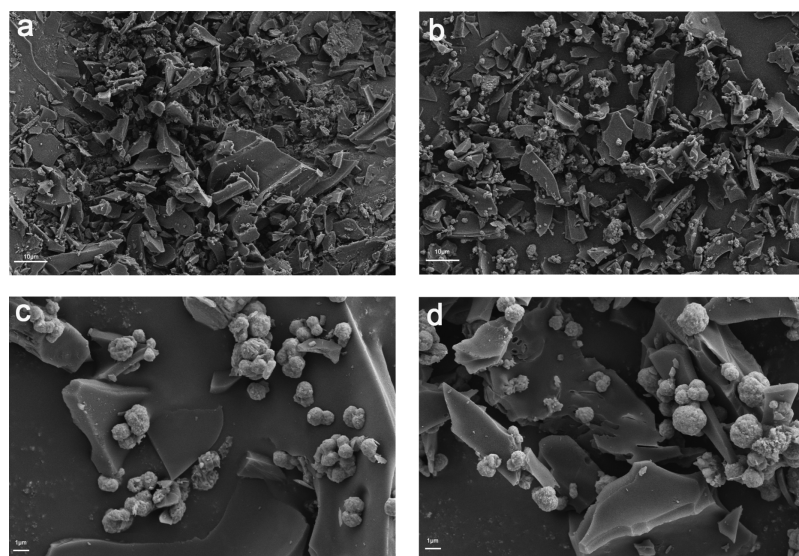

Figure 3. SEM images of BioC500 before Cd adsorption (a) and after Cd adsorption (b−d).

precipitates contain C, O, and Cd elements (Figure S6). There are a lot of CdCO$_3$ precipitates on the surface of biochar, speeding up the depositional rate of biochar by gravity. Therefore, biochars are separated from water by gravity within 20 min. Moreover, there were marked differences in the XRD patterns of BioC400 and BioC600 before and after adsorbing Cd, which are shown in Figure 1. After adsorption of Cd, Na$_2$CO$_3$ and NaCl on the biochar surface are decreased, while CdCO$_3$ is formed on the biochar surface. This result implies that surface precipitation is the main adsorption mechanism.

FTIR analysis further verified the changes in the surface functional groups of biochar. Figure 4 represents the characteristic peaks of biochar. The peaks at 3340 cm^{-1} are attributed to O−H stretching vibrations.[25] The peaks at 3340 cm^{-1} weakened after Cd adsorption using BioC300 or BioC400, indicating that hydroxyl functional groups on the biochar surface were involved in Cd removal. The bands at 1569 and 1694 cm^{-1} result from the C=O stretching vibrations of the −COOH group and ester C=O, respectively. After Cd adsorption, the C=O stretching vibrations at 1569 and 1694 cm^{-1} are obscured, indicating that the carboxylate anion involves the interaction with Cd. The peaks appearing at 880 and 750 cm^{-1} correspond to aromatic CH out-of-plane deformation vibrations.[26] The bands at 2925, 2865, and 1430 cm^{-1} are due to −CH$_2$ stretching vibrations.[27−29] The significant changes in the spectral features at 3340, 1694, and
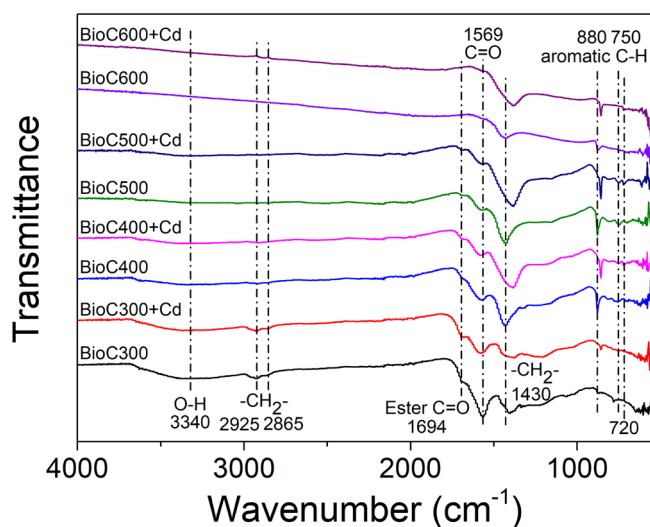
Figure 4. FTIR spectra of biochars before and after adsorption of Cd at different temperatures.

1569 cm^{-1} are observed on different biochar surfaces, illustrating that oxygen functional groups, such as $-OH$ and $-COOH$, decrease with increasing temperature. Oxygen functional groups play an important role in the adsorption of Cd by low-temperature biochar (such as BioC300). The peaks appearing at 720 cm^{-1} are likely due to the formation of Cd precipitates. The shift of 880 to 859 cm^{-1} may be ascribed to the interaction between the aromatic carbon of biochar as the π-donor and Cd^{2+} as the π-acceptor.

The XPS C 1s peaks of BioC300 and BioC600 before and after adsorbing Cd are shown in Figure S7. The binding energies of 283.86, 285.35, 287.73, and 289.94 eV were assigned to $C-C$, $C-O$, $C=O$, and $\pi-\pi^*$ transition for BioC300, respectively.[10,30−32] The slight shift of binding energies between BioC300 and BioC600 provides evidence for the influence of surface chemical composition on Cd adsorption. As shown in Table S2, C 1s relative atomic percentage indicates that the contents of $C-O$ and $C=O$ decrease with increasing pyrolysis temperature. The binding energies of $C-O$ and $C=O$ change before and after adsorbing Cd, indicating that the adsorption involves hydroxyl and carboxylic groups (Figure S7).[33] The deconvolution of the Cd 3d$_{5/2}$ and Cd 3d$_{3/2}$ spectra indicates that Cd bonding includes Cd^{2+} and $Cd-O$ states on the biochar surface (Figure S8).[34,35] As a π-acceptor, Cd^{2+} can interact with the aromatic carbon of biochar, which acted as an electron-rich aromatic oxygen donor. The $Cd-O$ bonding results from the interaction of Cd with oxygen-containing functional groups.

2.4. Contribution of Cd Removal Mechanisms Using Biochars. To study the contribution of different adsorption mechanisms, the untreated biochars and demineralized biochars were used to adsorb Cd. The contributions of the precipitation with minerals (Q_m), the oxygen functional group (Q_f), and $Cd-\pi$ binding (Q_π) are revealed in Figure 5.

It can be seen from Figure 5 that Q_f is a small fraction. As the temperature increases, the contribution ratio of oxygen functional groups decreases significantly. The Q_f and Q_f/Q_t values of BioC300 are 0.108 mg g^{-1} and 0.27%, while the Q_f and Q_f/Q_t values of BioC600 are 0.036 mg·g^{-1} and 0.023%, which indicate the oxygen functional group has only a marginal effect on the adsorption of Cd by biochar. Meanwhile, as compared with the Q_π values of BioC300 and BioC500 of
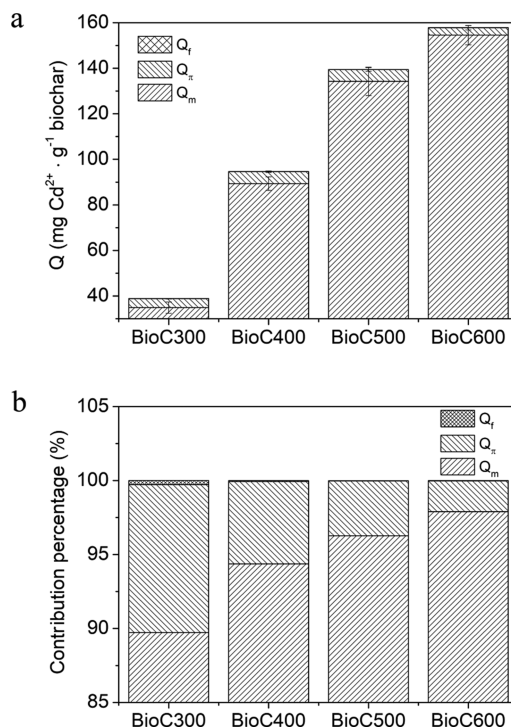

Figure 5. (a) Contribution of Cd removal using biochars and (b) contribution percentage of different mechanisms.

3.892 and 5.178 mg g^{-1}, the Q_π value of BioC600 was reduced to 3.284 mg·g^{-1}. The aromaticity of biochar increases with increasing temperature, implying that the contribution of $Cd-\pi$ binding increases, but a significant amount of minerals weakens the $Cd-\pi$ binding effect. However, compared to the contribution of the oxygen functional group and $Cd-\pi$ binding, the contribution of Q_m increases from 34.93 mg·g^{-1} for BioC300 to 154.54 mg·g^{-1} for BioC600. When the pyrolysis temperature increases from 300 to 600 °C, the contribution proportions of $Cd-\pi$ binding decrease from 9.99 to 2.08%, while the contribution proportions of minerals increase from 89.73 to 97.9%. This suggests that minerals play dominant roles in Cd adsorption. When pyrolysis temperature increases, modifying carbonate is conducive for mineral formation. The surface precipitation between minerals and Cd plays a decisive role in Cd adsorption. There is a large number of Cd precipitates on the surface of biochar, which make the biochar with buoyancy precipitate and separate quickly. Besides, as listed in Table 1, compared with other biochars, the prepared biochar has better Cd adsorption capacity and a shorter adsorption time.

3. MATERIALS AND METHODS

3.1. Materials. *P. acinosa* Roxb. was collected from Xiangtan City as the raw material for biochar preparation and was dried at 80 °C for several hours. Analytical grade reagents including $CdCl_2 \cdot 5/2H_2O$, HCl, $CaCl_2$, and Na_2CO_3 were purchased from the Sinopharm Chemical Reagent Co., Ltd.

3.2. Biochar Preparation. The dried *P. acinosa* Roxb. was dipped into a 2 M hydrochloric acid (HCl) solution for several days to remove impurities. The biomass was washed using distilled water until the pH value of the filtrate remains unchanged. The dried biomass was treated using 0.1 M $CaCl_2$ by the vacuum impregnation method for 4 h. The biomass was

Table 1. Cd Adsorption by Biochars of Different Biomass Feedstocks

raw materials	synthesis method	Cd maximum adsorption time and adsorption capacity	references
corn stalks and graphene	pyrolysis, 350 °C	120 min, 60−80%	Li et al.[36]
pinecone	pyrolysis, 350−400 °C	1−60 min, 87%	Teng et al.[37]
chicken feathers and KOH	pyrolysis, 450 °C	12 h, 80%	Chen et al.[38]
blue algae	pyrolysis, 400−600 °C	120 min, 81.5%	Liu et al.[39]
P. acinose Roxb., $CaCl_2$, and Na_2CO_3	pyrolysis, 300−600 °C	20 min, 100%	this work

washed several times to remove free $CaCl_2$ until the filtrate did not contain calcium ions by precipitation detection. Then, the biomass was dipped into 0.25 M Na_2CO_3 for another 4 h under vacuum impregnation. The biomass was cleaned again using distilled water until the filtrate did not contain carbonate by precipitation detection. The cleaned biomass was dried in an oven at 80 °C and stored in a dehydrator before use. The biomass was pyrolyzed at 300, 400, 500, or 600 °C under N_2 as a protective gas for 1 h. The heating rate was 10 °C min^{-1}. The biochars were cooled to room temperature and were ground using an 80-mesh sieve. BioC300, BioC400, BioC500, and BioC600 represent biochar prepared at 300, 400, 500, and 600 °C, respectively.

3.3. Removal and Adsorption Procedure. Jar tests were performed using a paddle mixer with four equal volume beakers. The adsorption procedure consisted of a flash mix of 150 rpm for 5 min, a slow mix of 50 rpm for 15 min, and a settling period of 30 min. After this proceeding, the Cd concentration was determined using an Agilent 200 Series AA atomic absorption spectrometer. The calculation formula for the Cd removal rate is shown in eq 1:

$$R\ (\%) = (C_i - C_f)/C_i \times 100\% \tag{1}$$

where C_i (mg L^{-1}) and C_f (mg L^{-1}) represent the initial Cd concentration and the final Cd concentration after adsorption, respectively.

3.4. Characterization of Biochar. 1 mg biochar was used to measure the pH of biochar after shaking 24 h in 20 mL ultrapure water.[40] The ash of biochar was analyzed using an electric furnace at 750 °C for 4 h. pH$_{zpc}$ (pH at zero point of charge) was identified with 0.01 M NaCl solution containing 1 mg·mL^{-1} biochar at different pH values for 48 h.[41] Elementar Analyzer Vario EL III (Elementar Analysensysteme GmbH) was used to analyze elements C, H, N, and S. Element O was calculated according to the conservation of mass. FTIR spectroscopy was performed using a Fourier transform infrared Nicolet 5700 spectrophotometer between 400 and 4000 cm^{-1} using a resolution of 4 cm^{-1}. The morphology of biochar was observed using a Zeiss Supra55 scanning electron microscope equipped with an energy-dispersive X-ray spectrometer. The specific surface area of biochar was measured by the Brunauer−Emmett−Teller method under liquid nitrogen conditions using a Belsorp Mini II gas adsorption apparatus. The pore volume was analyzed according to the Barrett−Joyner−Halenda method. X-ray diffraction (XRD) patterns were characterized using an X-ray diffractometer with Cu Kα

radiation (M21X, MAC Science Ltd.). XPS was carried out by using Thermo Fisher Scientific ESCALAB 250Xi.

3.5. Determination of Different Cd Removal Mechanisms. BioC300, BioC400, BioC500, or BioC600 was mixed into 1 M HCl for 12 h to remove minerals under agitation. The biochar was washed with distilled water until the pH value of the filtrate remained unchanged. The dipping and washing process was repeated three times. The contribution of different Cd adsorption mechanisms was analyzed using acid-treated and untreated biochar. The calculation of the contribution of Cd adsorption mechanisms was carried out according to previous reports.[42,43]

The acid-treated biochars have low or nonexistent levels of minerals. The oxygen functional group on the biochar surface does not change. The adsorption abilities of biochars before and after acid dipping could evaluate the contribution of minerals, the calculation was carried out using eq 2[44]

$$Q_m = Q_t - Q_a \tag{2}$$

where Q_m represents the content of adsorbed Cd due to the precipitation with minerals and Q_t and Q_a represent the amount of Cd adsorbed by the untreated biochar and the acid-treated biochar, respectively.

The pH of biochar changed before and after Cd adsorption because of the interaction between the carboxyl, hydroxyl groups, and Cd inducing H$^+$ release from the biochar surface. The contribution of the oxygen functional group could be calculated by monitoring the pH change, as shown in eq 3[45]

$$Q_f = \exp(-pH_f) - \exp(-pH_i) \tag{3}$$

where Q_f represents the content of Cd adsorbed by the oxygen functional group. pH_i and pH_f represent the pH of the solution before and after Cd adsorption, respectively.

The contribution of Cd−π interaction can be calculated using the following equation[45,46]

$$Q_\pi = Q_a - Q_f \tag{4}$$

where Q_π is the amount of Cd adsorption resulting from Cd−π binding. The contribution percent was calculated by the Q_m/Q_t, Q_π/Q_t, and Q_f/Q_t ratio.

4. CONCLUSIONS

In this study, biochar materials loaded with minerals were synthesized, which exhibited rapid adsorption and separation. Carbonate-modified biochars were prepared by vacuum impregnation with carbonate as a mineral at different pyrolysis temperatures. The adsorption of Cd by carbonate-modified biochar was controlled by multiple mechanisms, including surface complexation, Cd−π interaction, and surface precipitation, among which the surface precipitation provides a major contribution. The content of minerals on carbonate-modified biochar has a significant effect on Cd precipitation. A large number of Cd precipitates induce the rapid precipitation and separation of buoyant biochar. Besides, the higher surface hydrophobicity and the lower polarity are conducive to biochar separation from water. In general, the Cd removal method is based on enhancing surface precipitation on the biochar surface, which has the advantages of efficient adsorption and rapid separation.

ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02126.

SEM elemental maps of BioC500; SEM−EDX spectra of BioC500; photographs of biochars after Cd adsorption; pH at zero point of charge for biochars; SEM elemental maps of BioC500 after Cd adsorption; SEM−EDX spectra of BioC500 after Cd adsorption; XPS survey spectra of C 1s using BioC300 before and after Cd adsorption and using BioC600 before and after Cd adsorption; XPS survey spectra of Cd 3d using BioC300 and BioC600; physical and chemical properties of biochars; and C 1s relative atomic percentage for BioC300 and BioC600(PDF)

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Notes

The authors declare no competing financial interest.

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