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Research Article

Adsorption Characteristics of Chitosan-Modified Bamboo Biochar in Cd(II) Contaminated Water

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The purpose of this study was to fabricate a low-cost and eco-friendly adsorbent using bamboo biochar (BB), a kind of charcoal composed of high Brunauer–Emmett–Teller surface area and variety of functional groups, and chitosan as substrates for remediation of Cd(II) in Cd(II) contaminated water and characterized the functional group characteristics, surface morphology, and Cd(II) adsorption effect using the Fourier transform infrared (FT-IR), scanning electron microscope (SEM), and energy-dispersive X-ray spectrometer (EDS). Results showed that chitosan-modified bamboo biochar (CBB) provided more active adsorption sites (such as $-NH_2$, –COOH, –OH, and C=O) on the surface to enhance the Cd(II) removal efficiency in Cd(II) contaminated wastewater. Meanwhile, the optimal pH, contact time, and dose of CBB on the Cd(II) removal efficiency are 7, 120 min, and 600 mg, respectively. In addition, the adsorption isotherm results revealed that the possible adsorption mechanisms might include surface adsorption, electrostatic adsorption, and ion exchanges. Furthermore, the maximum adsorption capacity (Q_m) values predicted from the Langmuir model were 37.74 and 93.46 mg/g for BB and CBB, respectively, also indicating a potential application of CBB in practical wastewater. Desorption and regeneration of CBB were attained simultaneously and the results showed that even after five cycles of adsorption-elution, the adsorption and desorption of CBB exhibited a slight decline and still reached at 71.70% and 65.92%. Results from this study would provide a reference to functionalized CBB for Cd(II) adsorption in contaminated water.

1. Introduction

Water pollution is one of the most severe problems on our planet. It is a novel challenge to manage water resources sustainably under climate change and population growth in the 21st century [1, 2]. Because of the high toxicity and persistence of cadmium (Cd(II)) in natural water and farmland, it has become an increasing concern over the past decades [3]. In Japan, the main cause of the *itai-itai* disease was Cd(II) accumulation in the aquatic environment [4]. Meanwhile, according to the World Health Organization (WHO), as one of the most toxic heavy metals, Cd(II) could lead to Cd(II) accumulation to cause harmful effects on the human body and causes carcinogenicity and liver damage [3]. Hence, Cd(II) must be removed from the contaminated water and soil before they were disposed to the environment [5, 6]. During the past decades, many techniques, including ion exchange [7], membrane filtration [6], flocculation/coagulation [8], chemical precipitation [9], photocatalysis [10], phytoremediation [11], and adsorption [12], are performed to remove heavy metals from the contaminated water and soil. Especially, various physical and chemical techniques have been employed to lower the Cd(II) concentration to meet environmental standards, including chemical precipitation, ultrafiltration, membrane separation, electrochemical deposition, and adsorption [13]. However, these techniques have great limitations for heavy metals removal due to their higher cost of energy and sludge production.

Biochar is produced from sustainably sourced biomass and is used for nonoxidative applications in agriculture [14, 15]. If biochar is used as a fuel to burn and the carbon is

oxidized into CO_2, hence it is actually classified as charcoal. Activated carbon is produced from any carbon source, such as fossil, waste, and renewable, and engineered to be used as sorbents to remove contaminants from both gases and liquids [16, 17]. Thus, it is defined as a material for contaminant sorption without exigencies in regard to the sustainability of its production nor to the fate of the carbon after its use. The bio-based adsorption is a promising method for heavy metals removal because it has good potential application prospects with an abundance of functional groups. Recently, the recycling of agricultural wastes as renewable adsorbents has received more and more attention. As an eco-friendly material, biochar has been widely used to remediate heavy metals and organic pollutants in soil and water contaminants [18–20]. Bamboo biochar (BB), a kind of charcoal composed of high Brunauer–Emmett–Teller (BET) surface area and a variety of functional groups (e.g., $-NH_2$, –COOH, and –OH) that have gained more and more attention, is an eco-friendly, readily available, low-cost, and renewable biochar [18–20]. However, the BB adsorption performance for heavy metal removal is not so good since the surface functional groups are still insufficient. Therefore, to enhance the heavy metals removal performance of BB, in recent years, many attempts, for example, citric-acid modification, amino modification, polyethylenimine modification, and some other methods, have been performed to surface modification with more functional groups [21–24]. Chitosan, an abundant natural polysaccharide in the world, is a plentiful, inexpensive, and nontoxic product of the shellfish processing industry. In recent years, chitosan has been used as alternative sorbents in many industrial and environmental applications because their amine functional groups have a strong bonding ability to various heavy metals [25–28].

Herein, the objectives of this research were to (1) fabricate chitosan-modified bamboo biochar (CBB); (2) characterize the surface morphology, element abundance, and functional groups of CBB; (3) determine the Cd(II) adsorption effect of CBB in contaminated water; and (4) speculate the possible adsorption mechanisms of CBB in Cd(II) contaminated water.

2. Materials and Methods

2.1. Materials. The offcuts of bamboo (*Phyllostachys heterocycla* (Carr.) Mitford *cv. Pubescens*), collected from the bamboo forest (N26°29′49″ and E106°44′10″) in the Guizhou Academy of Forestry, Guizhou Province, China. The chemicals were purchased from Aladdin-reagent Co., Ltd. (Shanghai, China).

2.2. Preparation of BB and CBB. The BB and CBB samples were prepared by following the procedures reported previously with some modifications [29, 30]. The offcuts of bamboo were washed with deionized water for three times to remove the dirt contained in the samples. The washed samples were air-dried, chopped into a particle size below $1.0 \times 1.0 \times 1.0$ cm, and then oven-dried at 100 ± 5°C for 8 h before use. After that, the bamboo particles were pyrolyzed at 900°C for 4 h under N_2 flow (100 mL/min) using a vacuum annealing furnace. After pyrolysis, the samples were ground via a ball grinder and passed through a standard 200 mesh sieve to obtain a particle size of about 75.0 μm. The samples were rinsed several times with deionized water and then oven-dried at 80°C for 24 h to obtain BB products for further use. After that, 0.4 g of chitosan mixed with 2.0 g BB were added into 30 mL of water. The mixtures were stirred well with sonication for 2 d at 30°C and 75% relative humidity (RH) and then separated by vacuum filtration and dried at 100 ± 5°C to give rise to the CBB.

2.3. Characterization of BB and CBB. The particle size distribution and specific surface area of BB and CBB were measured using a laser Bettersize 2600 particle analyzer (Bettersize Instruments Ltd., Dandong, China). The Fourier transform infrared (FT-IR) spectra of BB and CBB were obtained using a Thermo Nicolet 380 FT-IR spectrometer (Waltham, MA, USA). The surface morphology and elements of BB and CBB were scanned using a Quanta 250 Scanning Electron Microscope (SEM; FEI, Oregon, USA) equipped with a Bruker Quantax X-Flash 5030 energy dispersive X-ray spectrometer (EDS; Bruker, Berlin, Germany). The zeta potential values of BB and CBB were measured by a zeta potential analyzer (Malvern Instruments Ltd., Malvern, UK).

2.4. Batch-Adsorption Experiments. Batch-adsorption experiments were performed to evaluate the maximum Cd(II) adsorption efficiency of BB and CBB in 30 mL Cd(II) contaminated water with a concentration of 10 μg/mL. Briefly, different BB or CBB amounts (100, 200, 400, 600, 800, and 1000 mg) with pH 7 and contact time of 2 h, different contact times (5, 10, 30, 60, 120, 180, and 240 min) with pH 7 and BB or CBB amount of 600 mg, and initial pH (3, 4, 5, 6, 7, and 8) with a contact time of 2 h and BB or CBB amount of 600 mg on the Cd(II) adsorption efficiency in Cd(II) contaminated water were studied systemically. Briefly, the mixtures were shaken in a rotary shaker at 20°C and 120 rpm. After adsorption, the suspension was filtered with a 0.2 μm syringe filter, the Cd(II) concentration in the filtrate was determined by an iCE 3500 flame atomic absorption spectrometer (FAAS; Thermo Fisher, MA, USA) and an inductively coupled plasma mass spectrometry (ICP-MS; Thermo Scientific, MA, USA). For experimental accuracy, each trial was repeated three times.

The adsorption rate R (%) and adsorption amount Q (mg/g) of Cd(II) in Cd(II) contaminated water by BB or CBB were calculated using equations (1) and (2), where C_0 (mg/L) and C_e (mg/L) represent the Cd(II) concentrations at the initial and adsorption equilibrium state, respectively, V (mL) represents the volume of the aqueous solution, and m (g) is the amount of BB or CBB.

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100\%, \quad (1)$$

$$Q(\%) = \frac{C_0 - C_e}{m} \times V. \quad (2)$$

2.5. Model for Equilibrium Study of Adsorption. The adsorption kinetics of Cd(II) was studied in Cd(II) contaminated water using the Langmuir and Freundlich isotherm models (3) and (4), where C_e (mg/L) is the equilibrium concentration, Q_m (mg/g) denotes the maximum adsorption capacity, Q_e (mg/g) represents the Cd(II) adsorbed amount at the equilibrium concentration, K_L (mg/g) and K_F (mg/g) are Langmuir and Freundlich isotherm constants, respectively, and $1/n$ relates to the adsorption capacity [31–34].

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}, \quad (3)$$

$$Q_e = K_F C_e^{1/n}. \quad (4)$$

2.6. Desorption and Regeneration. To investigate the possibility of repeated use of the adsorbent CBB, in this study, the generation experiment was also conducted through five consecutive adsorption-desorption processes with the essential pH, contact time, and dose. Meanwhile, for the desorption experiment after Cd(II) adsorption, the CBB was transferred to a flask containing 40 mL of 0.2 M HCl desorbing agent. The mixture was shaken at 200 rpm using a rotary shaker for 3 h. After elution, the CBB was rinsed three times with deionized water to remove any traces of acid and suspended again in Cd(II) solution for the next adsorption cycle. The adsorption-desorption cycle was repeated five times using the same CBB. The desorption rates of CBB were evaluated as

$$\text{desorption rate}(\%) = \frac{\text{released Cd(II)concentration}}{\text{initially sorbed Cd(II)concentration}} \times 100. \quad (5)$$

2.7. Statistical Analysis. Statistical analysis was conducted by ANOVA with software SPSS 17.0 (SPSS Inc, Chicago, USA).

3. Results and Discussion

3.1. Preparation of BB and CBB. This study successfully fabricated a new kind of CBB using BB and chitosan as substrates for Cd(II) remediation in Cd(II) contaminated water. Some previous studies reported by Zhou et al. [29] and Zhang et al. [30] had also explored the use of chitosan to modify the BB surface to fabricate chitosan-modified biochars (CMB) and chitosan-modified magnetic biochar (CMMB) to enhance their affinity to heavy metals (Cr(IV), Pb(II), Cu(II), and Cd(II)) in water. It is interesting to note that the preparation technology to fabricate CBB reported in our present study is relatively simple and environmentally friendly without using NaOH, $Fe_2(SO_4)_3$, and $FeSO_4{\cdot}7H_2O$. Therefore, as far as we know, it is the first report to fabricate CBB using the above method reported in our present study.

3.2. Characterization of BB and CBB. As shown in Table 1, after the modification, CBB has no significant impact on the specific surface area and particle size distribution of BB. However, contrary to our findings, many biochar with organic matter have been shown to register very low surface areas [35].

Figures 1(a)–1(c) show that the BB surface exhibits notable smoothness and has a rich pore structure and numerous small particles, which may be formed after the degradation of some bamboo tissue during high-temperature pyrolysis, whereas Figures 1(d)–1(f) show that the CBB is slightly rather rough due to the irregular stacking of the bamboo charcoal particles. Meanwhile, EDS showed that the abundances of C, K, N, and O elements, which were the essential components of active functional groups, such as $-NH_2$, –COOH, C=O, and –OH were found to be uniformly distributed along the surface of BB and CBB. In comparison, the abundances of C, K, N, and O were more densely distributed at CBB than BB, suggesting that CBB has abundant active ligand sites and has a positive contribution to the Cd(II) adsorption.

3.3. Zeta Analysis. The effect of pH on the zeta potential charge of BB and CBB surface is determined. As shown in Figure 2(a), the zeta potentials of BB and CBB decreased with the increase of the pH value, probably because of the deposition of more OH^- on the adsorbent surface [36]. Zeta potentials of BB were in the range of +18.90 to −22.10 mV as the initial pH of the suspensions increased from 3 to 8, whereas the zeta potentials of CBB increased (+35.80 to −5.26 mV) in the designed pH range from 3 to 8. The point of zero charge pH (pH_{pzc}) of BB is 5.2, whereas the pH_{pzc} of CBB increased to 7.6 after being modified by chitosan, suggesting that chitosan loaded on the BB surface increased the positive charge. Meanwhile, Figure 2(b) shows that, after Cd(II) adsorption, the zeta potentials of BB and CBB had an apparent increase at the pH of 7, illustrating that amino functionalization of chitosan had been adsorbed on the surface of CBB and the adsorption mechanism of CBB was based on electrostatic attraction [37, 38].

3.4. Infrared Spectroscopy Study. The surface functional groups information of BB and CBB before and after Cd(II) adsorption are presented in Figure 3. Figure 3 shows that the broad FT-IR band at 3420 cm^{-1} was attributed to the stretching vibrations of –OH and –NH– groups [39]. The bands at 2960 and 1750 cm^{-1} were associated with the stretching vibration of –CH– and C=O, respectively [40, 41]. The band at 1430 cm^{-1} was assigned to the in-of-plane bending vibration for $-COO^-$ and –OH of –COOH [42]. The band at 1160 cm^{-1} was ascribed to the stretching vibration of C–O of various groups [43, 44]. The band at 1070 cm^{-1} indicated the occurrence of the C–O group [45]. Figure 3 also shows that, compared to BB, the contents of the main

Table 1: The specific surface area and particle size distribution of BB and CBB.

Parameters	BB	CBB
Specific surface area (m^2/kg)	84.99	85.05
Volume mean diameter (μm)	83.45	82.61
Area mean diameter (μm)	26.15	26.13
Quantity mean diameter (μm)	0.907	0.912
D90 (μm)	186.8	187.0
D50 (μm)	63.05	62.37
D10 (μm)	13.25	12.81

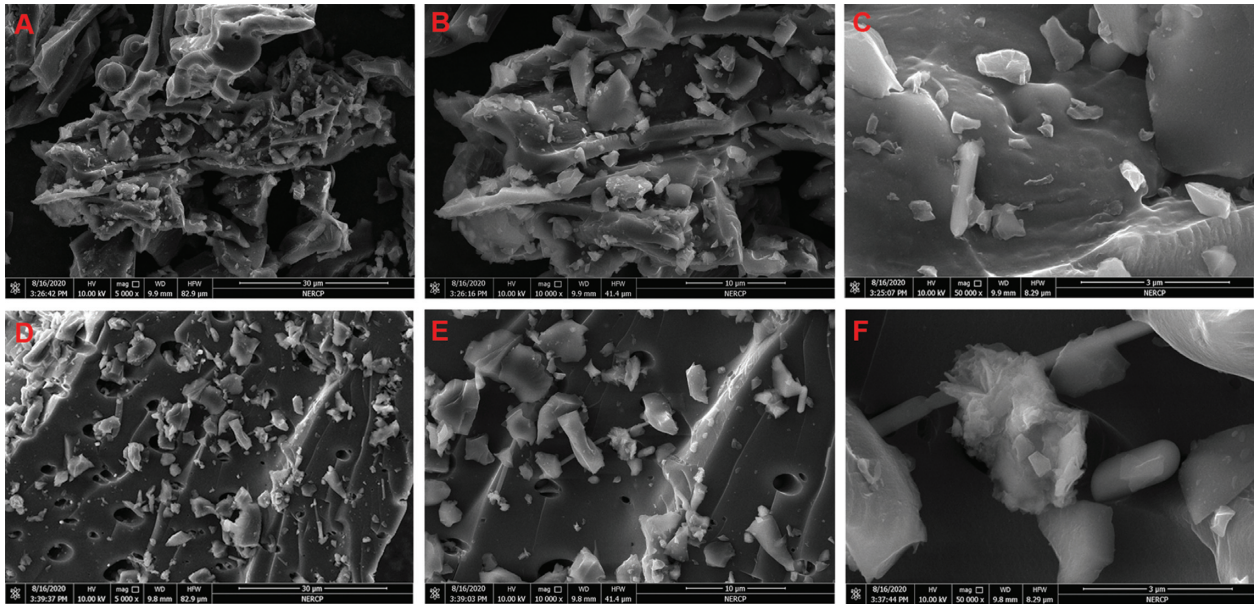

Figure 1: SEM images of BB (a–c) and CBB (d–f).

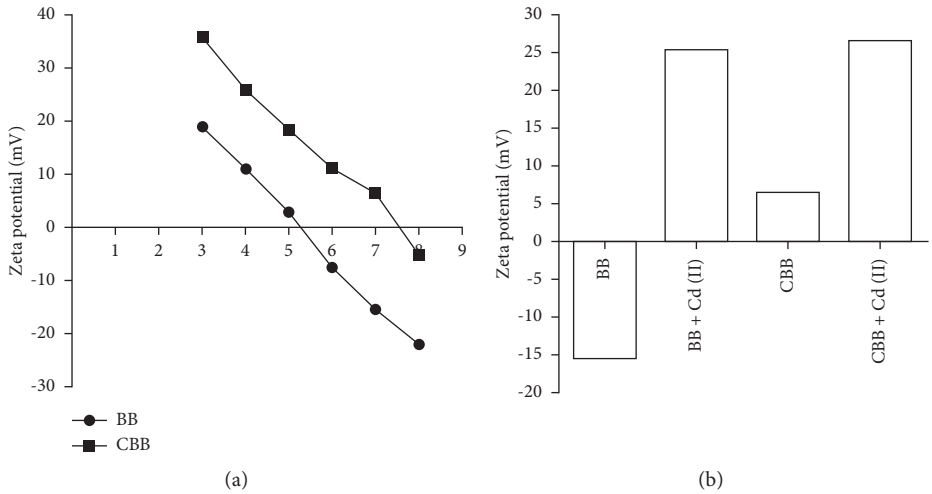

Figure 2: The zeta potential for BB and CBB in Cd(II) contaminated water at different pH values (a) and before and after Cd(II) adsorption at pH = 7 (b).

oxygen-containing functional groups, such as C–O, –COOH, C=O, and –OH, significantly increased during the preparation of CBB. Surfaces with abundant oxygen-containing functional groups could change the surface zeta potentials to strengthen the metal ions adsorbent in contaminated water [46].

3.5. Effect of pH, Contact Time, and Dose on the Cd(II) Adsorption. pH, an important parameter for affecting heavy metals adsorption, could affect the surface potential, counter ions concentration on the functional groups, and ionization degree of adsorbents [47–50]. To examine the effect of pH on the Cd(II) adsorption, the pH values were varied from 3 to 8.

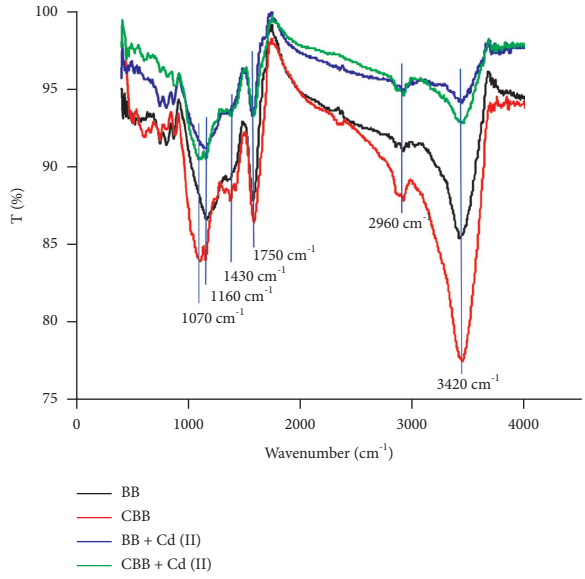

FIGURE 3: The FT-IR spectra of BB and CBB before and after Cd(II) adsorption.

As shown in Figure 4(a), the adsorption rates of BB and CBB in Cd(II) contaminated water depend on the pH values and show similar trends. The adsorption rates of CBB increased from 66.78% to 90.66%, respectively, over the pH values range from 3 to 7, while the adsorption of Cd(II) tends to be stable when pH is greater than 7. Therefore, the optimal pH of CBB on the Cd(II) removal efficiency is 7. This is consistent with the results reported for heavy metal removal from industrial wastewater using chitosan-modified oil palm shell charcoal which was in the pH values range of 6.8–7.1 [47]. Therefore, our results demonstrated that pH is one of the most essential parameters in the Cd(II) adsorption process and might change the function groups, mainly oxygen-containing groups, of CBB [51].

Contact time is one of the critical parameters for the contaminated water treatment system [52, 53]. To examine the effect of contact time on the Cd(II) removal efficiency, the contact time were varied from 5 to 240 min. As shown in Figure 4(b), the Cd(II) adsorption rates of CBB in Cd(II) contaminated water are higher than those of BB and increase with an increase in contact time before adsorption equilibrium is reached. It can be seen that the adsorption rates of CBB increase from 81.54% to 90.24% when the contact time increase from 5 to 120 min. Therefore, the optimum contact time for CBB is found to be 120 min, compared to that of BB which is 180 min. Hence, CBB requires a shorter contact time to reach adsorption equilibrium, demonstrating that the greater availability of various functional groups on the surface of chitosan could significantly improve the binding capacity and the adsorption of Cd(II) from wastewater [54–56].

The effect of different doses of BB and CBB on the Cd(II) adsorption was studied by varying the amount of adsorbents from 100 to 1000 mg, while keeping the pH value and contact time constant. Figure 4(c) shows that the Cd(II) removal efficiency of the BB and CBB adsorbents generally improves with the increasing adsorbent dose. This is expected that the higher dose of adsorbents added in Cd(II) contaminated water, the greater removal availability of adsorbents for Cd(II) removal, and then shows no further increase in Cd(II) adsorption after a certain amount of BB and CBB adsorbents were added [57, 58]. Meanwhile, the results, as shown in Figure 4(c), also indicate that the Cd(II) adsorption rates of CBB in Cd(II) contaminated water are higher than those of BB as well as increase with an increase in dose before equilibrium is reached. It can be seen that the adsorption rates of CBB increased from 73.33% to 90.66% when the doses of CBB were increased from 100 to 600 mg. Therefore, the optimum dose for CBB adsorbents is 600 mg, compared to that of BB which is 800 mg.

3.6. Adsorption Isotherms. To further investigate the adsorption mechanism of BB and CBB, the adsorption equilibrium isotherms of Cd(II) in Cd(II) wastewater were determined at 20°C with optimal conditions. Figure 5(a) shows the effect of contact time on the theoretical Cd(II) adsorption capacity by BB and CBB, and the adsorption curves of BB and CBB increased steeply within the first 180 min, indicating that the abundant adsorption sites on the BB and CBB surface were rapidly occupied by Cd(II) via surface absorption. Figure 5(b) shows the effect of C_e on the Cd(II) adsorption capacity by BB and CBB. When $C_e < 45$ mg/L, the Cd(II) adsorption capacity of the BB and CBB adsorbents was found to increase remarkably, which could be ascribed to the sufficient active sites on the BB and CBB surface. Meanwhile, as the C_e values continue to increase, the available active adsorption sites on the surface of the BB and CBB adsorbents tend to saturate, therefore resulting in a dynamic adsorption equilibrium for the Cd(II) adsorption capacity. Similar results were reported by Yan et al. [58]. The Langmuir and Freundlich fitting curves of BB and CBB are plotted in Figures 5(c) and 5(d) and the related parameters are presented in Table 2. Figures 5(c) and 5(d) as well as Table 2 show that the Langmuir and Freundlich models exhibit the best fit for BB and CBB with both the highest correlation coefficients exceeding 0.95, indicating that the BB and CBB surface are homogeneous [59]. Generally, $1/n$ represents the heterogeneity factor of the site energy on the functional groups, and the smaller $1/n$ is, the better the adsorption capacity is, such as $0 < 1/n < 1$ indicates favorable adsorption [60, 61]. This study shows that the $1/n$ values of BB and CBB are 0.24 and 0.21, respectively, indicating a favorable Cd(II) adsorption by the two adsorbents. The K_F obtained from the Freundlich model as well as K_L obtained from the Langmuir model could be the critical indicators of heavy metals adsorption [58]. Table 2 shows that the K_F and K_L values followed the order: BB > CBB, suggesting that CBB had an adsorption affinity toward Cd(II). Furthermore, the maximum adsorption capacity (Q_m) values predicted from the Langmuir model were 37.74 and 93.46 mg/g for BB and CBB, respectively. In recent years, many modified biochars were also prepared [61–65] and the comparison of the Q_m values of Cd(II) was listed in Table 3. Table 3 shows that the Q_m value of Cd(II) is higher than most of the reported modified biochars, indicating a potential application of CBB in practical wastewater.

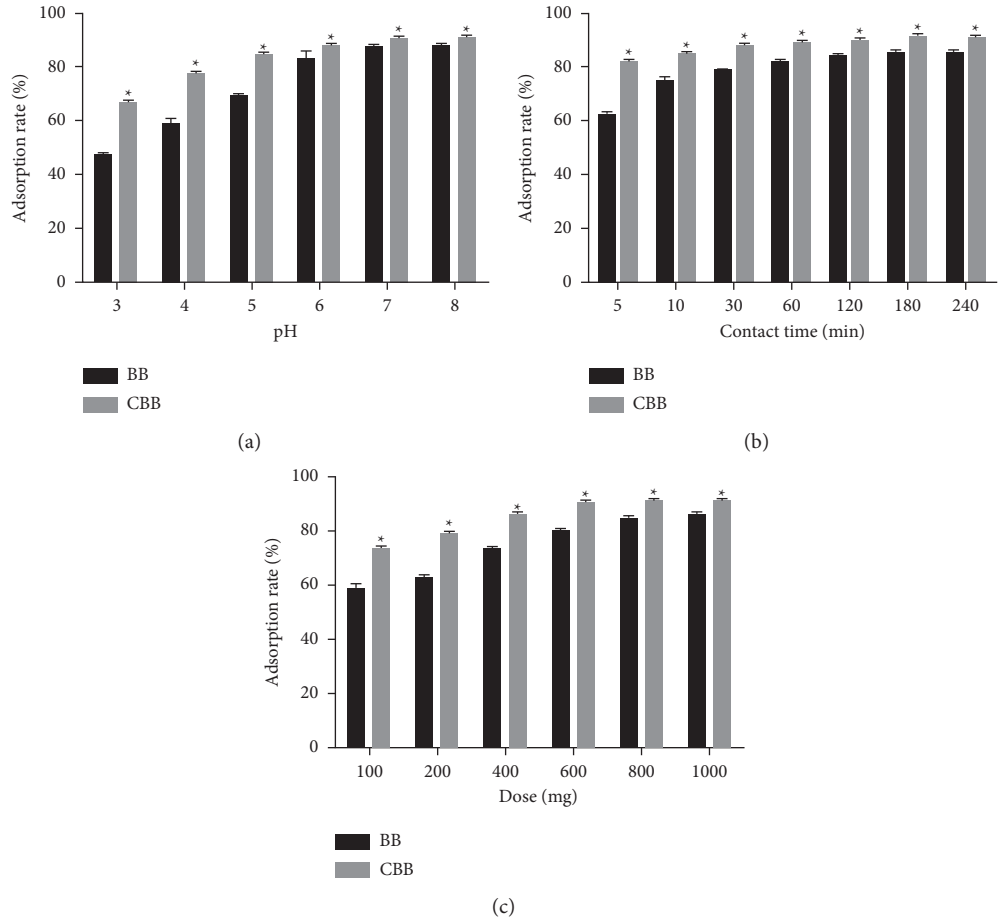

Figure 4: Effect of pH (a), contact time (b), and dose (c) on the adsorption rates of BB and CBB in Cd(II) contaminated water. Error bars mean the standard deviation. *indicates a significant difference ($p < 0.05$) between the adsorption rates of BB and CBB at different pH, contact times, and doses.

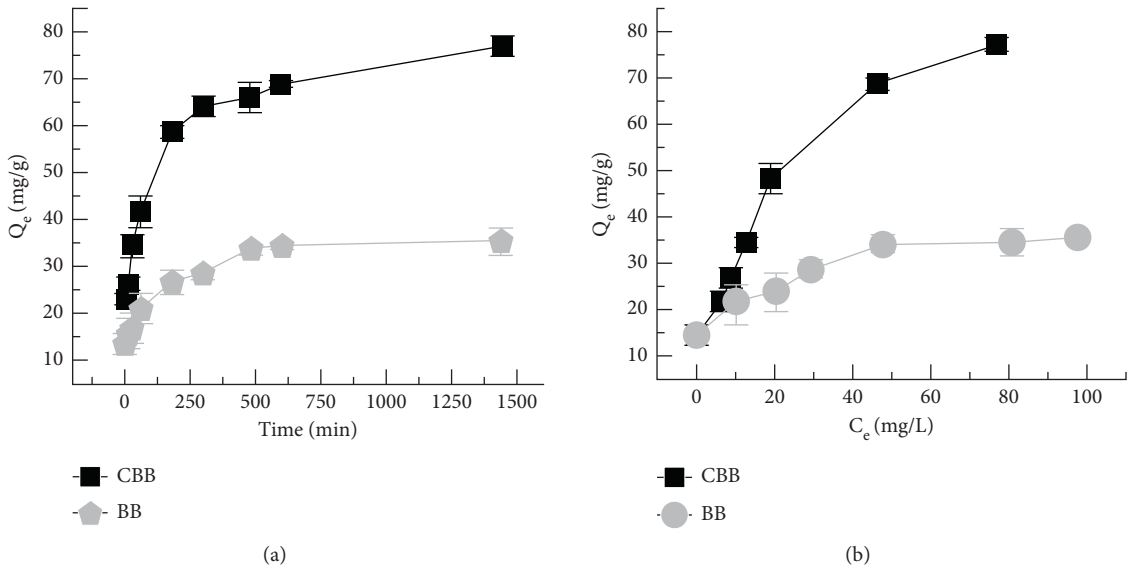

Figure 5: Continued.

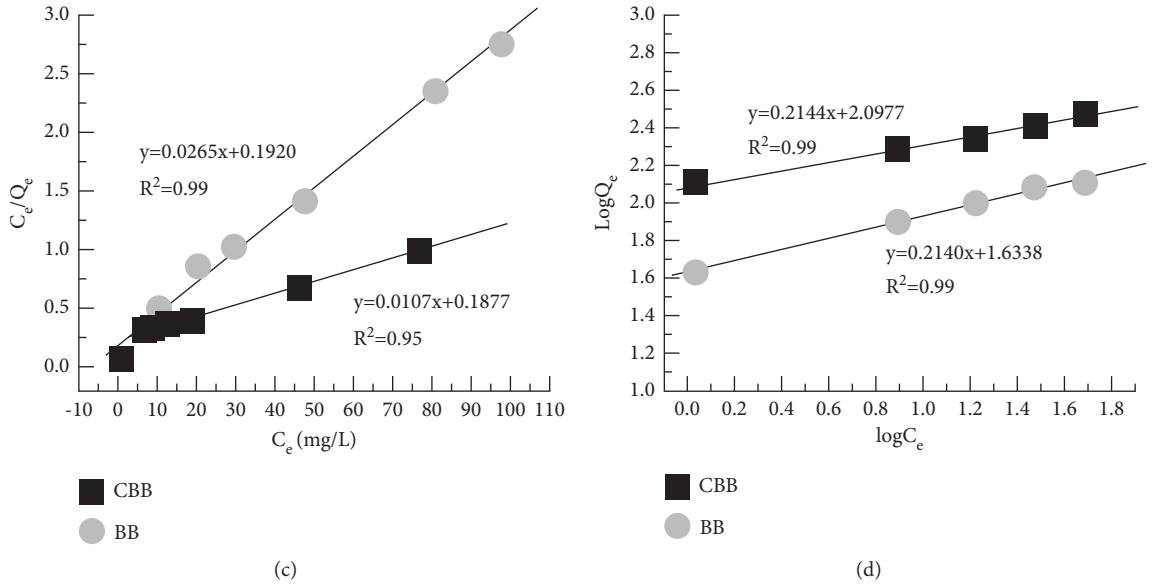

Figure 5: (a) Effect of contact time on equilibrium adsorbate concentration of the Cd(II) adsorption by CBB and BB; (b) effect of equilibrium adsorbate concentration on Cd(II) adsorption by CBB and BB; (c) Langmuir fitting curves; (d) Freundlich fitting curves. Error bars mean the standard deviation.

Table 2: Langmuir and Freundlich isotherm parameters for the adsorption of Cd(II).

Adsorbents	Langmuir			Freundlich		
	Q_m (mg/g)	K_L	R^2	K_F	$1/n$	R^2
BB	37.74	0.14	0.99	2.63	0.24	0.99
CBB	93.46	0.06	0.95	2.10	0.21	0.99

Table 3: Comparison of the Q_m values of Cd(II) of different modified biochars.

Absorbent	Q_m (mg/g)	Reference
CBB	93.46	This study
Chitosan-modified biochar	71.5	[29]
Phosphate-modified activated bamboo biochar	202.66	[61]
Fe-Mn binary oxide-biochar	72.9927	[62]
Ball-milled bone biochar	165.77	[63]
Sulfonated biochar	85.76	[64]
Magnesium oxide biochar-chitosan composite	68.223	[65]

3.7. Desorption and Reusability. The recyclability of adsorbent is one of the important performance indexes to evaluate the applicability of adsorbent in treating actual wastewater [66]. The adsorption and desorption rates of Cd(II) in five adsorption-desorption cycles were shown in Figure 6. It was found that after five cycles, the adsorption and desorption of CBB exhibited a slight decline and still reached at 71.70% and 65.92%, respectively. The good reproducibility indicated that CBB could be used as a desirable, economic, and recyclable adsorbent in practical wastewater.

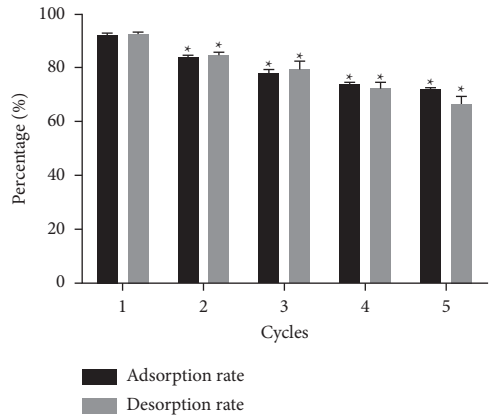

Figure 6: Five consecutive adsorption-desorption cycles of CBB for Cd(II) adsorption. Error bars mean the standard deviation. *indicates a significant difference at $p < 0.05$ compared with cycle 1.

3.8. Possible Adsorption Mechanism. Based on the above analysis and isotherm results, a possible mechanism for the adsorption of Cd(II) by CBB has been proposed and depicted in Figure 7. As shown in Figure 7, we speculate that the possible adsorption mechanisms include surface adsorption, electrostatic adsorption, and ion exchanges. More specifically, the surface of CBB has abundant pores and active functional groups (–NH_2, –COOH, –OH, and C=O), which could significantly improve the surface adsorption capacity. Meanwhile, abundant –OH and –COOH active functional groups on the surface of CBB could change the surface zeta potentials by loss of H^+ to form charged functional groups, thus strengthening the electrostatic adsorption of the adsorbent in Cd(II) contaminated water. In addition, after carbonization at high temperature, the abundant K of CBB are transformed into

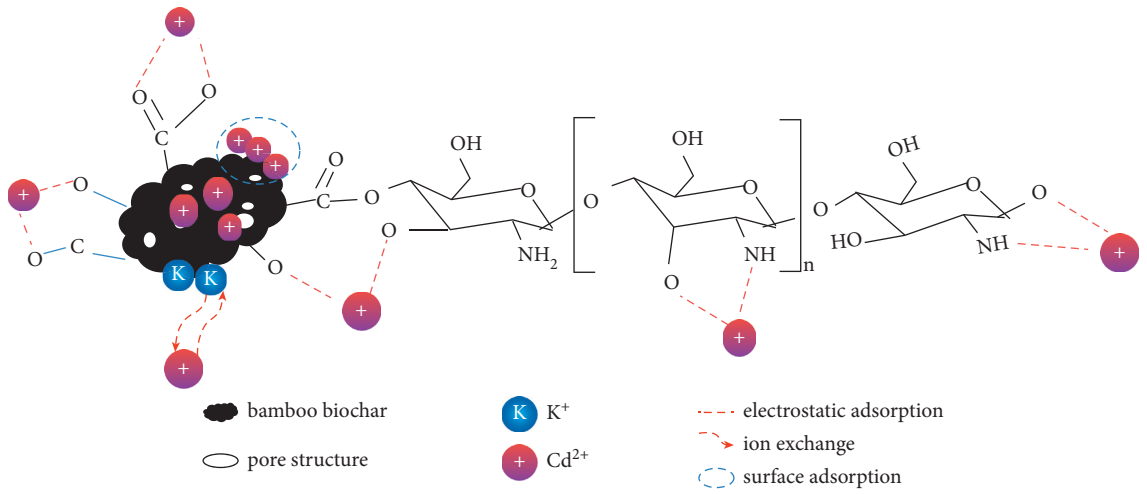

Figure 7: Diagram showing the possible adsorption mechanism of CBB on Cd(II) adsorption.

free K^+, which continuously exchange with Cd(II) in an aqueous solution, thus promoting the process of Cd(II) ion exchange.

4. Conclusions

In summary, a new eco-friendly and low-cost adsorbent for Cd(II) was prepared by the modification of BB with chitosan via a simple method. Results showed that the modification could significantly improve the surface properties and adsorption performance for Cd(II) adsorption. As well, the adsorption isotherm results show that the possible adsorption mechanisms include surface adsorption, electrostatic adsorption, and ion exchanges. Thus, the CBB can be considered as a feasible, promising, and high value-added approach for Cd(II) contaminated water recycling.

Data Availability

All data included in this study are available upon request by contacting the corresponding author.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

Acknowledgments

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