

Article

Adsorption Characteristics of Cd^{2+} Ions in Aqueous Solution on Modified Straw Biochar

Bo Tang ^{1,2,3,*}, Haopu Xu ¹, Fengmin Song ^{1,2,3} and Zhifeng Liu ^{1,2,3} 

¹ School of Chemistry and Environmental Science, Shaanxi University of Technology, Hanzhong 723001, China

² State Key Laboratory of Qinba Bio-Resource and Ecological Environment, Hanzhong 723001, China

³ Shaanxi Province Key Laboratory of Catalytic Foundation and Application, Hanzhong 723001, China

* Correspondence: czhatb@163.com

Abstract: Rice straw and corn straw were selected as raw materials to prepare biochar by anoxic carbonization and the biochar was loaded on the surface with FeCl_3 , MnCl_2 and $\text{Fe}(\text{NO}_3)_3$ & KMnO_4 , respectively, and then two types of straw biochar and six types of modified biochar were prepared. FT-IR, SEM, and XRD were used to characterize and analyze the physical and chemical properties of the biochar. The adsorption kinetics and adsorption isothermal tests of Cd^{2+} ions in aqueous solution were carried out. The results showed that modified biochars attached more active sites and surface group, especially iron-manganese-modified biochar (FMBC1, FMBC2). The kinetic adsorption tests showed that the adsorption process of eight kinds of biochar all conformed to the quasi-second-order kinetic equation, and chemisorption maybe dominated the adsorption process. The adsorption isothermal test showed that the adsorption process of Cd^{2+} ions by FeCl_3 -modified biochar (FBC1, FBC2) and $\text{Fe}(\text{NO}_3)_3$ & KMnO_4 -modified biochar (FMBC1, FMBC2) conforms to the Freundlich model, and the adsorption process of Cd^{2+} ions by MnCl_2 -modified biochar (MBC1, MBC2) conforms to Langmuir model. Compared with other kinds of biochar, the K_F value of $\text{Fe}(\text{NO}_3)_3$ & KMnO_4 -modified biochar of rice straw biochar (FMBC1) was the largest, reached $18.602 \text{ L} \cdot \text{mg}^{-1}$, and its $1/n$ value was the smallest, it reached 0.474, indicating that the adsorption effect on Cd^{2+} of FMBC1 was the best.

Keywords: biochar; modification; manganese modification; iron-manganese modification; Cd^{2+} ions



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1. Introduction

With the rapid development of industry and the increase in the types and quantities of agricultural chemical products, the pollution of heavy metals in natural water and soils caused by industrial wastes, pesticides, and fertilizers has become increasingly serious [1,2].

Cadmium (Cd) is a nonessential element in the human body and often exists in the form of minerals with other elements in nature, such as oxygen and sulfur [3,4]. Cd pollution in water bodies has become a global environmental problem and its main sources are smelting, chemical industry, electroplating, fertilizer manufacturing, waste incineration, and other industries [5,6]. Cadmium will spread in environmental waters, deposit in sediments and soil, and eventually, accumulate in the organism, causing the chronic and acute poisoning of humans and animals, and causing immeasurable harm to the entire ecological environment [7–10].

The adsorption method is one of the most effective methods to treat heavy metal pollution in water and soil. This method is easy to operate, has a wide range of applications, low material prices, and has a broad application space [11–15]. The most important link in the adsorption of heavy metals is the choice of the adsorbent. In recent years, biochar as an adsorbent has been increasingly used in experimental research on the treatment and remediation of heavy metal pollution. The main source materials for biochar preparation are straw, manure, and municipal waste [1,4–6]. Biochar is a high-carbon solid organic material that is pyrolyzed under high temperature and oxygen deficiency [16], and its surface

contains rich functional groups, such as carboxyl, hydroxyl, carbonyl, and other functional groups [17–19], functional groups are the majority in these groups. The adsorption mechanism of biochar for heavy metals is mainly as follows: (1) Surface adsorption through the affinity of heavy metals and π electrons on the surface of biochar [20,21]; (2) Heavy metal ions and surface functional groups can form hydroxides, phosphates, and carbonates [22,23]; (3) Heavy metal ions exchange ion with the negative charges on the surface of biochar [12,24]; (4) Surface complexation and electrostatic interact with oxygen-containing or carbon-containing functional groups on the surface of biochar [25,26]. Numerous test results show that biochar not only has a good effect on the treatment and restoration of heavy metal pollution in water and soil, but also can increase soil organic matter content, improve soil pH, strengthen soil enzyme activity and microbial activity, etc. In addition, the widespread application and promotion of biochar in the treatment of environmental heavy metal pollution can solve the problem of the final disposal of rural agricultural solid waste to a certain extent, reflecting the advanced environmental protection concept of waste treatment [15,27,28]. Due to the limited number of active functional groups contained in the original biochar structure, people often modify it to increase the active sites on the surface of the biochar to improve its adsorption efficiency. There are many ways to modify biochar, which are mainly divided into the physical method, chemical method, and biological method [12,16,29]. Among them, the chemical method is the most widely used, and the modification of biochar with acid-base or metal compounds is the most common chemical method [30–33].

The adsorption models are important ways to comprehensively understand the adsorption process of heavy metals and organic pollutants [4,6]. The models include sorption kinetics, adsorption isotherm, and adsorption thermodynamics [10]. The adsorption kinetics model can be used to study the adsorption mechanism of biochar and the influencing factors of the adsorption rate [10–12]. The isothermal adsorption model can be used to study the concentration relationship of organic molecules when they reach adsorption equilibrium at the interface of adsorbent and solution [10–12]. The parameters in the thermodynamic model can represent the coverage of the adsorbate on the surface of the adsorbent [11].

In this study, rice straw and corn straw were selected as raw materials to prepare biochar by anoxic carbonization, then the straw biochar was loaded with FeCl_3 , MnCl_2 , and $\text{Fe}(\text{NO}_3)_3$ & KMnO_4 on the surface, respectively. Then, two types of straw biochars and six types of modified straw biochars were prepared. Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), X-ray diffraction (XRD) were used to characterize and analyze the surface structure of the biochar. The adsorption kinetics and isothermal adsorption tests of Cd^{2+} ions in aqueous solution were carried out. The adsorption effect and adsorption mechanism of Cd^{2+} ions by eight types of biochar were compared and studied. The results hope to offer a better preparation method of biochar, explore its sorption effect toward Cd in the environment, and provide reference for the solid waste management of agricultural straw.

2. Materials and Methods

2.1. Experiment Material

$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, MnCl_2 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, KMnO_4 were all analytically pure and purchased from Sinopharm Chemical Reagent Co., Ltd. Rice straw and corn straw were collected in November 2021 from the agriculture experimental station (33°04'36'' N, 107°01'38'' E, 443.28 m a.s.l.), located in Hanzhong city, Shaanxi Province.

2.2. Preparation of Modified Biochar

2.2.1. Preparation of the Straw Biochar

The rice straw and corn straw were dried naturally and passed through the 20-mesh sieves. The straw biochar can be obtained after placing the rice straw and corn straw in the

muffle furnace at 600 °C and firing without oxygen for 2 h; the rice straw biochar and corn straw biochar were noted as BC1 and BC2, respectively.

2.2.2. Preparation of Fe-Modified Biochar

The prepared straw biochars BC1 and BC2 were soaked in FeCl₃ solution for 2 h, filtered, and washed with dH₂O to neutralize. The samples were placed in ovens at 80 °C, dried to a constant weight. Then, the samples were placed in a tube furnace under oxygen-limited conditions from 25 °C to 700 °C and kept for 1.5 h, naturally cooled to a constant temperature [19,34]. The rice straw and corn straw FeCl₃-modified biochar were obtained and noted as FBC1 and FBC2, respectively.

2.2.3. Preparation of Mn-Modified Biochar

The prepared straw biochars BC1 and BC2 were soaked in MnCl₂ (2 mol/L) solution for 2 h, filtered, and washed with dH₂O to neutralize. The samples were placed in ovens at 80 °C dried to a constant weight. Then, the samples were placed in a muffle furnace under an oxygen-limited condition at 500 °C for 1.5 h, naturally cooled to a constant temperature. The rice straw and corn straw MnCl₂-modified biochars were obtained and noted as FBC1 and FBC2, respectively [34].

2.2.4. Preparation of Fe-Mn Modified Biochar

The prepared straw biochars BC1 and BC2 were soaked in mixed solution of Fe(NO₃)₃·9H₂O and KMnO₄ [Fe:Mn = 10:1 (*w:w*), Fe:Mn = 3:1 (*n:n*)], respectively, dispersed in an ultrasonic cleaner for at 25 °C for 2 h; then, the sample were evaporated to dryness on the water bath at 95 °C. Then, the samples were placed in the muffle furnace under oxygen-limited conditions from 10 °C to 600 °C for 0.5 h, naturally cooled to a constant temperature [34,35]. The rice straw and corn straw Fe(NO₃)₃ & KMnO₄-modified biochars were obtained and denoted as FMBC1, FMBC2, respectively.

2.3. Structural Characterization of Biochar

Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), X-ray diffraction (XRD) were used to characterize and analyze the surface structure of the biochar.

2.4. Sorption Experiments

2.4.1. Sorption Kinetics

In the Cd²⁺ ions kinetics adsorption test, each of the total 8 types of biochar was added to a 50-mL tube containing 20 mL of CdCl₂ solution (40 mg/L), the mixtures were shaken in a thermostatic reciprocating shaker with 180 r min^{−1} at 25 °C. The samples were taken out at different times, at 0, 30, 60, 120, 180, 240, 300, 360, 420, 480, 540, 720, and 1500 min, respectively. Then, the solids and liquids were separated by centrifugation at 3900 rpm for 10 min. Finally, supernatants were filtrated through a 0.45 µm rounded filter membrane and stored at 4 °C for measuring Cd²⁺ ions' concentrations by inductively coupled plasma mass spectrometry (ICP-MS). The above isothermal adsorption tests were carried out in 3 sets of parallel tests.

The sorption kinetics was fitted with pseudo-first-order (1), pseudo-second-order model (2) [36,37].

$$Q_t = Q_e (1 - \exp(-k_1 t)) \quad (1)$$

where Q_t (mg/g) is the sorption amount at time t , k_1 is the pseudo-first-order rate constant (1/min), and Q_e (mg/g) is the sorption amount at equilibrium.

$$Q_t = k_2 Q_e^2 t / (k_2 Q_e t + 1) \quad (2)$$

where Q_t (mg/g) is the sorption amount at time t , k_2 (g/(mg·min)) is the pseudo-second-order rate constant, and Q_e (mg/g) is the sorption amount at equilibrium.

2.4.2. Sorption Isotherms

The Cd^{2+} ions' adsorption capacity of the biochar samples were investigated in aqueous solutions. In the Cd^{2+} ions' adsorption capacity experiment, 50 mg for each of the total 8 types of biochar was added to 50 mL tube containing 20 mL of CdCl_2 solution (2 mg/L). Then, the tube was shaken at 150 r min^{-1} at room temperature for 360 min, and the suspensions were filtered through $0.22 \mu\text{m}$ membrane filters [31]. The concentrations of Cd^{2+} ions in the filtered liquids were determined by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer 600 $\times$, Waltham, MA, USA). The Cd^{2+} ions sorption capacity of the biochar was calculated according to Equation (3), the Cd^{2+} ions' adsorption efficiency η of biochar was calculated according to Equation (4) [36,37]. The same procedures were repeated three times for each biochar, and their mean values were defined as the final capacity.

$$Q_e = V(C_0 - C_e)/m \quad (3)$$

$$\eta = (C_0 - C_e)/C_0 \quad (4)$$

where Q_e (mg/g) represents the biochar Cd^{2+} ions' sorption capacity; C_0 (mg/L) and C_e (mg/L) denote the Cd^{2+} ions concentration at initial and adsorption equilibrium, respectively; V (L) represents the volume of the Cd^{2+} ions solution used in the experiment; m (mg) denotes the dry weight of the biochar added to the Cd^{2+} ions solution.

The isothermal adsorption model of Cd^{2+} ions by biochar can be characterized according to Langmuir Equation (5) and Freundlich Equation (6) [38,39].

$$\text{Langmuir } Q_e = Q_m K_L C_e / (1 + K_L C_e) \quad (5)$$

$$\text{Freundlich } Q_e = K_F C_e^n \quad (6)$$

where C_e (mg/L) denotes the concentration of Cd^{2+} ions during adsorption equilibrium; Q_e (mg/g) denotes adsorption capacity at adsorption equilibrium; K_L (L/mg) denotes Langmuir constant; Q_m (mg/g) denotes maximum adsorption capacity under ideal conditions; K_F (L/mg) denotes Freundlich constant; n is an indicator of heterogeneity.

2.5. Data Processing

Data processing adopts Origin 2018, XRD analysis adopts MDI Jade 6 analysis.

3. Results and Analysis

3.1. Characterization of Biochar

3.1.1. FT-IR Characterization

As shown in Figure 1, FBC1, FMBC1, and FMBC2 had an obvious stretching vibration of the amino group ($=\text{NH}^+$ -) at $2317\sim 2311 \text{ cm}^{-1}$; all biochars had C-O stretching vibration at $1111\sim 1020 \text{ cm}^{-1}$ [40], which might be due to a small amount of oxygen entering into the formation of the C-O bond during the firing process; FBC1, FBC2, and FMBC1 had wide absorption peaks at 3296 cm^{-1} , 3312 cm^{-1} , and 3298 cm^{-1} , respectively, indicating that there was a stretching vibration of the intermolecular hydrogen bond ($-\text{OH}$), which might be due to the addition of metal ions to strengthen the intermolecular hydrogen bond in biochar [41]. FBC1, MBC1, and FMBC1 had a C-H out-of-plane bending vibration at 793 cm^{-1} , that was, there were aromatic compounds; it might be that after modification, BC1 had an aromatic compound. FBC1, FBC2, MBC2, FMBC1, and FMBC2 had obvious absorption peaks at the wave number of $1570\sim 1515 \text{ cm}^{-1}$, indicating the existence of solid-state N-monosubstituted amides [40,41]. The metal ions might increase the bond energy of the amide bond. In general, compared with the original biochar, the types of functional groups increased significantly on the surface of modified biochar.

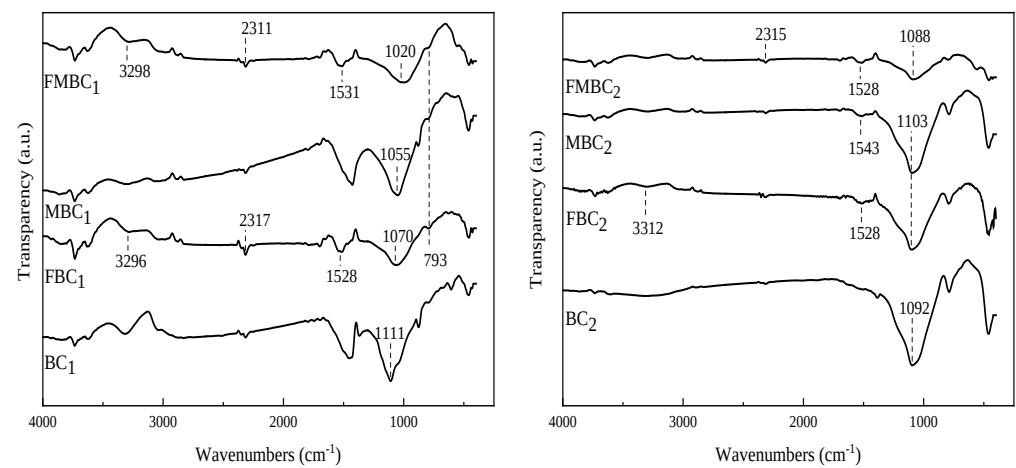


Figure 1. The FT-IR diagrams of biochars.

3.1.2. SEM Characterization

Shown in Figure 2, the SEM observation of the biochar surface showed that the pore size and micropore number of FBC₁, FBC₂, MBC₁, MBC₂, FMBC₁, and FMBC₂ increasing compared with the BC₁ and BC₂; moreover, the surface of the biochar became smoother, especially FBC₁ and FBC₂, while the surface of FMBC₁ and FMBC₂ was rougher, which might be due to the increase in modification strength, and it destroyed the surface structure of biochar itself.

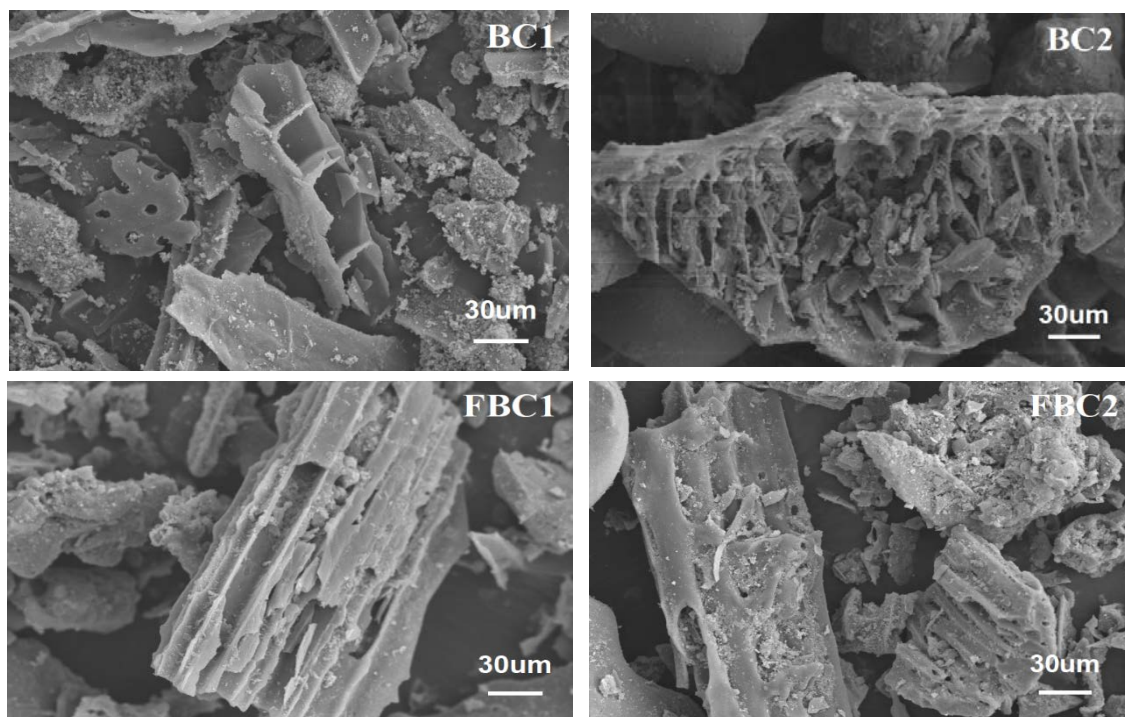


Figure 2. Cont.

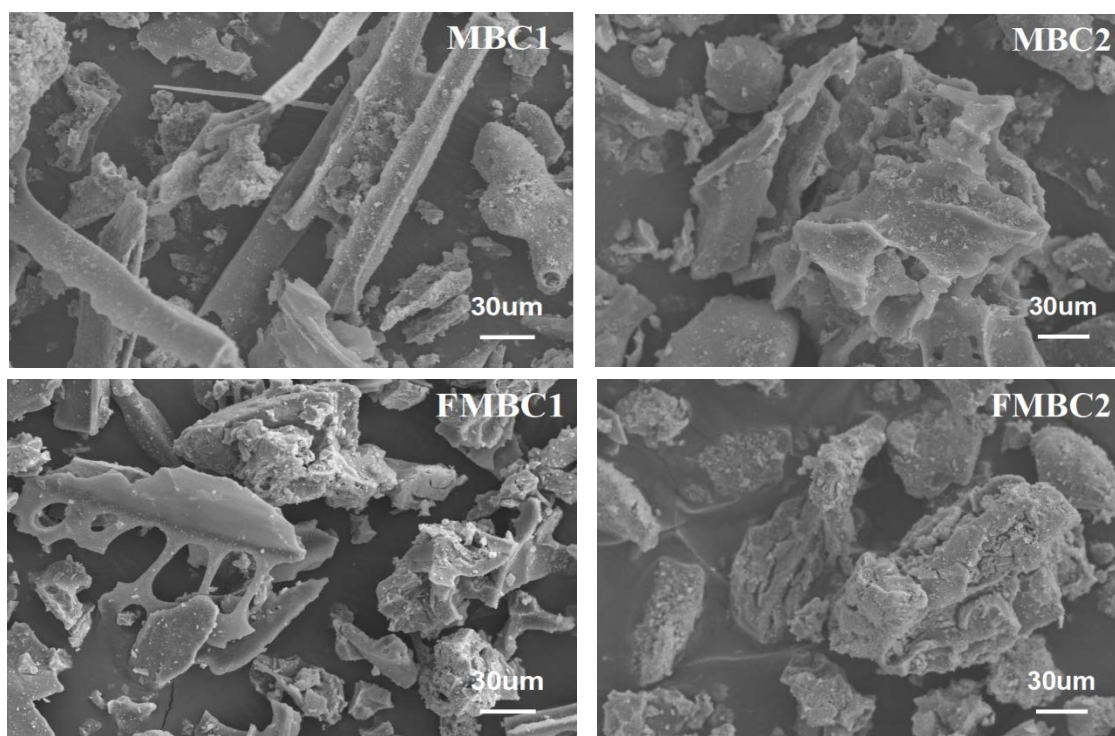
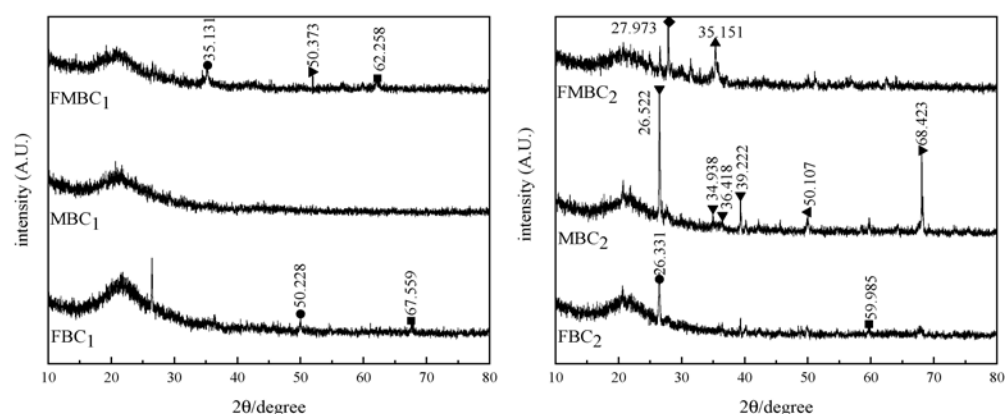


Figure 2. SEM images of biochars.

3.1.3. XRD Characterization

The XRD of the modified biochar is shown in Figure 3. The spectra of FBC1 and FBC2 were at $2\theta = 67.559^\circ$ (PDF#41-0586), 59.985° (PDF#41-0586), 50.228° (PDF#30-0226), 26.331° (PDF#42-1469), respectively. There were crystallization peaks of FeCO_3 and Fe_2O_3 , indicating that iron ions could be better combined with biochar and exist in a stereotyped form [42,43]. The crystal peak of MnCO_3 existing was observed at $2\theta = 68.423^\circ$ (PDF#02-0714), and the crystal peaks of Ca(OH)_2 and CaO were observed at $2\theta = 26.522^\circ$, 39.222° , 36.418° , 34.938° (PDF#24-0217), and 50.107° (PDF#22-0519) [44,45]; the results showed that element Mn was attached to BC2 and precipitated Ca(OH)_2 and CaO , but there was no crystallization peak in MBC1 spectrum. There were characteristic peaks of FeCO_3 , Fe_2O_3 , MnCO_3 , FeSO_4 , and MnO_2 in FMBC1 and FMBC2 spectra, which appeared at $2\theta = 62.258^\circ$ (PDF#36-0383), 35.131° (PDF#46-0291), 50.373° (PDF#02-0714), 35.151° (PDF#44-0605), and 27.973° (PDF#43-0185), respectively, which indicated that element Fe existed in the forms of FeCO_3 and Fe_2O_3 in the structure of FMBC1; element Mn existed in the form of MnCO_3 , while in FMBC2, element Fe existed in the form of FeSO_4 , element Mn existed in the form of oxides and in the form of stereotype [42–45].



Note: ●: Fe₂O₃; ■: FeCO₃; ▲: FeSO₄; ▼: Ca(OH)₂; ◆: CaO; ►: MnCO₃; ◆: MnO₂.

Figure 3. XRD diagrams of modified biochars.

3.2. Absorption Experiment

3.2.1. Effect of Concentration of CdCl₂ Solution on Adsorption Rate

At different Cd²⁺ ions concentrations, the adsorption rate of biochar to Cd²⁺ ions is shown in Figure 4, when the concentration of CdCl₂ was 20–80 mg/L, except for FeCl₂-modified biochars, the adsorption rate of rice straw biochars was higher than corn straw biochars (BC1 > BC2, MBC1 > MBC2, FMBC1 > FMBC2). The adsorption rate of Fe(NO₃)₃ & KMnO₄-modified biochars (FMBC1, FMBC2) was the highest. From the overall trend of the curve, it can be seen that the concentration of CdCl₂ had a greater influence on the adsorption rate of FBC1, FBC2, MBC1, and MBC2, while those of FMBC1 and FMBC2 were not obvious. This might because there were more types of functional groups on the surface of the modified biochar than on the original biochar [23,25], and as shown in Figure 1, the FT-IR diagrams of eight types of biochars, was discussed earlier in this paper.

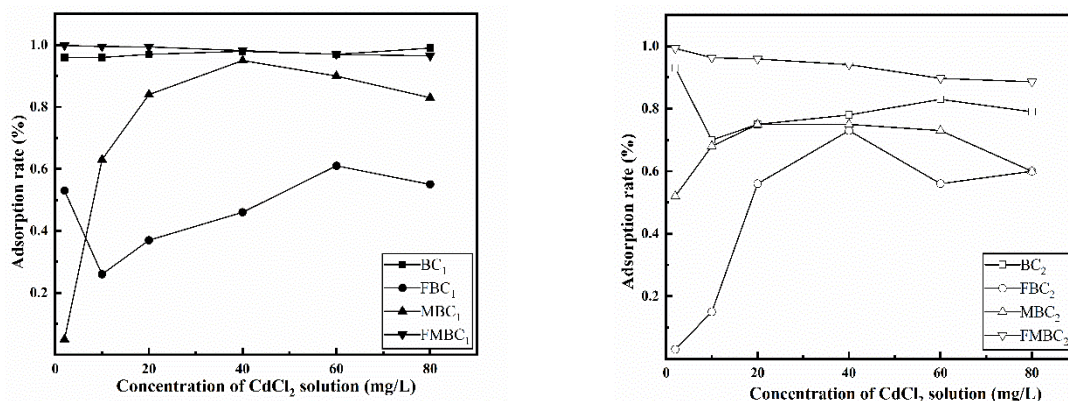


Figure 4. Adsorption rate of Cd²⁺ ions on biochars.

3.2.2. Adsorption Kinetics

The kinetic curves of Cd²⁺ ions' adsorption on biochar with time are shown in Figure 5; the adsorption capacities of eight types of biochars increased with time. Within 0–200 min, the adsorption amount of biochar gradually increased, and this period was the acceleration stage of adsorption. As shown in Figure 5d, FMBC1 and FMBC2 accelerated faster than the other six biochars, and tended towards equilibrium after 200 min. As shown in Figure 5b,c, FBC1, FBC2, MBC1, and MBC2 were in the acceleration stage when the adsorption reaction lasted for 150–400 min, and reached the adsorption equilibrium after 400 min. As shown in Figure 5a, BC1 and BC2 reached adsorption equilibrium at about 540 min, and the adsorption amount was the lowest. The rules of the adsorption capacity of eight types of

biochar can be obtained as: FMBC1 > MBC1 > FMBC2 > BC1 > BC2 > MBC2 > FBC2 > FBC1. The equilibrium adsorption quantity of FMBC1 was the highest; this might be because it was loaded with more active sites and functional groups, which was conducive to the adsorption of Cd^{2+} ions, thereby enhancing the complexation of biochar to Cd^{2+} ions and increasing the cation exchange of biochar quantity. The adsorption capacity of MBC2, FBC2, and FBC1 was lower than that of the original biochar; this showed that the modification of biochar increases its porosity, active sites, and functional groups, but it also caused the internal pore size of the biochar to become smaller, which prevented Cd^{2+} ions from entering the inside of the biochar. It could not significantly increase the adsorption capacity of Cd^{2+} ions; on the contrary, although the original biochar had small porosity, fewer active sites, and functional groups, its surface was smooth and there were no small particles in the interior, so the adsorption resistance was reduced, the adsorption capacity was higher than that of some modified biochar, and the adsorption capacity should be larger.

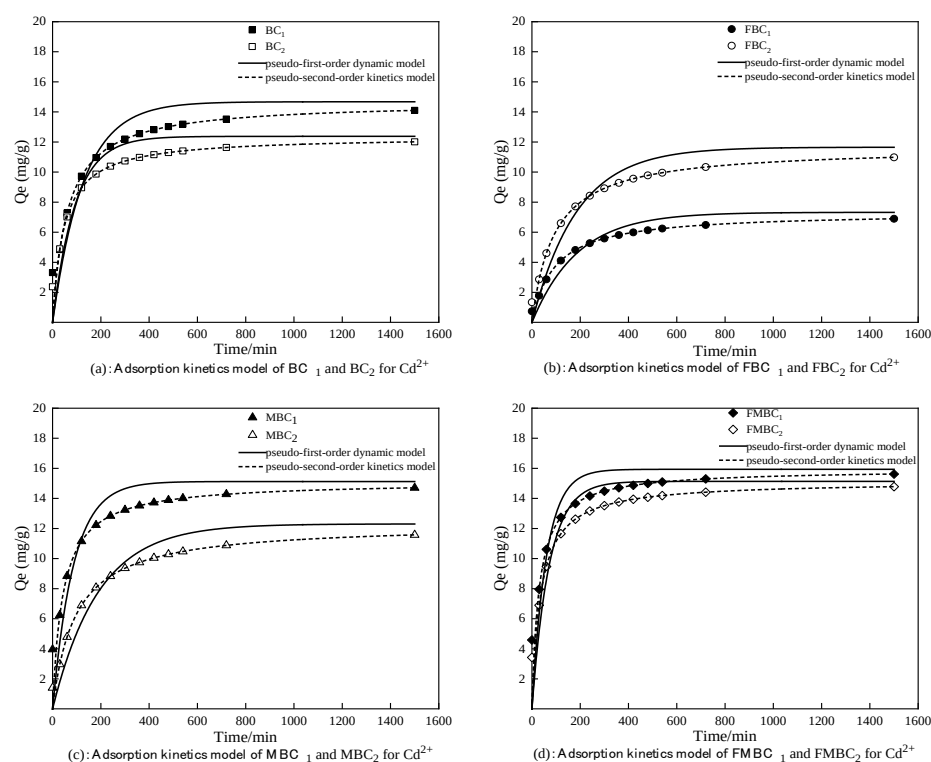


Figure 5. Adsorption kinetics diagrams of Cd^{2+} ions adsorption by biochars.

The curve fitted by the pseudo-first-order kinetic equation and the pseudo-second-order kinetic equation are shown in Figure 5. The fitting coefficient R^2 of the pseudo-second-order kinetic equation of each biochar was greater than that of the pseudo-first-order kinetic equation, so the adsorption process of eight types of biochar in accordance with the pseudo-second-order kinetic model and the adsorption mode was mainly chemical adsorption [46,47].

The kinetic adsorption test showed that the adsorption effect of FMBC1 on Cd^{2+} ions was better than other biochars, and the adsorption effect of the rice biochar was better than that of the corn biochar, which indicated that the rice straw biochar was more suitable for FeCl_3 , MnCl_2 , and $\text{Fe}(\text{NO}_3)_3$ & KMnO_4 modification than corn straw biochar.

3.2.3. Isothermal Adsorption

The isothermal adsorption curves of Cd^{2+} ions adsorbed by modified biochar are shown in Figure 6. The adsorption capacity increased slowly with the increase of equilibrium concentration. Generally speaking, the adsorption efficiency of BC1, FBC1, MBC1, and FMBC1 was higher than that of BC2, FBC2, MBC2, and FMBC2. As shown in Table 1, it was

found that the fitting coefficients R^2 in the Freundlich equation of FBC1, FBC2, FMBC1, and FMBC2 were greater than those in the Langmuir equation, while the fitting coefficient R^2 in the Freundlich equation of MBC1 and MBC2 were less than those in the Langmuir equation, indicating that the adsorption process of Cd^{2+} ions by FBC1, FBC2, FMBC1, and FMBC2 in accordance with the Freundlich model and the types of adsorption was multilayer adsorption. The adsorption process of Cd^{2+} ions by MBC1 and MBC2 were in accordance with the Langmuir model, and the type of absorption was monolayer adsorption.

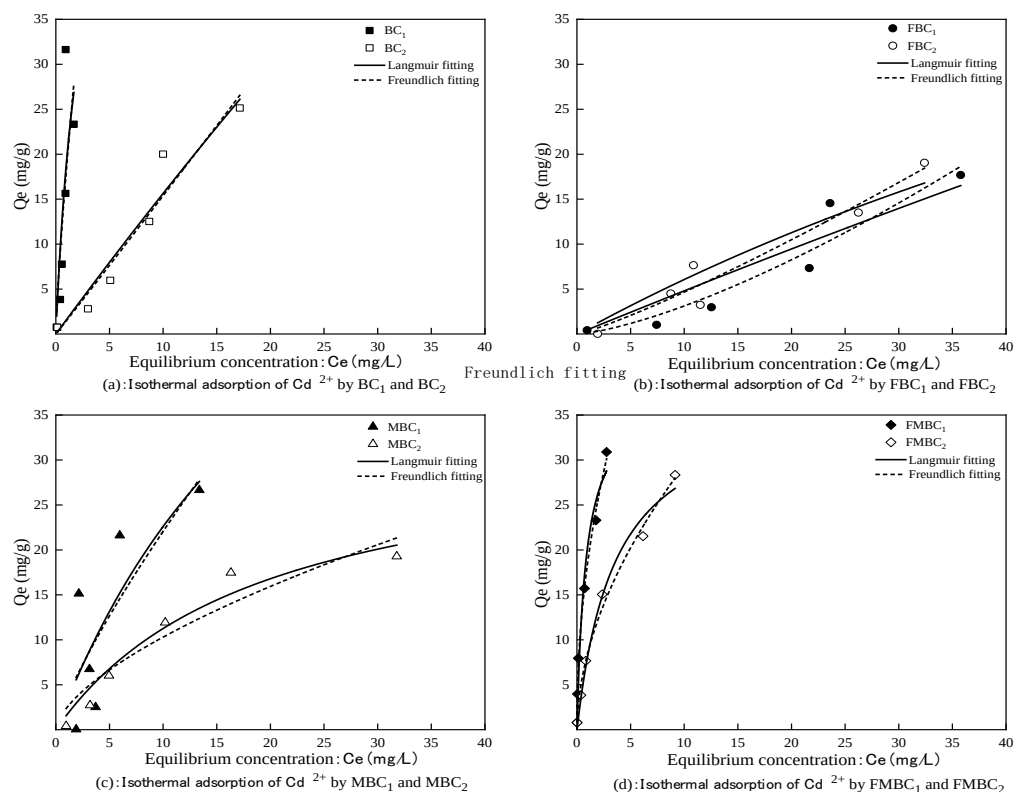


Figure 6. The adsorption isotherms of Cd^{2+} ions by biochars.

Table 1. Fitting parameters of the Cd^{2+} ions isotherm adsorption curve of original biochar and modified biochar.

Biochar Species	Langmuir Equation			Freundlich Equation		
	$K_L/(\text{L}\cdot\text{mg}^{-1})$	$Q_m/(\text{mg}\cdot\text{g}^{-1})$	R^2	$K_F/(\text{L}\cdot\text{mg}^{-1})$	$1/n$	R^2
BC1	0.417	20.304	0.953	8.553	0.782	0.942
BC2	0.004	30.371	0.921	1.503	1.010	0.920
FBC1	0.002	50.273	0.859	0.124	1.401	0.884
FBC2	0.008	93.748	0.911	0.316	1.170	0.934
MBC1	0.039	40.893	0.974	3.482	0.802	0.946
MBC2	0.052	33.018	0.947	2.418	0.630	0.887
FMBC1	1.198	37.453	0.955	18.602	0.474	0.995
FMBC2	0.281	37.284	0.983	8.507	0.538	0.989

In the Langmuir and Freundlich equations, K_L , K_F and $1/n$ reflected the adsorption efficiency of biochar for heavy metals [46–48]. Many studies have shown that the greater the K_L and K_F values, the better the biochar adsorption effect, and when $0.1 < 1/n < 0.5$, it was easy for the adsorption process to occur; when $1/n > 2$, the adsorption process was difficult [47,48]. As shown in Table 1, the K_F of FMBC1 was the largest, indicating that FMBC1 had the largest adsorption affinity for Cd^{2+} ions. The $1/n$ of FMBC1 was 0.474, which was smaller than that of other biochars, indicating that it was easier for FMBC1 to adsorb Cd^{2+} ions than for other biochars.

4. Conclusions

The kinetic adsorption test showed that the Cd^{2+} ions adsorption process of the eight types of biochar were in accordance with the quasi-two-stage kinetic adsorption model, and the adsorption mode was mainly chemical adsorption. The FMBC1 had the best adsorption capacity on Cd^{2+} ions in aqueous solution, while the FBC1 had the lowest adsorption capacity for Cd^{2+} ions. As a whole, the adsorption effect of rice straw biochars was better than that of the corn straw biochar, $\text{BC1} > \text{BC2}$, $\text{MBC1} > \text{MBC2}$, $\text{FMBC1} > \text{FMBC2}$.

Isothermal adsorption experiments showed that biochar modification could change its adsorption mechanism to some extent; the adsorption of Cd^{2+} ions by FMBC1, FMBC2, FBC1, and FBC2 conformed to the Freundlich equation, which was multi-layer adsorption, while BC1, BC2, MBC1, and MBC2 conformed to the Langmuir model, which was single-layer adsorption. Compared with other seven types of biochar, the K_F value of FMBC1 was the largest, and its $1/n$ value was the smallest, indicating that the adsorption effect on Cd^{2+} ions of FMBC1 was the best.

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Conflicts of Interest: The authors declare no conflict of interest.

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