Adsorption Mechanism of Hexavalent Chromium on Biochar: Kinetic, Thermodynamic, and Characterization Studies

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ABSTRACT: The adsorption mechanism of Cr\textsuperscript{6+} on biochar prepared from corn stalks (raw carbon) was studied by extracting the organic components (OC) and inorganic components (IC). Scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy were used to characterize the properties of three kinds of carbon. Kinetic and thermodynamic experiments were performed. The results showed that the experimental data were fitted well by the Freundlich model and the pseudo-second-order kinetic model, and the adsorptions on the three kinds of carbon were all spontaneous, endothermic processes. The adsorption of Cr\textsuperscript{6+} by biochar was in accordance with a chemisorption process. The adsorption contribution rate of the OC was 97%, which was much higher than that of the IC. Electrostatic attraction and redox reaction were the main mechanisms of adsorption, and among them, the contribution rate of the redox reaction accounted for 61.49%. The reduced Cr\textsuperscript{3+} could both exchange ions with K\textsuperscript{+} and dissociate into solution by electrostatic repulsion; the amount of Cr\textsuperscript{3+} released into the solution was approximately 17.07 mg/g, and the amount of Cr\textsuperscript{3+} ions exchanged with K\textsuperscript{+} was 0.29 mg/g. These results further elucidate the adsorption mechanism of Cr\textsuperscript{6+} by biochar.

1. INTRODUCTION

In recent years, heavy metal pollution has posed a serious challenge to the ecological environment and human health because of its cumulative, latent, and nondegradable characteristics. Chromium, a highly toxic pollutant, is produced from electroplating, mining, tanning, and other industrial processes. Chromium is a polyvalent metal which mainly exists in the form of Cr\textsuperscript{6+} and Cr\textsuperscript{3+} and has been identified as a top-priority contaminant by the U.S. Environmental Protection Agency because of its high teratogenicity. Therefore, it is of great significance to explore a simple and effective technique for the elimination of Cr\textsuperscript{6+} pollution. There are many methods to reduce Cr\textsuperscript{6+} contamination, such as chemical precipitation, membrane separation, adsorption, and so on. Among them, adsorption has attracted increasing attention because of its simple, low-cost, and high-efficiency characteristics.

Biochar, a low-cost and environmentally friendly adsorbent, is a carbon solid produced by relatively low-temperature pyrolysis of biomasses such as wood chips and straws (<700 °C). It has been demonstrated that biochar can effectively remove organic pollutants and heavy metals when used as an adsorption material.

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with alkaline substances such as CO$_3^{2-}$ in the IC.$^{17}$ It has been indicated that both the IC and OC in biochar play important roles in the adsorption of metal ions through different mechanisms. At present, research has focused on the removal of pollutants by biochar as a whole. However, studies on how the biochar components adsorb, the mechanisms by which they adsorb, and the quantification of adsorption for a particular metal ion are limited.

In this study, the OC and IC of biochar were prepared by pickling and high-temperature pyrolysis. The adsorption experiments for Cr$^{6+}$ were performed, and biochar before and after adsorption was characterized. Thermodynamic and kinetic experiments were conducted simultaneously, and the experimental data were fitted with the isotherm models and kinetic equations. The adsorption mechanisms of Cr$^{6+}$ on biochar were explored through experimental data analyses and characterizations, which provided empirical evidence and theoretical confirmation for the elucidation of the adsorption mechanism of Cr$^{6+}$ by biochar.

2. RESULTS AND DISCUSSION

2.1. XRD Analysis of the Different Components of Biochar before and after the Adsorption of Cr$^{6+}$. Carbon in raw carbon (RC) existed mainly in the form of graphite ($2\theta = 26.6$) and contained small amounts of KCl ($2\theta = 22.0$), SiO$_2$ ($2\theta = 29.4$), and CaCO$_3$ ($2\theta = 29.4$) (Figure 1a). The pH of the RC was alkaline because of the presence of CaCO$_3$ (Table 1). There was a small amount of KCl, consistent with the conclusion proposed by Guo and Thy et al. that KCl crystals in rice-based biochar are generated by pyrolysis at 500 °C.$^{18,19}$ There were some small peaks at 2$\theta = 74.3$ and 10.6, which were KCl and CaCO$_3$, respectively. The culprit was the silica—carbon components in the IC, and their melting and decomposition of KCl, CaCO$_3$, and CO$_3^{2-}$ effectively remove metal and inorganic ions such as Ca$^{2+}$, K$^+$, and CO$_3^{2-}$.$^{20}$ The pH of the OC was lower than that of the RC (Table 1), possibly due to the replacement of cations in the functional groups such as $-COOM$ (where M is a metal cation) with H$^+$ during the pickling process.$^{21}$ The proportion of C in the IC (the product of the RC pyrolyzed at 800 °C) was relatively decreased, whereas the quantities of KCl, CaSiO$_3$, and CaCO$_3$ had significantly increased (Figure 1a); these differences in the chemical compositions account for the higher pH of the IC, as compared with that of the OC. This finding is consistent with the conclusion that heat treatment could effectively remove metal and inorganic ions such as Ca$^{2+}$, K$^+$, and CO$_3^{2-}$.$^{20}$ The pH of the OC was lower than that of the RC (Table 1), possibly due to the replacement of cations in the functional groups such as $-COOM$ (where M is a metal cation) with H$^+$ during the pickling process.$^{21}$ The proportion of C in the IC (the product of the RC pyrolyzed at 800 °C) was relatively decreased, whereas the quantities of KCl, CaSiO$_3$, and CaCO$_3$ had significantly increased (Figure 1a); these differences in the chemical compositions account for the higher pH of the IC, as compared with that of the OC. This finding is consistent with the conclusion that heat treatment could effectively remove metal and inorganic ions such as Ca$^{2+}$, K$^+$, and CO$_3^{2-}$.$^{20}$ The pH of the OC was lower than that of the RC (Table 1), possibly due to the replacement of cations in the functional groups such as $-COOM$ (where M is a metal cation) with H$^+$ during the pickling process.$^{21}$ The proportion of C in the IC (the product of the RC pyrolyzed at 800 °C) was relatively decreased, whereas the quantities of KCl, CaSiO$_3$, and CaCO$_3$ had significantly increased (Figure 1a); these differences in the chemical compositions account for the higher pH of the IC, as compared with that of the OC. This finding is consistent with the conclusion that heat treatment could effectively remove metal and inorganic ions such as Ca$^{2+}$, K$^+$, and CO$_3^{2-}$.$^{20}$ The pH of the OC was lower than that of the RC (Table 1), possibly due to the replacement of cations in the functional groups such as $-COOM$ (where M is a metal cation) with H$^+$ during the pickling process.$^{21}$ The proportion of C in the IC (the product of the RC pyrolyzed at 800 °C) was relatively decreased, whereas the quantities of KCl, CaSiO$_3$, and CaCO$_3$ had significantly increased (Figure 1a); these differences in the chemical compositions account for the higher pH of the IC, as compared with that of the OC. This finding is consistent with the conclusion that heat treatment could effectively remove metal and inorganic ions such as Ca$^{2+}$, K$^+$, and CO$_3^{2-}$.$^{20}$ The pH of the OC was lower than that of the RC (Table 1), possibly due to the replacement of cations in the functional groups such as $-COOM$ (where M is a metal cation) with H$^+$ during the pickling process.$^{21}$ The proportion of C in the IC (the product of the RC pyrolyzed at 800 °C) was relatively decreased, whereas the quantities of KCl, CaSiO$_3$, and CaCO$_3$ had significantly increased (Figure 1a); these differences in the chemical compositions account for the higher pH of the IC, as compared with that of the OC. This finding is consistent with the conclusion that heat treatment could effectively remove metal and inorganic ions such as Ca$^{2+}$, K$^+$, and CO$_3^{2-}$.$^{20}$ The pH of the OC was lower than that of the RC (Table 1), possibly due to the replacement of cations in the functional groups such as $-COOM$ (where M is a metal cation) with H$^+$ during the pickling process.$^{21}$

![Figure 1. (a) XRD spectra before the adsorption of Cr$^{6+}$ by RC, OC, and IC; (b−d) XRD comparison patterns before and after adsorption by RC, OC, and IC.](https://example.com/figure1.png)

![Table 1. Change of pH before and after the Adsorption of Three Kinds of Carbon](https://example.com/table1.csv)
OC (Table 1). The oxygen-containing functional groups in the OC could reduce Cr$^{6+}$ to Cr$^{3+}$. Lyubchik et al. (2004) proposed that the adsorption mechanism of Cr$^{3+}$ by biochar was ion exchange or a combination of ion exchange and surface complexation. Therefore, the generated Cr$^{3+}$ may undergo ion exchange with K$^+$, which resulted in a significant reduction or elimination of KCl in the IC (Figure 1d).

2.2. SEM Analysis of Different Components of Biochar before the Adsorption of Cr$^{6+}$. The RC used here is a by-product of corn stalk, produced by oxygen-limited pyrolysis at 500 °C. Many regularly arranged pores in the RC were visible at a certain magnification (Figure 2a), which indicated that the fatty components had been completely decomposed at 500 °C. These macropores are what remained after the catheter structures in the plant tissue were pyrolyzed. The fiber bundles in the OC were more obvious than those in the RC, and many spherical crystals appeared (Figure 2b). Most of the ash and mineral components had been washed away from the RC by the erosion of the strong acids used for pickling, causing the apertures to become wider and the insoluble residual silica to aggregate as spherical crystals on the surface. The IC, prepared by pyrolysis at 800 °C for 4 h, contained many bar-shaped crystals on the surface (Figure 2c), which may be KCl crystals, according to the analysis shown in Figure 1d.

2.3. Analysis of the Optimal pH and the Adsorption Capacity. Many experiments have shown that the solution pH can significantly affect the removal of Cr$^{6+}$ by biochar. Because Cr$^{6+}$ as an anion contaminant is electronegative, the gravitation or repulsion between carbonaceous materials and Cr$^{6+}$ would dominate its adsorption behavior. Therefore, exploring the influence of solution pH on the adsorption of Cr$^{6+}$ was of great significance. The increases in the solution pH of the three kinds of biochar after adsorption were the largest when the pH was 2−4 before adsorption (Figure 3). However, as the initial solution pH increased, the increased value of the solution pH after adsorption gradually declined because the main adsorption mechanisms of Cr$^{6+}$ by biochar are adsorption—reduction—adsorption and desorption. During the adsorption process, the pH of the solutions always remained acidic and less than their respective pH$_{pzc}$ (Table 1), resulting in the three types of carbon having positive surface charges and surface functional groups that remained in a strong protonated state. Cr$^{6+}$ mainly existed in the form of
Table 2. Fitting Parameters of the F and D–R Adsorption Isotherm Models

| carbon | temperature (K) | $K_F$ | $1/n$ | $R^2$ | $\ln q_m$ | $E$ | $R^2$ |
|--------|----------------|-------|-------|-------|----------|-----|-------|
| RC     | 293            | 1.67  | 0.31  | 0.997 | 11.08    | 12.66 | 0.995 |
|        | 303            | 4.74  | 0.16  | 0.991 | 4.61     | 10.28 | 0.997 |
|        | 313            | 5.21  | 0.15  | 0.999 | 5.19     | 11.85 | 0.987 |
| OC     | 293            | 3.22  | 0.39  | 0.994 | 6.28     | 19.49 | 0.992 |
|        | 303            | 4.55  | 0.21  | 0.986 | 5.61     | 12.13 | 0.986 |
|        | 313            | 9.88  | 0.15  | 0.999 | 5.95     | 10.54 | 0.989 |
| IC     | 293            | 1.15  | 0.27  | 0.984 | 6.26     | 14.71 | 0.994 |
|        | 303            | 3.47  | 0.17  | 0.997 | 6.35     | 10.98 | 0.988 |
|        | 313            | 8.42  | 0.09  | 0.995 | 8.24     | 8.84  | 0.999 |

HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ under acidic conditions. Therefore, there was a strong electrostatic adsorption between Cr$^{6+}$ and the biochar surfaces, and H$^+$ in the solutions was consumed, causing the adsorption capacities to be gradually diminished as the pH increased.

XPS analysis showed the characteristic peaks at 577.5, 579.5 and 587.2, 588.2 eV, corresponding to the Cr 2p$_{1/2}$ orbital peak and Cr 2p$_{3/2}$ orbital peak, respectively. The peak at 579.0–578.0 eV was considered to be Cr$^{3+}$, and the peak at 579.0–579.5 eV was attributed to Cr$^{2+}$ (Figure 4a). A portion of Cr$^{6+}$ was reduced to Cr$^{3+}$ after being adsorbed by biochar (Figure 4a), which confirmed that reduction was one of the removal mechanisms of Cr$^{6+}$. Figure 4b shows the infrared spectra before and after the adsorption of Cr$^{6+}$ by the three kinds of carbon. The vibration absorption peaks of hydroxyl (O–H) at 3440 cm$^{-1}$ had decreased to varying degrees, and the absorbance of the RC and OC decreased from 0.8996 to 0.7612 and 0.8489 to 0.7192, respectively. At the same time, the absorbance also significantly decreased at 1480 cm$^{-1}$ after Cr$^{6+}$ was absorbed by the RC and OC, and the vibration peak at 1480 cm$^{-1}$ was attributed to a conjugated π-band (Figure 4b). Chen et al. (2020) proposed that the reduction of Cr$^{6+}$ was an electron-consuming process, and some electron-donor groups such as hydroxyl and aromatic π-conjugated systems could provide electrons to Cr$^{6+}$ because of the strong affinities for Cr$^{6+}$ under acidic conditions.$^{29-31}$

From what has been discussed above, we determined that acid conditions and oxygen-containing functional groups were favorable to the adsorption and the reduction of Cr$^{6+}$ into Cr$^{3+}$ according to the following formulas:

$$R-\text{OH}_2^+ + \text{HCrO}_4^- \rightarrow R-\text{OH}_2\text{CrO}_4^- + \text{H}^+$$ (1)

$$\text{HCrO}_4^- + 3e^- + 7\text{H}^+ \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}$$ (2)

In the adsorption and desorption stages, the reduced Cr$^{3+}$ existed as a cation. Meanwhile, the solution pH values after adsorption were still less than their respective pH$_{pzc}$ values (Table 1), which maintained a positive surface charge on the three kinds of biochar. This resulted in electrostatic repulsion between the reduced Cr$^{3+}$ and the carbon surface, and some of the Cr$^{3+}$ ions were released into the solution. At the same time, OH$^-$ hindered the affinity between Cr$^{6+}$ and oxygen-containing functional groups with the increase of pH$_1$, leading to the significantly lessened reduction of Cr$^{6+}$. Therefore, the adsorption capacity of Cr$^{6+}$ by biochar decreased greatly with the increase of the initial solution pH. However, the adsorption capacities of the RC and OC were much greater than that of the IC (Figure 3) because the IC contained fewer functional groups than the RC and OC (Figure 4b). As a result, the electron-donor ability of IC was weaker than that of the RC and OC. In other words, the removal of Cr$^{6+}$ by the IC was the result of adsorption, whereas that by the RC and OC was the result of double reactions of electrostatic adsorption and redox reaction. Therefore, the adsorption capacity of IC for Cr$^{6+}$ was smaller than that of the RC and OC and was not detectable using the XPS adsorption analysis of the IC (Figure 4a).

2.4. Adsorption Isotherm. In this study, three adsorption isotherm models [Langmuir (F), Freundlich (F), and Dubinin–Radushkevich (D–R)] were adopted to fit the adsorption data.$^{33,34}$ However, the experimental data were more consistent with the Freundlich model and the Dubinin–Radushkevich model.

The formula of the F model is as follows

$$\ln q_e = \ln K_F + \frac{-1}{n} \ln C_e$$ (3)

where $q_e$ is the adsorption capacity per unit mass adsorbent at equilibrium time (mg/g), $C_e$ is the concentration of adsorbate in the solution at equilibrium time (mg/L), $K_F$ is the Freundlich constant, and $n$ expresses the adsorption strength. The value of $n$ is usually greater than 1; adsorption occurs easily if $1/n$ is between 0.1 and 1, and a value otherwise would indicate that adsorption is difficult.$^{35,36}$ The formula of the D–R model is as follows

$$\ln q_m = \ln q_m - \beta e^2$$ (4)

where $\beta$ is the adsorption energy constant (mol$^2$/kJ$^2$) and $e$ is the Polanyi potential energy.

$$e = RT \ln \left(1 + \frac{1}{C_e}\right)$$ (5)

$$E = \frac{1}{\sqrt{2\beta}}$$ (6)

The average free energy ($E$) can be calculated using $\beta$. A physical adsorption process is indicated by $E < 8.0$ kJ/mol, and an ion-exchange mechanism is indicated by 8.0 kJ/mol $< E < 16.0$ kJ/mol.$^{37}$

The experimental data were applied to the above formulas, and the slopes, intercepts, adsorption constants, and correlation coefficients were obtained accordingly. The value of $K_F$ in the F model reflects the difference of adsorption performance with temperature. The $K_F$ values of the three kinds of carbon were all increased with an increase in temperature (Table 2), which indicated that the adsorptions of Cr$^{6+}$ by the three types of carbon were endothermic.
processes. The $1/n$ values of the three carbons were all between 0 and 1 (Table 2), indicating that the three kinds of carbon easily adsorbed Cr$^{6+}$.37 According to the D−R model, $E$ represents the average free energy of the adsorbate transferred from the solution to a solid surface, which is independent of temperature but is dependent on the nature of the adsorbent and adsorbate.38 The $E$ values of the three types of carbon were between 8 and 16 kJ/mol (Table 2), indicating that the adsorption processes of Cr$^{6+}$ by the three types of carbon occurred by ion exchange,33 which is consistent with the conclusion that the reduction of KCl was due to ion exchange with the reduced Cr$^{3+}$.

2.5. Adsorption Thermodynamics. Through the calculation of thermodynamic parameters such as adsorption enthalpy ($\Delta H$), adsorption free energy ($\Delta G$), and adsorption entropy ($\Delta S$), the adsorption mechanisms of Cr$^{6+}$ on biochar could be further elucidated. The specific formulas are as follows

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

(7)

where $K_d$ is the distribution coefficient, $T$ is the absolute temperature of the solution (K), and $R$ is the universal gas constant ($8.314 \text{ J/K mol}$); $\Delta H^0$ and $\Delta S^0$ can be obtained by calculating the slope and the intercept. $K_d$ and $\Delta G^0$ can be obtained from the following formula

$$K_d = \frac{q_e}{C_e}$$

(8)

where $q_e$ and $C_e$ are the same as in eq 3. The $\Delta G^0$ value can be calculated according to the van’t Hoff equation39

$$\Delta G^0 = -RT \ln K_d$$

(9)

The $\Delta G$ values of the three carbons at the different experimental temperatures were all negative, and their absolute values increased with an increase of temperature (Table 3), which indicated that the adsorptions of Cr$^{6+}$ by biochar were spontaneous, and the increases of temperature were beneficial to adsorption.40 However, the absolute values of $\Delta G$ at the same temperatures were reduced as the initial concentrations increased (Table 3), indicating that the mass transfer driving force was not the factor that controlled the adsorption process. It can be gleaned from the above discussion that the redox reaction between oxygen-containing functional groups and Cr$^{6+}$ impacted the adsorption process of Cr$^{6+}$.

The $\Delta H$ values of the three kinds of carbon at three different concentrations were greater than 0 (Table 3), indicating that the adsorption processes were endothermic, and the increase of temperature was favorable to adsorption, consistent with the conclusion of the F model. Generally, the heat of physical adsorption (8.37−62.8 kJ/mol) was less than that of chemical adsorption (125.6−418.68 kJ/mol). The $\Delta H$ values of the three carbons were basically in the latter range (Table 3), which indicated that the adsorption mechanism of Cr$^{6+}$ was chemisorption.41 In addition, if only ion exchange had occurred during the adsorption process, $\Delta H$ should be less than 8.4 kJ/mol.42 However, the $\Delta H$ values of the three types of carbon were much larger than 8.4 kJ/mol (Table 3), indicating that not only had ion exchange occurred, but other chemical reactions, such as the reduction of Cr$^{6+}$ to Cr$^{3+}$, had also occurred during the adsorption process. In short, the adsorption of Cr$^{6+}$ was a complicated chemical process.

The $\Delta S$ value was greater than 0 and increased with an increase of the initial concentrations (Table 3), indicating that both the free movement and the freedom degree of Cr$^{6+}$ in solution were increased.43 Lyubchik et al. (2004) proposed that the occurrences of ion exchange and displacement reactions lead to the formation of steric hindrance, which

| carbon | initial concentration (mmol/L) | $\Delta H$ (J/mol) | $\Delta S$ (J/mol K) | $\Delta G$ (kJ/mol) |
|--------|--------------------------------|-------------------|---------------------|-------------------|
| RC     | 1                              | 341.27            | 133.42              | 146.39            |
|        | 2                              | 139.61            | 57.78               | 128.95            |
|        | 3                              | 126.16            | 28.73               | 120.41            |
| OC     | 1                              | 387.11            | 147.15              | 142.65            |
|        | 2                              | 135.01            | 56.16               | 128.59            |
|        | 3                              | 122.83            | 14.54               | 124.39            |
| IC     | 1                              | 435.16            | 166.25              | 152.56            |
|        | 2                              | 236.59            | 57.14               | 129.86            |
|        | 3                              | 122.74            | 15.69               | 122.92            |

Table 3. Thermodynamic Parameters of Different Concentrations of Cr$^{6+}$ on the Three Kinds of Carbon

Figure 5. (a) PFO dynamic model diagram; (b) PSO dynamic model diagram.
types of carbon were analyzed with Origin 9. Great deviation between the experimental values were lower than those of the PSO kinetic model, which led to a constant (rate is controlled by the chemisorption mechanism, so the rate decreases with the removal of Cr6+ by the IC was correspondingly very weak. As a result, the adsorption contribution rates were numerically more similar, and the χ2 values for Cr6+ were stronger than that of the RC. Wan et al. (2019) proposed that the adsorption rate of Cr6+ was physically influenced by the porous structure, chemical functional groups, and adsorption sites. The Brunauer—Emmett—Teller (BET) value of the RC was much larger than that of the OC (Table 4), yet the K2 value of the OC was larger than that of the RC.44 This indicates that intraparticle diffusion was not the limiting step of adsorption.

### 2.7. Adsorption Contribution Rate of Each Component for Cr6+

The adsorption contribution rates of the biochar components for Cr6+ were estimated by considering the mass percentage of the OC and IC (Table 1). The experimental and theoretical contribution rates were close to 1 (Table 4) because of the complexity of the biochar components; a small amount of SiO2 in the OC was not picked off, and a small amount of C remained in the IC (Figure 1). However, the theoretical and experimental contribution rates were numerically more similar, and χ2 analysis showed that there was little deviation between them, indicating that the adsorption of Cr6+ conformed more to the PSO kinetic model. The contribution rate of the OC reached 96–97%, indicating that the OC played an important role in the removal of Cr6+.

Figure 6a illustrates the adsorption conversion process of Cr6+ by biochar. The adsorption capacity of the RC for Cr6+ was 27.76 mg/g (Table 4), and the content of Cr3+ in solution was 1.48 mg/g when equilibrium was reached (Figure 6b).
Therefore, a total of 26.28 mg/g chromium (Cr(VI) and Cr(III)) had adsorbed on the RC surface. As can be seen in Figure 4a, Cr(VI) accounted for 40.69% and Cr(III) accounted for 59.31% (mass percentages) after Cr(VI) was adsorbed by the RC, so the contents of Cr(VI) and Cr(III) were 10.69 and 15.59 mg/g, respectively. Cr(III) was equal to the sum of Cr(III) and Cr(III) when the adsorption reached equilibrium. According to the above analysis, the Cr(III) content was 17.07 mg/g, which accounted for 61.49% of the experimental adsorption value (27.76 mg/g) and 39.63% of the initial chromium content. The maximum leaching content of K+ reached 0.63 mg/g with the extension of the adsorption time, indicating that there was ion exchange between 0.29 mg/g Cr(III) and K+.

2.8. Adsorption Mechanism of Biochar for Cr(VI). In recent years, adsorption has become the main method for the removal of Cr(VI), and the exploration of the adsorption mechanisms of Cr(VI) through adsorption thermodynamics and adsorption kinetics has become the primary focus of research. The adsorption parameters of Cr(VI) by various adsorbents have been listed in the literature (Table 5). The mechanisms of adsorption by the adsorbents were all consistent with the PSO kinetic model, indicating the adsorption of Cr(VI) by these materials occurs by chemisorption. Some isotherm types conform to the Langmuir equation, and some conform to the Freundlich equation, depending on the heterogeneity of the adsorbent surface. The optimum adsorption pH of Cr(VI) in all studies was 2 because the acidic conditions are conducive to the chromium content. The maximum leaching content of K+ of the IC was much larger than that of the OC, and K+ could be released into the solution by ion exchange with K+.

4.4. Adsorption Experiments. 4.4.1. Adsorption Thermodynamics Experiment. Different concentrations of K2Cr2O7 solutions were prepared, and the components of biochar were added to a solid–liquid ratio of 1:200 (mass/volume), followed by mixing in a reciprocating oscillator at 150 rpm for 12 h at 20, 30, or 40 °C. The concentrations of Cr(VI) in the supernatants were determined by atomic absorption spectrophotometry after centrifugation, and the concentration of Cr(VI) was obtained by subtracting the concentration of Cr(III) from the total amount of chromium.

4.4.2. Adsorption Kinetics Experiment. A 2.0 mM K2Cr2O7 solution was prepared. In accordance with a specific solid–liquid ratio of 1:200, the various components of biochar were added, and the mixture was agitated at 150 rpm in a reciprocating oscillator at 25 °C. The concentrations of Cr(VI) were determined after centrifugation at regular intervals until they remained constant. The concentrations of Cr(VI) and K+ in the solutions were determined simultaneously. All tests were conducted in triplicate.
4.4.3. Calculation of Adsorption Capacity. The amount of Cr(VI) adsorbed on biochar was calculated by the following formula

\[ q_e = \frac{V(C_0 - C_e)}{m} \]  \hspace{1cm} (12)

where \( q_e \) and \( C_e \) are the same as in eq 4. \( C_0 \) is the initial concentration, \( V \) is the volume of the solution (L), and \( m \) is the mass of the adsorbent.

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