Adsorption characteristics and mechanisms of Cd$^{2+}$ from aqueous solution by biochar derived from corn stover

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Corn stover could be pyrolysed to prepare biochar for removing pollutants in water and realizing the resource utilization of biomass. The aims of the present study were to investigate the optimal preparation and adsorption conditions of biochar and to reveal the adsorption characteristics and mechanisms of Cd$^{2+}$ in water by biochar. For this purpose, with Cd$^{2+}$ as the target pollutant, the pyrolysis conditions involved in the pyrolysis temperature, retention time, and heating rate were evaluated and optimized. Additionally, the characteristics, mechanisms and optimal adsorption conditions of Cd$^{2+}$ by biochar were determined. A series of characterization techniques was employed, including scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and specific surface area analysis ($S_{BET}$). The optimum pyrolysis parameters were a pyrolysis temperature of 700 °C, a retention time of 2.5 h, and a heating rate of 5 °C/min. Acid/base modification did not improve the adsorption capacity of biochar. The Langmuir and the Elovich model were the most suitable isotherm and kinetic models for equilibrium data, respectively. The maximum adsorption capacity fitted by Langmuir model was 13.4 mg/g. Furthermore, mineral precipitation and π electron interactions were shown to be the main adsorption mechanisms of Cd$^{2+}$. The optimum adsorption conditions for Cd$^{2+}$ in water were a CaCl$_2$ electrolyte solution of 0.01 mol/L, a pH level of 6.7, and a biochar dosage of 0.4 g. Our results indicated that corn stover biochar was an appropriate approach for improving the status of water with Cd$^{2+}$ contamination in the short term and for promoting a new perspective for the rational utilization of corn stover and the low-cost pollution control of heavy metals in water.

**Abbreviations**

- SEM: Scanning electron microscopy
- FTIR: Fourier transform infrared spectroscopy
- XRD: X-ray diffractometer
- TG/DTG: Thermogravimetric/Differential Thermogravimetry
- $S_{BET}$: Specific surface area
- CEC: Cation exchange capacity
- BC: Biochar
- BC-H: Biochars modified by acid
- BC-OH: Biochars modified by alkali

Cadmium (Cd$^{2+}$) is a harmful heavy metal element that is ubiquitous in aquatic environments$^{1,2}$. Cd$^{2+}$ has the characteristics of strong mobility, high biological toxicity, and difficulty in removal after entering the food chain$^{3}$. Cd$^{2+}$ can cause a series of adverse effects on animals and plants, such as oxidative stress, photosynthesis inhibition, and liver damage$^{4}$. Research has indicated that Cd$^{2+}$ can lead to the abnormal electrocardiogram of zebrafish$^{5}$. Additionally, Cd$^{2+}$ can affect the activities of key enzymes, such as lipoprotein lipase and liver lipase,
in liver metabolism, causing lipid and lipoprotein metabolism disorders and resulting in the fatty liver of fish\(^6\). Moreover, Cd\(^{2+}\) can inhibit plant growth and photosynthesis, interfering with ion metabolism and free radical formation\(^7\). Due to its strong ecological and toxicological effects, the control and remediation of Cd\(^{2+}\) pollution in water has attracted extensive attention. The removal of Cd\(^{2+}\) in water mainly includes physicochemical and bioremediation methods. Among these methods, adsorption has received extensive attention from researchers because of its simple operation, easy recovery and low cost\(^8\),\(^9\). Therefore, the selection of an adsorbent is essentially important for the removal of Cd\(^{2+}\) from water.

Biochar (BC) is a carbon-rich material obtained by the pyrolysis of biomass raw materials under anoxic and oxygen-limited conditions\(^10\). BC is often used as an adsorbent due to its large specific surface area and abundant functional groups. Previous studies have shown that BC prepared from different biomasses has a better removal effect on Cd\(^{2+}\) in water\(^11\)–\(^13\). Northern China is a major corn-growing region. The comprehensive utilization of a large amount of corn stover has always been an urgent problem to be solved. Therefore, solving this problem by preparing corn stover into biochar and using it to remove Cd\(^{2+}\) from water is a very good technique. To prove the feasibility of this view in this research, Cd\(^{2+}\) is taken as the target pollutant and corn stover as the biomass material for biochar. Orthogonal experimental design is used to optimize the factors affecting the preparation of biochar (pyrolysis temperature, retention time, and heating rate) with the removal rate of Cd\(^{2+}\) in water as the target. In this test stage, the Cd\(^{2+}\) removal performance is compared to the original biochar and the acid/base-modified biochar under the corresponding preparation conditions. Only BC with a good Cd\(^{2+}\) removal effect is further studied. This decision not only greatly reduces the workload of the experiment but also makes the characterization of the samples more targeted; thus, the produced biochar has a better Cd\(^{2+}\) removal effect. Subsequently, adsorption isotherms and kinetics are studied, combined with a series of characterization methods, to more comprehensively reveal the mechanism of Cd\(^{2+}\) removal by corn stover biochar. This study provides a systematic theoretical basis and support for the promotion and application of biochar in the treatment of cadmium-containing wastewater.

### Materials and methods

**Chemicals and materials.** All the chemicals in this experiment were obtained from Qinhuangdao Chemical Reagents Company (China) and were of analytical grade. We collected corn stover from local farmers, in Qinhuangdao, China.

**Preparation of corn stover biochar.** After cleaning, the corn stover was dried at 70 °C for 10 h and then pulverized. Then, corn stover was pyrolysed into biochar in a tube furnace under a nitrogen atmosphere. The optimal preparation conditions were screened by a three-factor, four-level orthogonal experiment. Sixteen biochars prepared under different conditions were labelled C1, C2, C3, C4, C5, C6, C7, C8, C9, C10, C11, C12, C13, C14, C15, and C16. The orthogonal experiment is shown in Table 1. Finally, the pyrolytic biochar was ground with a mortar and passed through a 200-mesh standard sieve.

Biochar modification was as follows: the biochars were mixed with 1 mol/L HCl (or NaOH) at a ratio of 1:10 (w/v), followed by ultrasonication for 10 min, then pressure filtration, and finally, the sample was washed to a neutral pH. Corn stover biochars modified by acid/alkali were labelled BC-H/BC-OH, respectively. The biochar preparation process is shown in Fig. 1.

**Characterization of corn stover biochar.** The S\(_\text{BET}\) of the biochar was measured by a specific surface area analyser (SSA-4000, BUILDER, China), and the functional groups of the biochar were determined by Fou-

### Table 1. Orthogonal experimental parameters.

| Sample | Temperature (°C) | Retention time (h) | Heating rate (°C/min) |
|--------|----------------|-------------------|----------------------|
| C1     | 400            | 1                 | 5                    |
| C2     | 400            | 1.5               | 10                   |
| C3     | 400            | 2                 | 15                   |
| C4     | 400            | 2.5               | 20                   |
| C5     | 500            | 1                 | 10                   |
| C6     | 500            | 1.5               | 5                    |
| C7     | 500            | 2                 | 20                   |
| C8     | 500            | 2.5               | 15                   |
| C9     | 600            | 1                 | 15                   |
| C10    | 600            | 1.5               | 20                   |
| C11    | 600            | 2                 | 5                    |
| C12    | 600            | 2.5               | 10                   |
| C13    | 700            | 1                 | 20                   |
| C14    | 700            | 1.5               | 15                   |
| C15    | 700            | 2                 | 10                   |
| C16    | 700            | 2.5               | 5                    |
rier transform infrared spectroscopy (FTIR) (8400S, SHIMAZU, Japan). The apparent structure of the biochar was characterized by scanning electron microscopy (SEM) (Supra55 Sapphire, ZEISS, Germany and COXEM, OPTON, China). Thermogravimetric (TG) analysis of corn stover was performed using a thermogravimetric analyser (Setsy Evolution, SETARAM, France), and the surface phases of biochar were analysed by X-ray diffraction (XRD) (SmartLab (9), RIGAKU, Japan). Biochar yields were calculated as the ratio between the weights of the corn stover before and after pyrolysis. The sample was added to deionized water at a ratio of 1:20 (w/v), and the suspension was shaken for 1 h and allowed to stand for 5 min. The pH was measured by a pH meter. The surface functional groups of biochar were determined by improved Bohem titration14,15, and the cation exchange capacity (CEC) of biochar was measured by sodium acetate-flame photometry14.

**Adsorption experiment.**  Optimization of biochar. Cadmium chloride hydrate (CdCl2·2.5H2O) was dissolved to prepare the Cd2+ stock solution and then diluted to various concentrations for adsorption experiments. Corn stover biochars (0.20 g original, acid modified and base modified) were added into a 50 mL polyethylene centrifuge tube containing 20 mL Cd2+ solution (100 mg/L) and 0.01 mol/L CaCl2 as the background electrolyte. After shaking at 25 °C and 150 rpm for 24 h, the mixture was passed through a 0.45 μm filter membrane. Finally, the concentration of Cd2+ in the solution was determined by flame atomic absorption spectrometry (AA-6800F/G, Shimazu, Japan). The equilibrium adsorption capacity (qe, mg/g) of biochar was calculated based on the differences in the Cd2+ contents in the solution before and after adsorption. The removal rate (Rr, %) was calculated by the ratio of adsorption capacity to Cd2+ content before adsorption. The adsorption capacity and the removal rate of Cd2+ were calculated according to Eqs. (1) and (2), respectively. Through the experiment, the biochar with the best adsorption performance for Cd2+ was screened.

\[ q_e = \frac{(C_0 - C_e) \times V}{m} \]  
\[ R_r(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \]  

**Adsorption isotherm experiment.** The biochar optimized in “Optimization of biochar” section was used for adsorption isotherm and adsorption kinetics experiments. Adsorption isotherm experiments were conducted with CdCl2 solutions of different initial concentrations (10, 50, 100, 200, 300, 400 and 500 mg/L). Other experimental steps were the same as those in “Optimization of biochar” section. The adsorption isotherm was drawn and fitted by Langmuir and Freundlich adsorption isotherm models16.

The Langmuir isotherm is as follows (Eq. 3):

\[ q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e} \]  

where \( q_{\text{max}} \) (mg/g) is the maximum adsorption capacity of the adsorbent at equilibrium, \( C_e \) (mg/L) is the equilibrium concentration of adsorbate, and \( K_L \) (L/mg) is the Langmuir isotherm constant.

The Freundlich isotherm is as follows (Eq. 4):

\[ q_e = K_F C_e^{1/n} \]  

where \( K_F \) (mg\(^{1-n}\) g\(^{-1}\) L\(^n\)) is the Freundlich isotherm constant and \( n \) is a constant.
Adsorption kinetics experiment. The concentration of Cd$^{2+}$ was measured at 13 points in time from mins to 1440 min. The adsorption experiment method was the same as that in “Optimization of biochar”. The adsorption capacity of biochar on Cd$^{2+}$ in water at different time points was fitted by pseudo-first-order (Eq. 5), pseudo-second-order (Eq. 6), Elovich (Eq. 7), and Webber–Morris intraparticle diffusion models (Eq. 8)$^{16-18}$:

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

\[
q_t = \frac{k_2 q_e^2 t}{1 + q_e t} 
\]

\[
q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t 
\]

\[
q_t = K_{id} t^{0.5} + C_i 
\]

where $q_t$ (mg/g) is the amount of adsorbate at time $t$, $K_1$ (h$^{-1}$) and $K_2$ (g mg$^{-1}$ h$^{-1}$) are the pseudo-first-order and pseudo-second-order reaction rate constants, respectively, $a$ (mg g$^{-1}$ min$^{-1}$) and $b$ (mg/g) are the initial adsorption rate and the desorption constant of the Elovich model, respectively, $t$ (h) is the reaction time, $K_{id}$ (mg g$^{-1}$ min$^{-0.5}$) is the intraparticle diffusion rate constant, and $C_i$ is a constant.

Factors influencing Cd$^{2+}$ adsorption by biochar. The biochar optimized in “Optimization of biochar” section was used to explore the optimal adsorption conditions. In this study, the experimental steps were the same as those in “Optimization of biochar” section, only increasing the Cd$^{2+}$ solution to 25 mL.

Electrolyte solution concentration. The concentrations of the electrolyte CaCl$_2$ solution were 0.01, 0.04, 0.08, 0.12, 0.16, and 0.3 mol/L, and the other factors remained unchanged. The optimal concentration of electrolyte solution was determined according to the removal rate of Cd$^{2+}$.

Initial pH value. Based on the research in “Electrolyte solution concentration” section, the influence of the initial pH value on the Cd$^{2+}$ removal rate was further discussed. We used 0.1 mol/l HCl or NaOH to adjust the initial pH values to 2, 3, 4, 5, 6, and 7.

Biochar dosage. Combined with the optimal electrolyte concentration and pH, the influence of biochar addition on the Cd$^{2+}$ removal rate was revealed. The biochar additions were 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g.

Results and discussion
Thermogravimetric/differential thermogravimetry analyses of corn stover. Thermogravimetric/Differential Thermogravimetry (TG/DTG) curves are shown in Fig. 2. The pyrolysis process of corn stover could be divided into three stages. The first stage was the dehydration stage, which occurred at approximately 55–125 °C, and the weight loss was mainly accounted for by water$^{19}$. The second stage was the pyrolysis stage, which occurred at approximately 200–400 °C and mainly involved the decomposition of cellulose, hemicellulose and a small amount of lignin. This process involved the generation of CO and CO$_2$, and the breaking of carbonaceous polymer bonds$^{20}$. In addition, a shoulder peak in the range of 265 to 300 °C in the DTG diagram could be caused by side chain decomposition and glycosidic bond cleavage of xylan during the pyrolysis of corn stover$^{21}$. The third stage was the carbonization stage, which occurred above 400 °C; this stage mainly involved the decom-
position of lignin. The carbonization process was relatively slow after 600 °C; this process was called the passive pyrolysis stage. In general, the TG loss in the pyrolysis process of corn stover was mainly from the moisture in the biomass sample in the first stage. Hemicellulose and cellulose decomposition occurred in the second stage, and lignin decomposition occurred in the third stage. In this experiment, the minimum pyrolysis temperature for the preparation of biochar was 400 °C. Therefore, the pyrolysis of biochar was relatively complete.

Characterization of biochar. Yield and specific surface area analyses. The yield and $S_{\text{BET}}$ are presented in Table 2. BC, BC-H and BC-OH represent the origin, acid-modified, and base-modified biochar, respectively. The yield of corn stover biochar exhibited a negative correlation with the temperature and decreased from 39.65% to 28.26% when the pyrolysis temperature increased from 400 to 700 °C. This phenomenon could have occurred due to the loss of more volatile substances and the thermal degradation of lignocellulose with increasing temperature, thus reducing the yield of biochar. The $S_{\text{BET}}$ of the original biochar showed little difference below 700 °C but increased significantly at 700 °C. Combined with the SEM analysis (Fig. 3), at low temperatures, more ashes on the surface of biochar could block its pores so that the change in $S_{\text{BET}}$ was not obvious. At 700 °C, because the ash content significantly reduced and the pyrolysis was more sufficient, the pores of the biochar were more developed, and the $S_{\text{BET}}$ significantly increased. The $S_{\text{BET}}$ of the acid/base-modified biochar increased with increasing temperature. The $S_{\text{BET}}$ of biochar was larger than that of the original biochar after acid and base modification at 400–600 °C. This phenomenon occurred because the porous structure of biochar was enhanced by acid and base modification. Moreover, pickling removed most of the inorganic substances in biochar and reduced ash content, while alkali washing removed the tar on the surface of biochar to a certain extent. However, at 700 °C, the $S_{\text{BET}}$ of biochar after acid/base modification was lower than that of the original biochar. Combined with the SEM (Fig. 4), the acid/base modification caused the nanopores of biochar to collapse into mesopores or macropores. Therefore, the well-developed pore structure of the biochar prepared at 700 °C was destroyed by acid/base modification, resulting in a significant decrease in $S_{\text{BET}}$.

Table 2. Yield and $S_{\text{BET}}$ of different biochars.

| Sample | Yield (%) | $S_{\text{BET}}$ (m$^2$/g) |
|--------|-----------|--------------------------|
|        | BC        | BC-H        | BC-OH        | BC        | BC-H        | BC-OH        |
| C1     | 38.104    | 32.477      | 36.322       | 3.960     | 6.050       | 5.512        |
| C2     | 39.653    | 31.953      | 37.917       | 4.143     | 6.601       | 5.734        |
| C3     | 35.221    | 31.791      | 32.563       | 4.334     | 7.277       | 6.284        |
| C4     | 35.472    | 30.438      | 32.431       | 4.401     | 5.998       | 5.766        |
| C5     | 32.106    | 28.583      | 30.639       | 4.554     | 11.899      | 6.179        |
| C6     | 33.701    | 31.023      | 32.042       | 3.849     | 12.597      | 5.231        |
| C7     | 30.268    | 26.657      | 29.313       | 4.679     | 22.027      | 6.457        |
| C8     | 31.864    | 28.054      | 29.083       | 4.780     | 15.927      | 5.618        |
| C9     | 29.319    | 26.442      | 26.628       | 3.745     | 39.018      | 6.53         |
| C10    | 29.103    | 26.133      | 29.141       | 4.045     | 20.546      | 7.621        |
| C11    | 30.622    | 27.989      | 28.427       | 4.228     | 20.496      | 10.644       |
| C12    | 30.047    | 27.053      | 28.372       | 3.792     | 33.216      | 8.494        |
| C13    | 28.258    | 24.855      | 24.913       | 6.271     | 14.047      | 6.333        |
| C14    | 28.653    | 26.203      | 27.224       | 30.439    | 25.261      | 8.948        |
| C15    | 28.391    | 25.534      | 26.766       | 81.682    | 17.684      | 58.25        |
| C16    | 30.024    | 27.171      | 28.135       | 52.156    | 17.469      | 25.305       |

Scanning electron microscopy analysis. The C1, C8, C12 and C16 biochars had the highest Cd$^{2+}$ removal rates at 400, 500, 600 and 700 °C, respectively. Therefore, these BCs were selected for SEM analysis. Figure 3 clearly showed that as the pyrolysis temperature increased from 400 to 700 °C, the pore structure of biochar became more developed, with a smaller pore size and more pores. Although there were numerous pores at 500 °C, the pores were not fully developed and were blocked inside. At 700 °C, the skeleton structure appeared, and the particle size of ash blocked in the pores decreased.

By taking C16 biochar with the highest removal rate of Cd$^{2+}$ as the research object, the changes in the biochar surface before and after modification were compared. C16-H and C16-OH represent acid-modified and base-modified biochar, respectively. After acid/base modification, the ash content on the surface of biochar decreased, and the pore size increased (Fig. 4). Therefore, some skeleton structures could collapse after corrosion, which was consistent with the previous $S_{\text{BET}}$ results. Sun et al. discovered that citric acid-modified biochar would lead to micropore wall collapse and micropore loss, resulting in a reduction in $S_{\text{BET}}$. This finding was in agreement with the results of our study.

Fourier transform infrared spectroscopy analysis. The FTIR spectra of biochar at different pyrolysis temperatures are presented in Fig. 5a.
As the pyrolysis temperature increased from 300 to 700 °C, the absorption peak intensity showed a downwards trend. There was a remarkable decrease in features associated with stretch O–H (3400 cm⁻¹) [32]. The vibration peaks of C–H (2924 cm⁻¹) and C=O (1610 cm⁻¹) decreased with increasing temperature, which could be due to the reduction in –CH₂ and –CH₃ groups of small molecules and the pyrolysis of C=O into gas or liquid byproducts at high temperatures [33]. In addition, the peak at 1435 cm⁻¹ was identified as the vibration of C=C bonds belonging to the aromatic skeleton of biochar. A decrease in the absorbance peaks was found at 1115 cm⁻¹, which corresponded to C–O–C bonds. The ratio of intensities for C=C/C=O (1550–1650 cm⁻¹) and C–O–C (1115 cm⁻¹) to the shoulder (1100–1200 cm⁻¹) gradually decreased, and the loss of –OH at 3444 cm⁻¹ indicated that the oxygen content in biochar reduced. The cellulose and wood components were dehydrated, and the degree of biochar condensation increased at higher temperatures. The bending vibration peaks of Ar–H at 856 and 877 cm⁻¹ changed little at different temperatures, which showed that the aromatic rings were relatively stable below 700 °C [34]. Combined with the above analysis the condensation degree of biochar increased gradually above 400 °C [35,36].

As the pyrolysis temperature increased, the degree of aromatization of biochar improved, and the numbers of oxygen-containing functional groups decreased continuously. Figure 5b showed that after acid/base modification, the absorbance peaks at 3444 cm⁻¹, 1610 cm⁻¹ and 1115 cm⁻¹ increased, indicating that the number of oxygen-containing functional groups increased. However, the stretching vibration peak of aromatic ring skeleton C=C (1435 cm⁻¹) and the bending vibration peaks of Ar–H (856–877 cm⁻¹) changed little. The number of functional groups of acid-modified biochar increased more than that of alkali-modified biochar. Mahdi et al. found that acid modification increased the number of functional groups in a study of biochar modification [37]. After acid/base modification, the number of oxygen-containing functional groups, such as hydroxyl and carboxyl groups, increased.

**Optimization of biochar.** Figure 6 illustrates that the removal rates of Cd²⁺ by corn stover biochar (original, acid-modified, and base-modified biochars) consistently increased with increasing pyrolysis temperature. The highest removal rate reached 95.79% at 700 °C. The removal rate decreased after modification, especially after pickling. The results showed that C16 biochar had the best removal effect on Cd²⁺.

Intuitive and variance analyses were employed to explore the influences of biochar preparation conditions on the removal rate of Cd²⁺.

1. **Intuitive analysis**

   The intuitive analysis of the orthogonal experiment is shown in Table 3 and Fig. 7. The pyrolysis temperature had the most significant influence on the removal of Cd²⁺, followed by the retention time and finally the heating rate. Therefore, the optimal conditions for biochar preparation were a pyrolysis temperature of 700 °C, a retention time of 2.5 h, and a heating rate of 5 °C/min.
2. Variance analysis

Variance analysis showed that the effect of pyrolysis temperature on the removal rate of Cd2+ was very significant (Table 4). The effects of retention time and heating rate were not significant. This phenomenon was consistent with the conclusions obtained in the intuitive analysis.

Analysis of adsorption mechanism. The \( S_{\text{BET}} \) of the unmodified biochar did not change significantly with temperature, which indicated that \( S_{\text{BET}} \) could potentially not be a critical factor for Cd\( ^{2+} \) adsorption. Qi et al. obtained a similar conclusion when studying the adsorption of Cd\( ^{2+} \) in water by chicken litter biochar. In addition to \( S_{\text{BET}} \), the four primary mechanisms involved in the removal of heavy metal ions by biochar were as follows: (1) Ion exchange: the alkali or alkaline earth metals in biochar (K\(^{+}\), Ca\(^{2+}\), Na\(^{+}\), and Mg\(^{2+}\)) were the dominant cations in ion exchange. (2) The complexation of oxygen-containing functional groups mainly
Figure 5. FTIR spectra of corn stover biochar: (a) different pyrolysis temperatures and (b) different modification treatments.

Figure 6. Cd$^{2+}$ removal rate of different biochars (BC: original biochar, BC-OH: alkali-modified biochar, and BC-H: acid-modified biochar).
### Table 3. Intuitive analyses of influencing factors of biochar preparation.

| Sample | Pyrolysis temperature (°C) | Retention time (h) | Heating rate (°C/min) | Removal rate (%) |
|--------|-----------------------------|---------------------|------------------------|------------------|
| C1     | 400                         | 1                   | 5                      | 36.42            |
| C2     | 400                         | 1.5                 | 10                     | 35.17            |
| C3     | 400                         | 2                   | 15                     | 26.86            |
| C4     | 400                         | 2.5                 | 20                     | 30.47            |
| C5     | 500                         | 1                   | 10                     | 26.87            |
| C6     | 500                         | 1.5                 | 5                      | 30.24            |
| C7     | 500                         | 2                   | 20                     | 43.82            |
| C8     | 500                         | 2.5                 | 15                     | 52.62            |
| C9     | 600                         | 1                   | 15                     | 59.72            |
| C10    | 600                         | 1.5                 | 20                     | 69.76            |
| C11    | 600                         | 2                   | 5                      | 69.98            |
| C12    | 600                         | 2.5                 | 10                     | 73.92            |
| C13    | 700                         | 1                   | 20                     | 84.85            |
| C14    | 700                         | 1.5                 | 15                     | 89.00            |
| C15    | 700                         | 2                   | 10                     | 91.37            |
| C16    | 700                         | 2.5                 | 5                      | 95.79            |
| Average value 1 | 32.230                   | 51.965              | 58.108                 |
| Average value 2 | 38.388                   | 56.043              | 56.833                 |
| Average value 3 | 68.345                   | 58.008              | 57.050                 |
| Average value 4 | 90.253                   | 63.200              | 57.225                 |
| Range  | 50.023                      | 11.235              | 1.275                  |
| Factor priority | A > B > C               |
| Best combination | A_4B_4C_1                |

### Figure 7. Intuitive analysis diagram of influencing factors for biochar preparation.

### Table 4. Variance analysis. P < 0.01 indicates a very significant difference represented by **.

| Element                      | Sum of square of deviations | Degree of freedom | F ratio | F critical value | Significance |
|------------------------------|-----------------------------|-------------------|---------|------------------|--------------|
| Pyrolysis temperature (°C)   | 8776.187                    | 3                 | 13.361  | 4.760            | **           |
| Retention time (h)           | 261.416                     | 3                 | 4.760   | 4.760            |              |
| Heating rate (°C/min)        | 3.755                       | 3                 | 0.398   | 4.760            |              |
| Error                        | 1313.750                    | 6                 | 0.006   | 4.760            |              |

Table 3. Intuitive analyses of influencing factors of biochar preparation.

Figure 7. Intuitive analysis diagram of influencing factors for biochar preparation.

Table 4. Variance analysis. P < 0.01 indicates a very significant difference represented by **.
peak position of CaCO_3 at 2θ = 29.369° was very close to Cd(OH)_2 at 2θ = 29.454°. At low concentrations, the functional groups were not the main adsorption mechanism. π-electron interactions could play a dominant role in Cd^{2+} adsorption on high-temperature pyrolysis biochar. In adsorption, when the concentrations of cadmium solution were 100 mg/l and 200 mg/l, respectively. The results showed that new peaks appeared at 30.275° and 36.546° after adsorption, corresponding to CdCO_3. The spike at 29.454° was due to Cd(OH)_2. Additionally, the intensity of the CdCO_3 peak increased significantly from C16-100Cd to C16-200Cd, indicating that mineral precipitation occurred in adsorption. Liu et al. found similar results in a study on removing Cd^{2+} from water by blue algae biochar. However, as the concentration of Cd^{2+} increased from 0 to 200 mg/L, the diffraction peak at 2θ = 29.454° first increased and then decreased. This because the peak position of CaCO_3 at 2θ = 29.369° was very close to Cd(OH)_2 at 2θ = 29.454°. At low concentrations, the number of acidic functional groups decreased gradually, while the number of alkaline functional groups increased. The main functional groups used to remove Cd^{2+} were generally considered acidic oxygen-containing functional groups. However, the number of these functional groups decreased with increasing pyrolysis temperature, which weakened the complexation on the surface of biochar. However, this result was contradictory to the results of Cd^{2+} adsorption. Therefore, the functional groups were not the main adsorption mechanism.

To further explore the adsorption mechanism of Cd^{2+}, the biochar before and after the adsorption of Cd^{2+} was characterized by XRD. As shown in Fig. 7a, C16-100Cd and C16-200Cd represented the biochar after Cd^{2+} adsorption when the concentrations of cadmium solution were 100 mg/l and 200 mg/l, respectively. The results showed that new peaks appeared at 30.275° and 36.546° after adsorption, corresponding to CdCO_3. The spike at 29.454° was due to Cd(OH)_2. Additionally, the intensity of the CdCO_3 peak increased significantly from C16-100Cd to C16-200Cd, indicating that mineral precipitation occurred in adsorption. Liu et al. found similar results in a study on removing Cd^{2+} from water by blue algae biochar. However, as the concentration of Cd^{2+} increased from 0 to 200 mg/L, the diffraction peak at 2θ = 29.454° first increased and then decreased. This because the peak position of CaCO_3 at 2θ = 29.369° was very close to Cd(OH)_2 at 2θ = 29.454°. At low concentrations, the production of Cd(OH)_2 was greater than that of CdCO_3. When the initial concentration of Cd^{2+} increased, more CO_3^{2−} released by CaCO_3 combined with Cd^{2+} to form CdCO_3, resulting in a reduction in the diffraction peak.

As presented in Fig. 8b, the peak intensities of CdCO_3 and Cd(OH)_2 gradually increase with increasing pyrolysis temperature. On the one hand, this could be ascribed to the increase in the mineral content of biochar with increasing pyrolysis temperature. On the other hand, the pH value of biochar increased with increasing pyrolysis temperature. In this way, more OH− was released, thus forming more Cd(OH)_2. Wang et al. obtained similar results. Moreover, the peak intensity of KCl at 2θ = 28.347° decreased after adsorption, as shown in Fig. 8a, which indicated that ion exchange took part in adsorption.

In addition, the FTIR spectra showed that the number of functional groups, such as C=C and C=O, in biochar decreased with increasing pyrolysis temperature, leading to the weakening of cation–π interactions between Cd^{2+} and C=C and C=O. In contrast, due to the enhanced aromatization of functional groups on the surface of biochar, many lone pair electrons existed in the electron-rich domains of the graphene-like structure, which in turn enhanced the cation–π interactions. Harvey et al., based on the study of Cd^{2+} adsorption by plant biochar, concluded that the electron-rich domain bonding mechanism between Cd^{2+} and the graphene-like structure on the surface of biochar played a more significant role in biochar with a high degree of carbonization. Therefore, π-electron interactions could play a dominant role in Cd^{2+} adsorption on high-temperature pyrolysis biochar. Moreover, the results showed that the number of alkaline functional groups increased while acidic functional groups decreased with the increase in pyrolysis temperature. It is generally believed that acidic functional groups could withdraw electrons, and basic functional groups could donate electrons. The biochar with higher pyrolysis temperature contained more alkaline functional groups, which improved the electron donating ability of biochar and enhanced the cation–π electron effect.

In summary, mineral precipitation and π electron coordination were the main mechanisms of removing Cd^{2+} from water by corn stover biochar. This phenomenon explained why the Cd^{2+} removal rate of acid/base–modified biochar decreased. After modification, the functional groups on the surface of biochar increased, but the inorganic minerals were removed. Pickling resulted in the loss of soluble minerals and alkaline functional groups on the surface of biochar, which was not conducive to adsorption. After alkaline washing, more PO_4^{3−}, CO_3^{2−} and HCO_3− were released, thereby reducing the mineral precipitation. Since NaOH had a weaker destructive effect than HCl and introduced some OH−, alkaline washing had little effect on the removal rate of Cd^{2+}.

| Sample | CEC (cmol/kg) | pH | Acid functional groups (mmol/g) | Alkaline functional groups (mmol/g) |
|--------|--------------|----|-------------------------------|-------------------------------------|
| C1     | 45.763 ± 0.133d | 7.86 ± 0.03d | 1.030 ± 0.027a | 1.325 ± 0.032a |
| C8     | 47.518 ± 0.124c | 9.61 ± 0.07c  | 0.651 ± 0.013b | 1.625 ± 0.028b |
| C12    | 52.212 ± 0.341b | 10.24 ± 0.04b | 0.621 ± 0.021bc | 1.652 ± 0.023b |
| C16    | 44.164 ± 0.262a | 11.09 ± 0.03a | 0.613 ± 0.010c | 1.791 ± 0.048a |

Table 5. Physicochemical properties of biochar at different pyrolysis temperatures. Different letters (a, b, c, d, e) represent significant differences (p < 0.05) between treatments in same physicochemical properties.
Figure 8. XRD images: (a) before and after adsorption of Cd$^{2+}$ on C16 biochar and (b) Cd$^{2+}$ adsorption by biochar at different pyrolysis temperatures.

Figure 9. Adsorption isotherm.
Adsorption isotherm and adsorption kinetics. Adsorption isotherm. The adsorption isotherms were fitted with Langmuir (Eq. 3) and Freundlich (Eq. 4) models, as shown in Fig. 9, and the fitting parameters are listed in Table 6.

The Langmuir model ($R^2 > 0.963$) was more suitable than the Freundlich model ($R^2 > 0.919$), indicating that the adsorption sites of biochar were evenly distributed, and adsorption was mainly monolayer. Parameter $K_L$ reflected the difficulty of adsorption and was generally divided into four types: unfavourable ($K_L > 1$), favourable ($0 < K_L < 1$), linear ($K_L = 1$), or irreversible ($K_L = 0$). The $K_L$ values obtained by fitting were all between 0 and 1, suggesting that it was easy to adsorb. According to the fitting parameters of the Langmuir model, it could be inferred that the maximum adsorption capacity of corn stover biochar for $\text{Cd}^{2+}$ was 13.4 mg/g. This result was higher than the maximum adsorption capacity of $\text{Cd}^{2+}$ by biochar derived from oil seed rape, miscanthus and wheat in other studies (6.77, 11.33 and 12.35 mg/g, respectively). The maximum adsorption capacity of Hickory wood biochar before and after sodium hydroxide modification for $\text{Cd}^{2+}$ was 0.2 mg/g and 0.98 mg/g, respectively, which was lower than the biochar derived from corn stover in this study.

Adsorption kinetics. Pseudo-first-order (Eq. 5), pseudo-second-order (Eq. 6) and Elovich (Eq. 7) models were employed to fit the adsorption kinetics process, and the results are presented in Fig. 10a and Table 7.

According to the fitting parameters of the kinetic model, the fitting effect of the pseudo-second-order model was better than that of the pseudo-first-order model. This phenomenon indicated that adsorption could be
controlled by chemisorption, which could be roughly divided into two stages: rapid adsorption within 4 h and slow adsorption after 4 h. The adsorption capacity reached 6.98 mg/g at 4 h, accounting for 72.9% of the total adsorption capacity. In the fast adsorption stage, due to the existence of numerous active adsorption sites on the sample, the adsorption capacity increased significantly with time. With the decrease in the number of adsorption sites, the samples entered the slow stage, and the adsorption rate slowed and gradually approached equilibrium. In comparison, the Elovich model had the best fitting effect on adsorption (R^2 > 0.944), indicating that the adsorption of Cd^{2+} by corn stover biochar occurred by heterogeneous chemisorption. The results were consistent with the previous adsorption mechanism.

The Webber–Morris intraparticle diffusion model (Eq. 8) is often used to predict the possibility of intraparticle diffusion. The adsorption process could be divided into different stages according to the adsorption characteristics. The Webber–Morris intraparticle diffusion model showed that adsorption consisted of two stages, as reflected in Fig. 10b. The first stage was the diffusion of Cd^{2+} to the surface of the biochar. The second stage was the adsorption of Cd^{2+} on biochar. Since K_{1d} was greater than K_{2d} (Table 8), the second stage was the control step of adsorption. Neither of the two fitting lines passed through the origin, indicating that intraparticle diffusion was not the only rate-determining step in adsorption. The adsorption process could be affected by liquid film diffusion and the physicochemical interaction between Cd^{2+} and biochar. Similar results were obtained by Pholosi et al. using magnetite-coated biomass to adsorb Cr(VI).

**Optimal conditions for Cd^{2+} adsorption by biochar.**  Electrolyte concentration. Figure 11a showed that the electrolyte concentration was negatively correlated with the removal rate and adsorption capacity. The removal rate of Cd^{2+} decreased from 74.465 to 36.02% as the CaCl_2 concentration increased from 0.01 to 0.3 mol/L, which could be caused by the competitive adsorption between Ca^{2+} and Cd^{2+} and the formation of a water-soluble metal–anion complex (CdCl^+)61,62. Therefore, the removal rate of Cd^{2+} was the highest when the concentration of CaCl_2 was 0.01 mol/L.

pH. As shown in Fig. 11b, the removal rate of Cd^{2+} improved significantly with the initial pH increase, and the upwards trend gradually slowed after the pH value reached 4, which could be explained by the competitive adsorption of Cd^{2+} and H^+, the electrostatic repulsion between Cd^{2+} and the positive charge on the adsorbent surface. With the increase in pH and the decrease in protons, more binding sites were exposed, promoting the adsorption of Cd^{2+}. In addition, mineral precipitates dissolved at low pH values, affecting adsorption. The optimal pH value was 7. Considering the economic benefits, combined with the Cd^{2+} removal rate, the pH value should be selected in a neutral range.

**Biochar dosage.** The biochar dosage had an important effect on the adsorption of Cd^{2+} (Fig. 11c). As the biochar dosage increased, the removal rate of Cd^{2+} gradually increased to 97.96% and then stabilized. This phenomenon could have occurred because with the increase in biochar dosage from 0.1 to 0.4 g, the surface adsorption sites increased rapidly, thus enhancing the adsorption of cadmium and increasing the removal rate of cadmium. When the biochar dosage was higher than 0.4 g, the removal rate did not increase, indicating that the Cd^{2+} in the solution reached adsorption equilibrium. However, the adsorption capacity decreased from 11.42 to 4.14 mg/g with increasing biochar dosage. This phenomenon could have occurred because although the adsorption sites increased with the addition of biochar dosage, the amount of adsorbate remained constant; thus, the mass of Cd^{2+} adsorbed per unit mass of biochar decreased. Additionally, due to the aggregation and overlap of adsorption sites, which could be caused by the increase in biochar dosage, the effective adsorption area decreased, and the diffusion path length increased, reducing the adsorption capacity. Therefore, under the experimental concentration, the optimal addition amount of biochar was 0.4 g.

| Electrolyte concentration | pH | CaCl_2 (mol/L) | Removal rate (%) |
|---------------------------|----|----------------|------------------|
| CaCl_2 0.01               | 4  | 61.27          | 74.465           |
| CaCl_2 0.1               | 4  | 61.27          | 74.465           |
| CaCl_2 0.3               | 4  | 61.27          | 74.465           |
| CaCl_2 0.01               | 7  | 97.96          | 97.96            |
| CaCl_2 0.1               | 7  | 97.96          | 97.96            |
| CaCl_2 0.3               | 7  | 97.96          | 97.96            |

Table 7. Fitting parameters of the pseudo-first-order, pseudo-second-order and Elovich models.

| First stage of intraparticle diffusion | Second stage of intraparticle diffusion |
|---------------------------------------|----------------------------------------|
| K_{1d} (mg g^{-1} min^{-1/2}) | C_1 | R^2 | K_{2d} (mg g^{-1} min^{-1/2}) | C_2 | R^2 |
| 2.049 | 2.999 | 0.948 | 0.988 | 4.677 | 0.917 |

Table 8. Fitting parameters of the Webber–Morris intraparticle diffusion model.
Conclusion
This study demonstrated that corn stover biochar could effectively remove Cd\textsuperscript{2+} from water. The preparation conditions of corn stover biochar were optimized by the orthogonal test method. The results showed that when the pyrolysis temperature was 700 °C, the residence time was 2.5 h, and the heating rate was 5 °C/min, biochar with the highest removal rate of Cd\textsuperscript{2+} was produced. Under the same conditions, the acid/base-modified biochar did not improve the removal rate of cadmium compared to the original biochar. To further investigate the adsorption mechanism of cadmium in water by biochar, a series of chemical and characterization analyses (SBET, CEC, SEM, XRD, FTIR) were conducted, indicating that mineral precipitation and π electrons were the main removal mechanisms. Moreover, the isotherm and kinetic models were studied. The results showed that adsorption was consistent with the Langmuir adsorption isotherm, Elovich kinetic and Webber–Morris intraparticle diffusion models. The theoretical maximum adsorption capacity was 13.4 mg/g. In addition, to better understand the application conditions of biochar adsorption of Cd\textsuperscript{2+} in water, the optimal adsorption conditions were screened. When the concentration of CaCl\textsubscript{2} was 0.01 mol/L, the pH was 7, and the amount of biochar was 0.4 g, the removal...
rate of Cd²⁺ by biochar was the highest. Although the natural water environment could be more complex and the application of corn stover biochar needs further investigation, this study provided a systematic and comprehensive theoretical basis for a better understanding of adsorption and the mechanisms of Cd²⁺ removal from water by corn stover biochar; this study provided a powerful data guarantee for the future application of corn straw biochar in the field of water pollution control.

Data availability

The raw data supporting the conclusions of this article are available from the corresponding author upon reasonable request.

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Author contributions
F.C., Y.S., and Q.Y. contributed to the study conception and design. Material preparation and data collection were performed by F.C., Y.S., T.Y., C.L., S.M., Y.D., and M.Y.; F.C., Y.S., and Q.Y. analysed the data. The first draft of the manuscript was written by F.C., and Y.S., and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.
Competing interests
The authors declare no competing interests.

Additional information
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