

Article

Preparation of Corncob Biochar Film and Its Efficiency in Removing Cr(VI) in Wastewater

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Abstract: With the advancement of China's agricultural modernization and scientific and technological progress, there has been a substantial increase in corn production, resulting in significant agricultural waste of materials such as corncobs. Conventional incineration methods fail to efficiently utilize the recyclable resources present in corncobs. In this investigation, corncob biochar film (CBC) was synthesized through the pyrolysis of corncob. Single-factor and orthogonal experiments were used to determine the conditions needed to prepare biochar film with the best Cr(VI) adsorption effect. The experiments showed that at a heating rate of 5 °C/min, pyrolysis temperature of 500 °C and pyrolysis time of 120 min, the Cr(VI) removal rate of prepared biochar film reached 73.55% and the adsorption capacity was 18.39 mg/g. Meanwhile, the factors affecting the removal of Cr(VI), including pH value, initial concentration of Cr(VI) solution, dosage of adsorbent, adsorption kinetics and isothermal adsorption, were analyzed in detail. The structures of CBC before and after Cr(VI) adsorption were analyzed by SEM, FTIR, XRD, XPS, and BET. These findings demonstrate the efficacy of corncob biochar film in Cr(VI) removal.

Keywords: corncob; biochar film; Cr(VI) adsorption



Academic Editor: Hideyuki Kanematsu

Received: 18 November 2024

Revised: 28 December 2024

Accepted: 30 December 2024

Published: 31 December 2024

Citation: Zuo, J.; Jiang, S.; Yang, T.; Li, J.; Xia, Z.; Wang, Y.; Tan, C. Preparation of Corncob Biochar Film and Its Efficiency in Removing Cr(VI) in Wastewater. *Coatings* **2025**, *15*, 25. <https://doi.org/10.3390/coatings15010025>

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1. Introduction

The advancement of science and technology in our nation has led to an increase in the level of agricultural modernization, resulting in a rise in the annual output of agricultural products. Corn, as a principal food crop in China, boasts an annual output of approximately 280 million tons, with corncobs, a by-product of corn production, yielding about 56 million tons annually [1,2]. These statistics underscore the substantial scale of agricultural development in China and the abundance of corn resources. Formerly regarded as waste, corncobs now hold significant resource potential [3], offering ample opportunities for the utilization of agricultural waste resources, thereby fostering rural economic growth and enhancing farmers' income [4–6]. Consequently, harnessing and leveraging corncob resources not only enhances resource utilization efficiency but also fosters the sustainable development of the agricultural industry, thereby bolstering rural economic prosperity [7].

Traditionally, due to budget constraints and technological limitations, the prevailing practice has been to stack and incinerate corncobs [8,9]. Although this method is convenient, its adverse environmental impact on the soil and the atmosphere cannot be overlooked. Moreover, the direct return of corncobs to the field or their use as a fuel resource falls short of meeting environmental protection standards. Research indicates that corncobs are rich in carbon elements, polysaccharides, cellulose, lignin, and hemicellulose [10], rendering them

suitable for the production of functional biochar film [11]. Presently, common methods for biochar film preparation include pyrolysis, hydrothermal carbonization, and microwave carbonization [12]. Among these, pyrolysis stands out for its simplicity, efficiency, and environmental friendliness, thus enjoying widespread application in biochar film production [13]. Hydrothermal carbonization, characterized by its ease of operation and ability to yield biochar film with an abundant pore structure and high specific surface area, is gaining prominence for its environmental benefits [14,15]. Additionally, the microwave carbonization method offers advantages such as uniform heating, rapidity, and low energy consumption [16,17].

Corncob is often relegated to waste [18,19]. However, this ostensibly discarded material represents a valuable carbonaceous resource that can undergo thermochemical conversion processes to yield biochar film. Biochar film, characterized by high stability and a well-defined pore structure, possesses surface functional groups that render it an exceptional adsorbent, particularly in the treatment of heavy metal-contaminated wastewater [20–22]. Chromium (VI), a highly toxic industrial wastewater pollutant, poses significant environmental and human health risks [23,24]. Given the drawbacks of traditional treatment methods, including high costs and secondary pollution, there is an urgent need to develop economically viable, efficient, and sustainable treatment approaches. By repurposing them [25], not only can the utilization scope of corncob be broadened, but a novel approach to agricultural waste recycling can be provided, thereby achieving the dual objectives of waste management and environmental pollution mitigation [26].

The rapid growth of contemporary industries has exacerbated environmental pollution stemming from chromium (Cr) discharge in wastewater [27,28]. This study focuses on the removal of Cr from sewage by preparing corncob biochar film. The influence of pyrolysis parameters on biochar film adsorption performance was investigated [29,30], with discussions on Cr(VI) removal efficiency elucidated by variations in initial Cr(VI) concentration, material dosage, and pH. Characterization techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) were employed to analyze samples before and after adsorption, facilitating a deeper understanding of the adsorption mechanism.

2. Materials and Methods

2.1. Preparation of Biochar Film Materials

The main chemicals and reagents are shown in Table 1.

Table 1. Chemical reagents in experiment.

Drug	Chemical Formula	Purity	Supplier
Dibenzoyl dihydrazine	$C_{13}H_{14}N_4O$	Analytically pure	Fuchen (Tianjin) Chemical Reagent Co., LTD. (Tianjin, China)
Concentrated sulfuric acid	H_2SO_4	Analytically pure	Tianjin Guangfu Fine chemical Research Institute. (Tianjin, China)
Phosphoric acid	H_3PO_4	Analytically pure	Tianjin Fuyu Fine Chemical Co., LTD. (Tianjin, China)
Potassium dichromate	$K_2Cr_2O_7$	Analytically pure	Tianjin Fuchen chemical reagent factory. (Tianjin, China)
Acetone	C_3H_6O	Analytically pure	Nanjing Chemical Reagent Co., LTD. (Nanjing, China)
Hydrochloric acid	HCL	Analytically pure	Nanjing Chemical Reagent Co., LTD. (Nanjing, China)
Sodium hydroxide	NaOH	Analytically pure	Tianjin Mainland chemical reagent factory. (Tianjin, China)
Anhydrous ethanol	CH_3CH_2OH	Analytically pure	Tianjin Tianli Chemical Reagent Co., LTD. (Tianjin, China)

Table 2 lists the main instruments.

Table 2. Instrument required in experiment.

Instrument	Model Number	Producer
Ultraviolet–visible spectrophotometer	UV-51	Shanghai Yuan analysis Instrument Co., LTD. (Shanghai, China)
Infrared spectrometer	Spectrum Two	Shanghai Perkinelmer Enterprise Management Co., LTD. (Shanghai, China)
Electronic balance	FA2004	Shanghai Yue Ping Scientific Instrument Co., LTD. (Shanghai, China)
Blast-drying oven	DHG-9055A	China Shanghai Yiheng Scientific Instrument Co., LTD. (Shanghai, China)
pH meter	PHS-2F	Shanghai Yi Electrical Scientific Instruments Co., LTD. (Shanghai, China)
Water bath shaker	SHC-C	Shanghai Jingqi Instrument Co., LTD. (Shanghai, China)
Chinese herbal medicine crusher	1000C	Dongguan City Fangtai Electric Co., LTD. (Dongguan, China)
High-temperature combustion tube furnace	SK-2-13	Beijing Yongguang Medical Instrument Co., LTD. (Beijing, China)

2.2. Preparation Method of Corncob Biochar Film

Biochar film is a new type of inorganic film material prepared by high-temperature carbonization in isolated air or in a vacuum. The pyrolysis method stands as a widely employed approach for biochar film preparation, involving the thermal decomposition or carbonization of biomass at elevated temperatures, resulting in a series of physical and chemical transformations. This process typically encompasses pretreatment, drying, pyrolysis or carbonization, cooling, and additional treatment steps. The characteristics and composition of the raw materials significantly influence the quality and properties of the resulting biochar. In this experimental procedure, the corncob is first dried in a blast oven at 60 °C and then placed in a tubular furnace with nitrogen. High-temperature pyrolysis is conducted under varying conditions, including carbonization times (30 min, 60 min, 120 min, 180 min, and 240 min), carbonization temperatures (400 °C, 500 °C, 600 °C, and 700 °C), and heating rates (5 °C/min, 10 °C/min, 20 °C/min, 30 °C/min, and 50 °C/min). Upon completion of pyrolysis and subsequent cooling, the resultant corncob biochar film is retrieved and stored in a drying dish for subsequent use [31].

2.3. Characterization and Principle of Materials

2.3.1. Scanning Electron Microscope (SEM) Determination

In this experiment, the morphology of the samples was observed and analyzed by a Hitachi SU5000 scanning electron microscope, EHT = 20 KV. The sample was dried thoroughly and spray gold was applied before testing began.

2.3.2. Specific Surface Area (BET) and Aperture Analysis

The specific surface area, total pore volume, and average pore diameter of corncob biochar film samples were measured by the nitrogen adsorption–desorption method, and the pore structure was evaluated by analyzing the types of desorption curves. The instrument used was a 3H-2000PS pore structure analyzer with a specific surface area.

2.3.3. X-Ray Diffraction (XRD) Determination

In this experiment, the crystal structure of the material was determined by an X-ray diffractometer. The instrument used was the ARL EQUINOX 100 X-ray diffractometer. The test conditions were as follows: a scanning angle of 5–90° and a scanning speed of 5°/min.

2.3.4. X-Ray Photoelectron Spectroscopy (XPS) Determination

In this experiment, the composition and valence information of the sample elements were determined by X-ray photoelectron spectroscopy. The instrument used was the Thermo Scientific K-Alpha X-ray photoelectron spectrometer. All energy spectra (C1s(C-107C284.8eV)) underwent corrections.

2.3.5. Fourier Infrared Spectroscopy (FTIR) Determination

The structure of the sample was characterized by a PerkinElmer SpectrumTwo infrared spectrometer with a spectral range of 4000–400 cm^{-1} and a resolution of 0.5 cm^{-1} .

2.4. Adsorption Experiment

2.4.1. Cr(VI) Standard Curve Drawing

The Cr(VI) standard curve was drawn according to the national standard GB7467-87 [32].

(1) Preparation of reagents.

To prepare the Cr(VI) standard solution, potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) of 0.2829 ± 0.001 g, with superior purity, is precisely weighed and subsequently dissolved in water to produce a chromium standard storage solution of 100 mg/L concentration. From this stock solution, 5 mL is withdrawn and diluted to 500 mL, yielding a chromium standard solution with a concentration of 1 mg/L.

For the color-developing agent, dibenzoyl dihydrazine ($\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$) is weighed at 2 g and dissolved in 50 mL of acetone, followed by dilution with distilled water to reach a final volume of 100 mL. This solution is stored in a brown bottle at low temperature. Prior to utilization, it is imperative to inspect the color of the solution, as any darkening indicates its unsuitability for use. The reaction between Cr(VI) and $\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$ results in the formation of a purple-red compound.

(2) Cr(VI) determination

In a colorimetric tube, 50 mL of distilled water is taken and supplemented with 0.5 mL of sulfuric acid solution (sulfuric acid—distilled water = 1:1) and 0.5 mL of phosphoric acid solution (phosphoric acid—distilled water = 1:1), followed by thorough agitation. Subsequently, 2 mL of the color developer is added, and the solution is vigorously shaken then allowed to stand for 5–10 min. The absorbance is then measured at a wavelength of 540 nm and utilized as a blank test. Prior to testing (with a Cr(VI) concentration < 0.05 mg/L), the sample is diluted to 50 mL, and absorbance is determined in a similar manner. The concentration of Cr(VI) is calculated by subtracting the absorbance value of the blank test and employing the standard curve.

(3) Drawing of standard curves

The Cr(VI) standard solution is added to the 50 mL colorimetric tube in different volumes (0 mL, 1 mL, 2 mL, 5 mL, 10 mL, 20 mL, 30 mL, 40 mL, and 50 mL), diluted to the line, and the absorbance is measured according to the established steps, and then the concentration–absorbance curve is drawn accordingly [33]. Then, subsequent adsorption experiments are conducted. Figure 1 shows the standard curve.

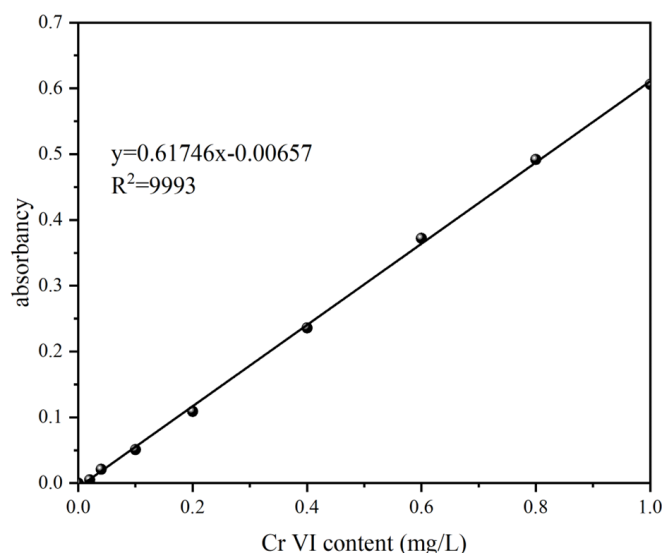


Figure 1. The standard curve of Cr(VI).

2.4.2. Adsorption Test Method

First, 0.1 g biochar film and 50 mL Cr(VI) solution (50 mg/L, pH = 2) are oscillated in a water bath at 25 °C and 130 r/min for 24 h in the adsorption experiment. After the adsorption, 0.22 µm filter membrane is used for filtering and sampling, and the remaining concentration of Cr(VI) is measured by standard curve to evaluate the adsorption performance of biochar. The adsorption capacity and removal rate are calculated by the initial and residual mass concentrations of Cr(VI). The removal rate R and adsorption capacity Q are calculated according to the Formulas (1) and (2):

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

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

Formula:

C_0 —Cr(VI) initial mass concentration (mg/L);

C_t —Cr(VI) mass concentration at time t (mg/L);

V —solution volume (L);

t —adsorption time (min);

m —the dosage of biochar.

2.5. Adsorption Kinetics Experiment

Next, 0.1 g biochar film is added to 50 mL Cr(VI) solution (50 mg/L). Oscillation is performed for 0 min, 10 min, 30 min, 60 min, 90 min, 120 min, 180 min, 360 min, 540 min, 720 min, and 1440 min in a constant-temperature water bath oscillator at 25 °C, 130 r/min. The absorbance of residual Cr(VI) in the solution is measured by 0.22 µm filter membrane, and the removal rate R and adsorption amount Q are calculated.

2.6. Isothermal Adsorption Experiment

A series of Cr(VI) solutions with concentrations of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L, 75 mg/L, and 100 mg/L (pH = 2) are prepared and 0.1 g biochar film is added. After shaking for 24 h in a constant-temperature water bath oscillator at 25 °C and 130 r/min, 0.22 µm filter membrane is used for filtering and sampling, and the removal rate R and adsorption capacity Q are calculated.

2.7. Adsorption Cycle Regeneration Experiment

Next, 0.1 g of adsorbent is added to 50 mL Cr(VI) solution (50 mg/L, pH = 2) and oscillated in a constant-temperature water bath oscillator at 25 °C and 130 r/min for 24 h. After saturation adsorption, the adsorbent is placed in 50 mL, 0.1 mol/L NaOH, and shaken under the same conditions to release Cr(VI). After that, the removal experiment of Cr(VI) is carried out with the adsorbent treated by regeneration, and the removal efficiency is measured.

2.8. Data Processing

Microsoft Excel 2019 is used for data processing and Origin is used for mapping. Differences and correlations are analyzed using IBM SPSS Statistics 26.0.

3. Results and Discussion

3.1. Parameter Optimization of Biochar Film Preparation Process

The preparation process parameters examined in this experiment include pyrolysis time, pyrolysis temperature, and heating rate, and the optimum preparation process parameters are determined by factor analysis.

3.1.1. Analysis of Single-Factor Test Results

(1) Influence of pyrolysis time on the removal of Cr(VI) from biochar film.

Figure 2 depicts the impact of pyrolysis time on the efficiency of Cr(VI)'s removal from biochar film. When the heating rate is 5 °C/min and the pyrolysis temperature is 500 °C, the results illustrate that as the pyrolysis time increases, the efficacy of Cr(VI)'s removal from biochar film exhibits a relatively consistent trend. Concurrently, the adsorption capacity remains relatively stable, indicating minimal influence of pyrolysis time within the specified range. In summary, while the initial stages of the experiment show a significant effect of pyrolysis time on Cr(VI) removal, this influence stabilizes over time. This phenomenon may be attributed to alterations in surface functional groups and the stability of the microstructure of biochar film.

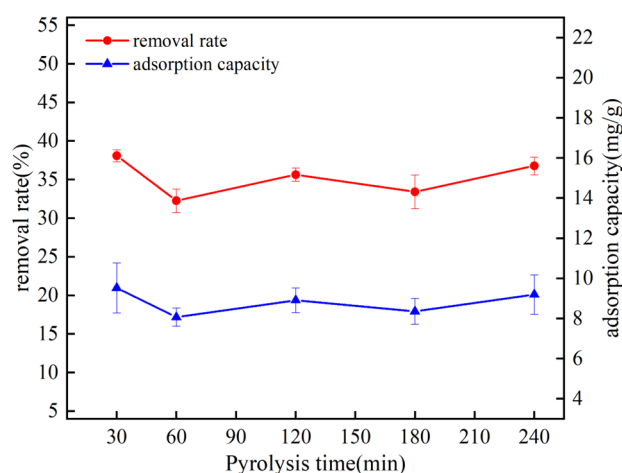


Figure 2. Effect of pyrolysis time on Cr(VI) removal from BC.

(2) Influence of pyrolysis temperature on the removal of Cr(VI) from biochar film.

Figure 3 illustrates the impact of pyrolysis temperature on Cr(VI)'s removal from biochar film. When the heating rate is 5 °C/min and the pyrolysis time is 120 min, the results indicate that pyrolysis temperature has a pronounced influence on both the efficiency and adsorption capacity of Cr(VI) removal. Initially, the removal rate increases, reaching its peak at 500 °C, suggesting optimal conditions for Cr(VI) adsorption onto biochar film.

However, as the temperature surpasses this point, the removal rate diminishes, possibly due to detrimental alterations in the biochar film's microstructure, such as pore collapse or reduction in active sites. Similarly, the adsorption capacity attains its maximum at 500 °C, declining thereafter with rising temperatures. This decline may be attributed to changes in the biochar film's pore structure and surface functional groups, which impact its Cr(VI) adsorption capacity.

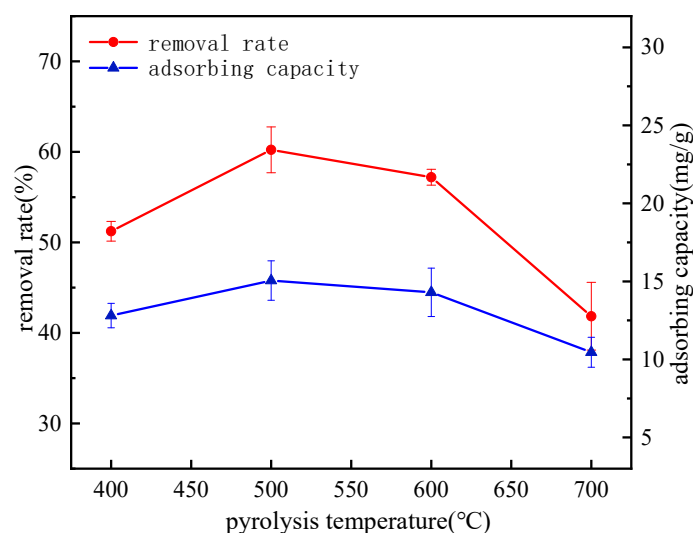


Figure 3. Effect of pyrolysis temperature on Cr(VI) removal from BC.

(3) The effect of heating rate on the removal of Cr(VI) from biochar film.

Figure 4 illustrates the impact of heating rate on Cr(VI)'s removal from biochar film. When the pyrolysis temperature is 500 °C and the pyrolysis time is 120 min, the heating rate has a noticeable influence on both the efficiency and adsorption capacity of Cr(VI)'s removal from biochar film. Specifically, lower heating rates correspond to higher Cr(VI) removal rates, with a rapid decline observed as the heating rate increases. Eventually, a stable removal rate is reached at a certain heating rate. This trend suggests that a slower heating rate allows for the formation of pore structures and functional groups within the biochar film that are conducive to Cr(VI) adsorption. Conversely, excessively fast heating rates may impede the pyrolysis reaction within the biochar film, thereby adversely affecting its adsorption performance.

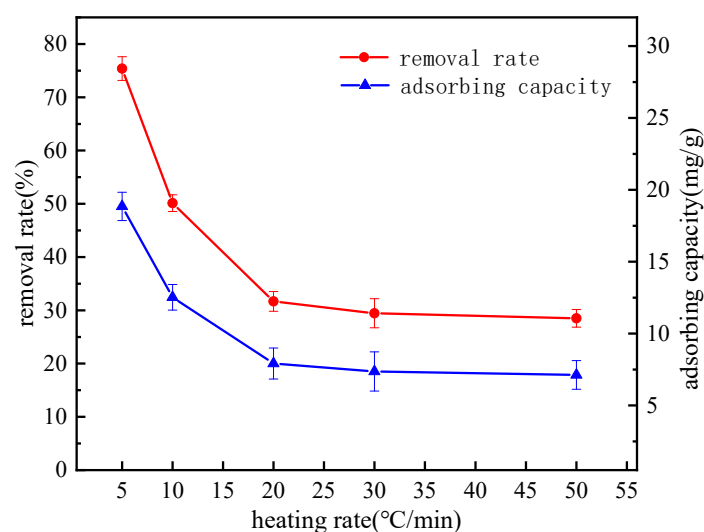


Figure 4. Effect of heating rate on Cr(VI) removal from BC.

A similar trend in adsorption capacity is evident in Figure 4. Higher adsorption capacities are observed at lower heating rates, while they decrease with increasing heating rates. This suggests that excessive heating rates may disrupt the pore structure of biochar film, thereby diminishing the availability of effective adsorption sites and resulting in decreased adsorption capacity. Consequently, controlling the appropriate heating rate emerges as a crucial factor in enhancing the adsorption performance of biochar film for Cr(VI) removal from wastewater.

3.1.2. Establishment and Analysis of Orthogonal Experiment

Based on the results of single-factor tests, the main factors of pyrolysis temperature, heating rate, and pyrolysis time were identified. Subsequently, a three-factor, three-level orthogonal test was conducted to ascertain the optimal preparation conditions for corncob biochar film, as delineated in Table 3.

Table 3. The factors and levels of orthogonal experiment.

Level	Factor		
	A Heating Rate (°C/min)	B Pyrolysis Temperature (°C)	C Pyrolysis Time (min)
1	5	400	60
2	10	500	120
3	20	600	180

According to the orthogonal test data, the significance of the influencing factors was detected by analysis of variance (ANOVA). The orthogonal experimental results and variance analysis of various factors pertaining to the Cr(VI) removal efficiency of CBC are shown in Tables 4 and 5.

Table 4. The design and results of orthogonal experiment.

Test Number	Factor			Removal Rate (%)
	A	B	C	
1	1	1	1	64.93
2	1	2	2	64.93
3	1	3	3	62.45
4	2	1	2	39.84
5	2	2	3	42.89
6	2	3	1	40.02
7	3	1	3	27.15
8	3	2	1	35.36
9	3	3	2	30.22
K ₁	67.383	43.973	46.770	
K ₂	40.917	51.007	48.277	
K ₃	30.910	44.230	44.163	
R	36.473	7.033		
Primary and secondary factors		A > B > C		
Optimal scheme		A ₁ B ₂ C ₂		

Table 5. Analysis of variance for orthogonal experiment.

Source	Deviation Sum of Squares	Degree of Freedom	Mean Square	F	p	Significance
Heating rate	2130.922	2	1065.461	567.973	0.002	*
Pyrolysis temperature	95.457	2	47.728	25.443	0.038	*
Pyrolysis time	25.984	2	12.992	6.926	0.126	
Error	3.752	2	1.876			

Note: $p < 0.05$ —significant “*”.

According to the analysis presented in Table 4, the influence of the three factors on the removal rate of Cr(VI) follows the order A > B > C, indicating that the heating rate

exerts the greatest influence, followed by pyrolysis temperature and pyrolysis time. The optimal process condition for preparing CBC is identified as $A_1B_2C_2$, resulting in a removal rate of 74.77%. This condition has been validated through three repeated tests, yielding an average removal rate of 73.55%. Thus, the optimum preparation conditions for CBC are determined as a heating rate of 5 °C/min, pyrolysis temperature of 500 °C, and pyrolysis time of 120 min. According to the results of variance analysis in Table 5, the heating rate and pyrolysis temperature significantly influence the removal of Cr(VI) by CBC, whereas the pyrolysis time demonstrates no significant impact. At the same time, when biochar adsorption Cr(VI) is repeated three times, the average removal rate is 68.26%. Yu Y [34] showed that the removal rate of Cr(VI) adsorbed by raw walnut shell biochar was 14.97%. Cheng H [35] synthesized sulfide nano zero-valent iron (S-nZVI) on the surface of corn stalk biochar (BC). The removal rate of Cr(VI) was 42%. Dai X [36] synthesized activated biochar nanoparticles (AS-BC) using squid ink. The removal rate of Cr(VI) was 62.1%. The results showed that under the best conditions, the biochar prepared by corncob had strong adsorption capacity and high use value.

3.2. Study on the Cr(VI) Removal Performance of Biochar Film

3.2.1. Exploring the Factors Affecting Cr(VI) Removal Efficiency

The factors affecting the removal of Cr(VI), including the pH value, initial concentration of Cr(VI) solution, dosage of adsorbent, adsorption kinetics, and isothermal adsorption, were analyzed in detail.

(1) The influence of solution pH on the removal of Cr(VI) by CBC.

The concentration of Cr(VI) solution was 50 mg/L, and the pH of the solution was adjusted with HCl and NaOH solutions (the pH gradients were set to 2, 3, 4, 5, 6, 7, 8, and 9). The dosage of adsorbent was 0.1 g.

Figure 5 illustrates the efficiency of Cr(VI) removal by CBC and the adsorption capacity as the pH of the solution varies. A significant decrease in both removal rate and adsorption capacity is observed with increasing pH values. In particular, within the pH range of 2 to 4, a sharp decline in adsorption capacity and removal rate is evident. The peak removal rate and adsorption capacity, reaching 61.36% and 15.34 mg/g, respectively, are attained at pH 2. Subsequently, as the pH increases from 4 to 9, the removal rate and adsorption capacity stabilize. At pH 9, the removal rate diminishes to 18.71% while the adsorption capacity reduces to 4.68 mg/g.

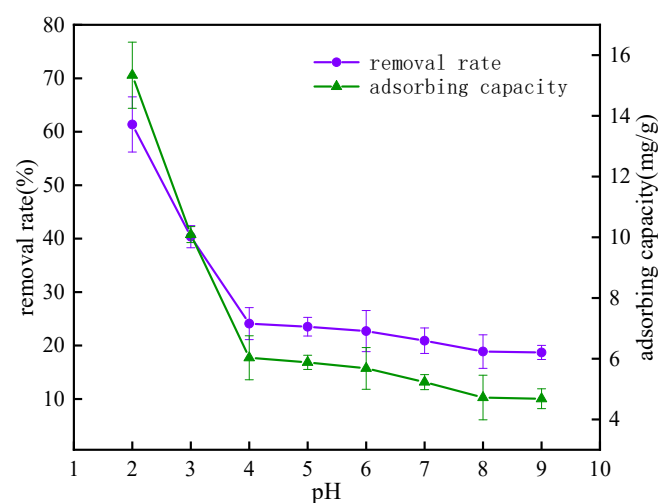


Figure 5. Effect of pH on Cr(VI) removal.

The behavior of Cr(VI) in solution is profoundly influenced by pH. Cr(VI) predominantly exists as H_2CrO_4 , $\text{Cr}_2\text{O}_7^{2-}$, and CrO_4^{2-} species, which undergo transformations at different pH levels. At $\text{pH} < 1$, H_2CrO_4 prevails, while $\text{Cr}_2\text{O}_7^{2-}$ emerges at $1 < \text{pH} < 3$ and a transition to $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} occurs between $\text{pH} 3$ and 7 , contributing to the excellent removal efficacy observed at $\text{pH} < 3$.

Furthermore, under acidic conditions, the surface of CBC may acquire a positive charge, facilitating the attraction of negatively charged CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions in solution, thereby enhancing their adsorption onto the CBC's surface. Conversely, in alkaline environments, the surface charge of the CBC may become negative, and the increase in OH^- ions competes with Cr(VI) for adsorption sites, resulting in reduced adsorption efficiency.

In conclusion, the efficacy of Cr(VI) removal by CBC is highly contingent on solution pH, with optimal performance achieved under acidic conditions. Thus, adjusting the pH of Cr(VI)-containing wastewater to the acidic range is recommended to enhance CBC removal efficiency.

(2) The effect of Cr(VI) initial concentration on the removal of Cr(VI) by CBC.

The solution concentration of Cr(VI) was 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 75 mg/L, 100 mg/L, the pH was 2, and the dosage of adsorbent was 0.1 g.

In Figure 6, as the Cr(VI) concentration gradually increases, distinct trends are observed in the removal rate and adsorption capacity. Specifically, as the concentration of Cr(VI) rises, the removal rate of Cr(VI) by CBC decreases from 97.59% to 35.66%, while the adsorption capacity increases from 4.88 mg/g to 17.83 mg/g. This phenomenon may arise due to sufficient adsorption sites being available at lower concentrations, allowing each Cr(VI) molecule to readily locate adsorption sites. However, as the initial concentration increases, the removal rate begins to decline, suggesting the onset of adsorption site saturation. With a higher initial concentration, the initial driving force for adsorption becomes more pronounced, resulting in an increase in adsorption capacity. Nonetheless, as the Cr(VI) concentration continues to escalate, a limited number of CBC adsorption sites approach or reach saturation, causing a deceleration in the growth trend of adsorption capacity.

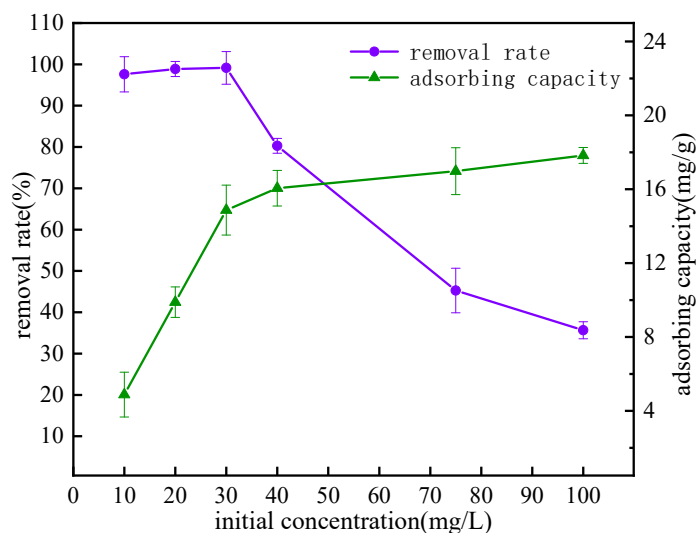


Figure 6. Effect of initial concentration on Cr(VI) removal.

(3) The effect of adsorbent dosage on the removal of Cr(VI) by CBC.

The dosage of adsorbents was 0.05 g, 0.1 g, 0.2 g, 0.3 g, and 0.4 g, respectively, the pH was 2, and the concentration of Cr(VI) solution was 50 mg/L.

In Figure 7, as the dosage of CBC increased from 0.05 g to 0.4 g, the removal rate of Cr(VI) increased similarly, eventually plateauing at 97.59%. Notably, a significant increase

in the removal rate occurred as the dosage escalated from 0.05 g to 0.3 g. Concurrently, the adsorption capacity of CBC declined as the dosage increased.

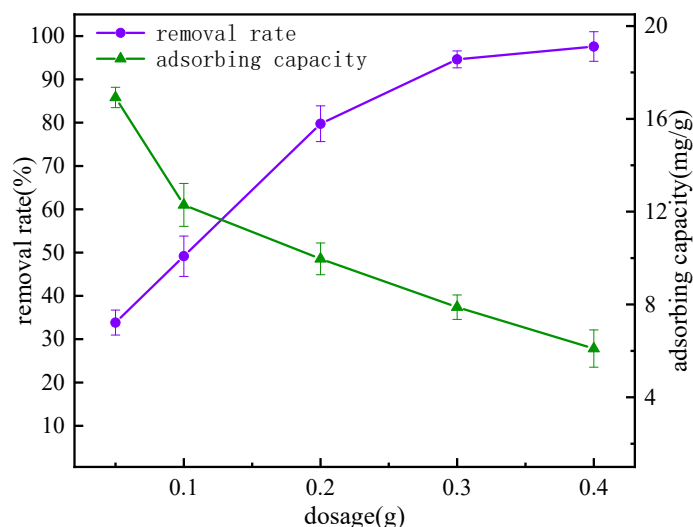


Figure 7. Effect of CBC dosage on Cr(VI) removal.

This observation suggests that the augmentation of the CBC dosage augments the number of available adsorption sites, thereby enhancing the contact area between Cr(VI) and CBC, resulting in an escalating removal rate. However, the rate of removal rate growth decelerated as the CBC amount increased, ultimately stabilizing. This phenomenon may be attributed to the potential blockage of effective adsorption sites by newly added CBC particles.

Moreover, the decrease in Cr(VI) adsorption capacity with increasing dosage indicates a reduction in the number of chromium ions available for adsorption per gram of CBC. Consequently, the average adsorption capacity per gram of CBC diminishes, and some adsorption sites may remain underutilized due to limitations in the Cr(VI) concentration. At the same time, when the removal rate is close to 100%, the driving force for adsorption will lessen, resulting in its decline. Therefore, in 50 mL Cr(VI) solution, the optimal dosage of biochar is 0.4 g; that is, the optimal dosage concentration is 8 g/L.

3.2.2. Adsorption Kinetics Experiment

The adsorption process of Cr(VI) removal from water by biochar film can be characterized by Lagergren's quasi-first-order kinetic model, quasi-second-order kinetic model, and Weber–Morris's intra-particle diffusion model. These models serve to delineate the rate-controlling steps in the adsorption process. Specifically, the quasi-first-order and quasi-second-order kinetic models elucidate the adsorption process and properties of Cr(VI) adsorbed by CBC, while the intra-particle diffusion model is employed to analyze the diffusion process of Cr(VI) within CBC particles.

(1) Quasi-first-order kinetic equation expression:

$$\ln(Q_e - Q_t) = \ln Q_e - K_c t \quad (3)$$

Formula:

Q_e —saturated adsorption capacity, mg/g;

Q_t —adsorption capacity at time t , mg/g;

K_c —quasi-first-order kinetic model rate constant, min^{-1} ;

T —Contact time, min.

(2) Quasi-second-order kinetic equation:

$$\frac{t}{Q_t} = \frac{1}{K_s \cdot Q_e^2} + \frac{1}{Q_t} \quad (4)$$

Formula:

K_s —Rate constant of a quasi-second-order kinetic model, min^{-1} .

(3) Diffusion equation in particles:

$$Q_t = K_j \cdot t^{\frac{1}{2}} + C \quad (5)$$

Formula:

K_j —Rate constant of diffusion reaction in particles, $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$;

C —The thickness of the boundary layer, mg/g .

The fitting curves of the quasi-first-order dynamic model and quasi-second-order dynamic model of CBC adsorbing Cr (VI) prepared under optimal conditions are shown in Figure 8, and the fitting parameters are shown in Table 6.

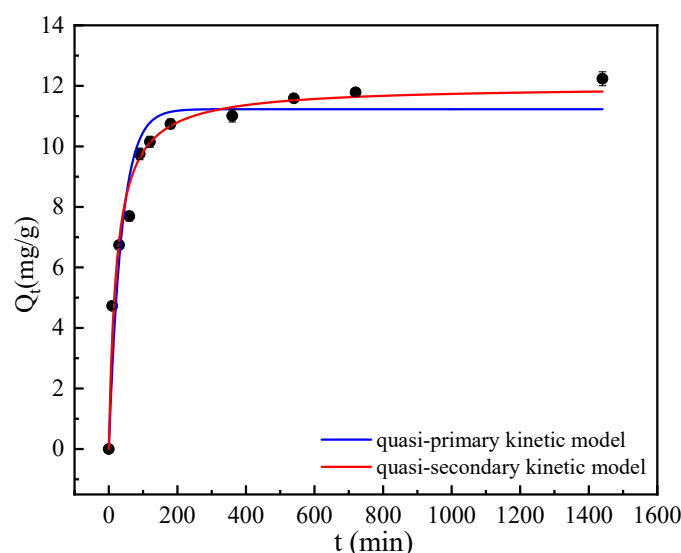


Figure 8. Kinetic fitting curve of Cr(VI) adsorption by CBC.

Table 6. Kinetic fitting parameters of Cr (VI) adsorption by CBC.

Sample	Q_e (mg/g)	Quasi-First-Order Dynamics			Quasi-Second-Order Dynamics		
		Q_t (mg/g)	k_c (min^{-1})	R^2	Q_t (mg/g)	k_s ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)	R^2
CBC	12.24	11.23	0.02688	0.9384	11.99	0.003750	0.9823

According to Table 6, the adsorption of Cr(VI) by CBC conforms more closely to the quasi-second-order kinetic model. The high fitting degree, indicated by the fitting R^2 of 0.98229 for CBC using the quasi-second-order kinetic model, surpasses that of the quasi-first-order kinetic model. Additionally, the equilibrium adsorption capacity of 11.9945 mg/g obtained from the model closely aligns with the experimental result of 12.235 mg/g . During the initial 120 min of adsorption, the rapid increase in Cr(VI) adsorption capacity can be attributed to the abundant active functional groups and large specific surface area of newly added CBC, facilitating numerous available adsorption sites.

Therefore, in comparison with the quasi-first-order kinetic model, the quasi-second-order kinetic model more accurately characterizes the dynamics of Cr(VI) adsorption over

time following the addition of CBC, indicating that the adsorption process is predominantly governed by chemisorption mechanisms. Furthermore, the rate constant $k_s < 1$ suggests rapid reaction kinetics.

According to Table 7 and Figure 9, the adsorption behavior of Cr(VI) by biochar film can be delineated into two primary stages based on the intra-particle diffusion model: the initial phase characterized by rapid membrane diffusion, followed by the subsequent intra-particle diffusion stage. The adsorption rate during the first stage notably exceeds that of the second stage, suggesting that the swift reaction of Cr(VI) on the CBC surface corresponds to the membrane diffusion phase. Moreover, the diffusion within the particles emerges as the key limiting factor governing the overall adsorption rate. The deviation of the fitting line from the origin indicates the influence of additional mechanisms, such as surface adsorption, alongside intra-particle diffusion, on the adsorption rate.

Table 7. Adsorption particle diffusion fitting parameters for CBC on Cr(VI).

	R^2	The First Stage		R^2	The Second Stage	
		k_j ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$)	C (mg/g)		k_j ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$)	C (mg/g)
CBC	0.9512	0.6093	3.199	0.9011	0.05939	10.06

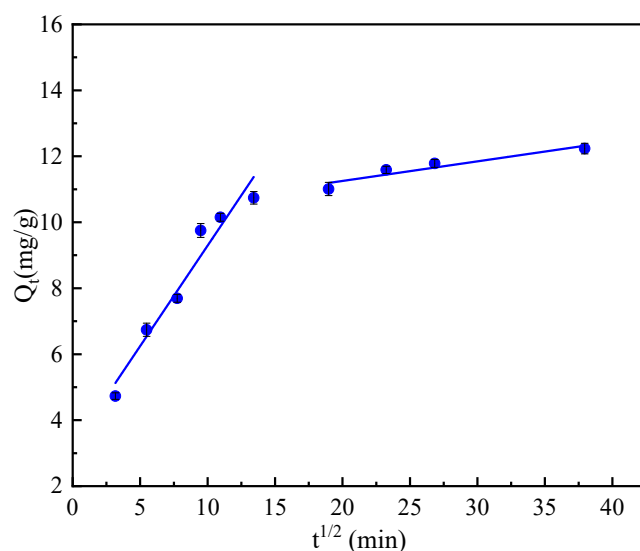


Figure 9. Particle diffusion fitting curves of CBC adsorption Cr(VI).

3.2.3. Isothermal Adsorption Experiment

In order to further explore the concentration relationship when corncob biochar film reached equilibrium during Cr(VI) adsorption, Langmuir and Freundlich isothermal adsorption models were used to describe and fit the isothermal adsorption data. These two models can reveal the adsorption characteristics and mechanism of Cr(VI) adsorption by biochar film, and provide a more comprehensive perspective for understanding the adsorption process. The two equations are expressed as follows:

$$\text{Langmuir equation : } Q_e = \frac{Q_m \cdot K_1 \cdot C_e}{1 + K_1 \cdot C_e} \quad (6)$$

Formula:

Q_e —adsorption capacity at equilibrium concentration, mg/g;

C_e —equilibrium concentration of adsorbed substance in solution, mg/L;

Q_m —the maximum adsorption capacity when the adsorbent surface is saturated, mg/g;

K_L —Langmuir adsorption constant.

$$\text{Freundlich equation : } Q_e = K_f C_e^{\frac{1}{n}} \quad (7)$$

Formula:

K_f —Freundlich adsorption constant;

$\frac{1}{n}$ —index of adsorption strength: $\frac{1}{n} < 1$ indicates that the stronger the adsorption capacity, the easier the adsorption process.

As depicted in Table 8 and Figure 10, both the Langmuir and Freundlich adsorption isotherm models exhibit a high degree of fit, with correlation coefficients exceeding 0.9. However, the Langmuir model yields a more significant correlation coefficient (R^2) compared to the Freundlich model, suggesting that the adsorption process of Cr(VI) by CBC predominantly adheres to the Langmuir model. This implies that the adsorption sites are uniformly distributed, and the adsorption occurs via monolayer adsorption. Additionally, the K_L value in the Langmuir model is less than 1, indicating favorable adsorption and an easier reaction process. These findings underscore the potential of CBC as a highly efficient adsorbent for Cr(VI) removal, with adsorption properties consistent with monolayer adsorption theory.

Table 8. Isotherm model parameters.

	Langmuir Model			Freundlich Model		
	Q_m (mg/g)	K_L (L/mg)	R^2	K_f (L/mg)	$1/n$	R^2
CBC	19.70	0.03058	0.9959	2.169	0.4266	0.9802

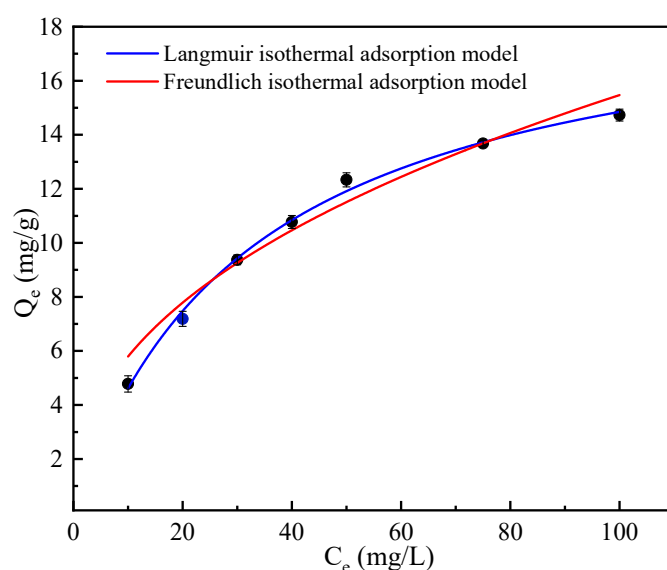


Figure 10. Isothermal adsorption fitting curve of Cr(VI) by CBC.

3.2.4. Adsorption Cycle Regeneration Experiment

In practical applications, assessing the efficacy of biochar film extends beyond its adsorption capacity to encompass considerations regarding its reusability. As depicted in Figure 11, the removal efficiency of Cr(VI) by CBC diminishes notably after five cycles of use. This decline in performance may stem from the relatively fragile internal structure of CBC, which is prone to pore structure collapse. Additionally, certain heavy metal ions may prove resistant to removal via simple washing procedures, further contributing to reduced removal efficiency. Consequently, the removal rate of CBC decreases to approximately

20% after five cycles of recycling. Thus, enhancing the Cr(VI) removal efficiency of CBC necessitates modifications aimed at improving its recyclability.

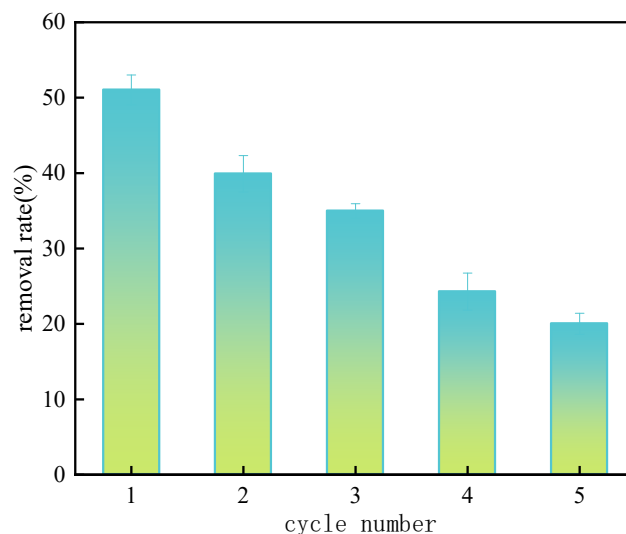


Figure 11. The ability of CBC recycling to adsorb Cr(VI).

3.2.5. Material Characterization and Removal Mechanism Analysis

(1) SEM analysis before and after Cr(VI) adsorption.

The apparent morphology of corncob biochar film can be elucidated through scanning electron microscopy (SEM) analysis. Figure 12 presents SEM images of CBC before and after Cr(VI) adsorption. Figure 12a–c depict SEM images of CBC prior to adsorption. Notably, Figure 12a,b reveal the presence of a developed pore structure with varying pore sizes on the surface of CBC. Figure 12c further illustrates the abundance of small holes on the CBC's surface, which are indicative of a relatively large specific surface area. This phenomenon may be attributed to the destruction of the fiber structure of corncob during high-temperature thermal cracking. These pore structures are formed during pyrolysis as a result of the release of internal water and volatile substances, as well as the oxidation etching of carbon elements, thereby endowing CBC with favorable adsorption capacity.

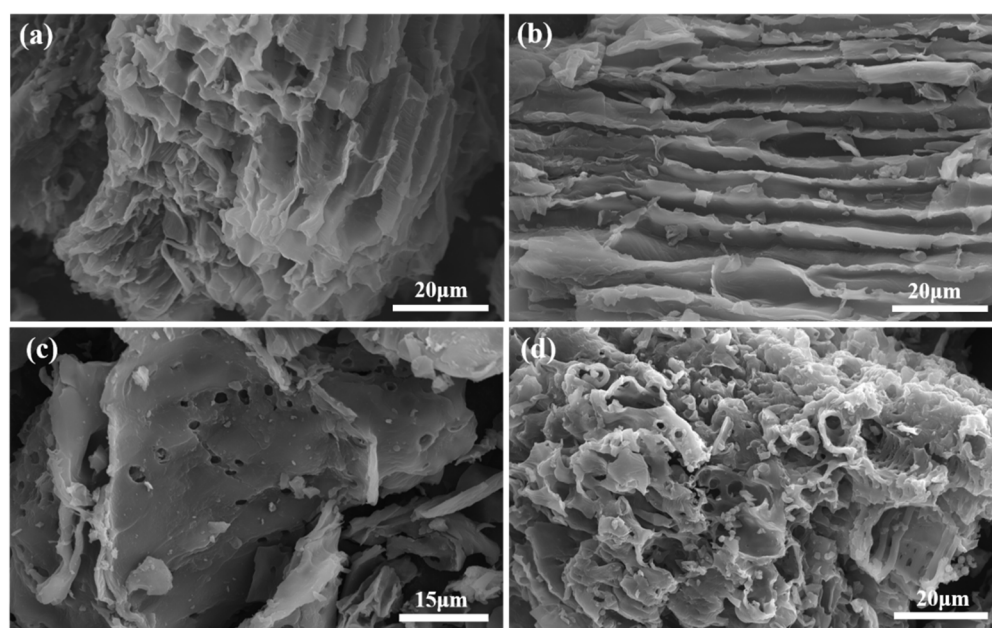


Figure 12. SEM before and after adsorption of CBC: (a–c) Before adsorption; (d) after adsorption.

Figure 12d illustrates the morphology of CBC after Cr(VI) adsorption, revealing the appearance of new particles within the pores and surface of CBC. These particles may correspond to Cr(VI) entities, leading to partial or complete pore closure and a reduction in pore count. Additionally, the surface appears rougher post-adsorption, which is attributed to Cr(VI) deposition.

(2) Specific surface area (BET) and aperture analysis.

As depicted in Table 9, the BET surface area of corncob biochar film is $235.571257 \text{ m}^2/\text{g}$, signifying a substantial specific surface area that is conducive to enhanced adsorption performance by providing ample active sites for molecular adsorption. The presence of both micropores and mesopores in CBC is indicated by a mesoporous volume of $0.143878 \text{ cm}^3/\text{g}$ and a micropore volume of $0.069950 \text{ cm}^3/\text{g}$. Micropores exhibit high efficacy in adsorbing small molecules, while mesopores facilitate the transport pathway of adsorbed molecules. The average pore size of 3.615407 nm falls within the mesoporous range, facilitating the adsorption and diffusion of larger molecules, such as Cr(VI), thus enhancing its removal efficiency.

Table 9. Parameters of specific surface area and pore structure of CBC.

Sample	BET Surface Area (m^2/g)	$V_{\text{mesoporous}}$ (cm^3/g)	$V_{\text{Micropore}}$ (cm^3/g)	Average Pore Ize (nm)
CBC	235.6	0.1439	0.06995	3.615

Figure 13 illustrates the N_2 adsorption–desorption isotherm of CBC, which predominantly conforms to a mixed isotherm exhibiting characteristics of type I and type II isotherms. The non-coincidence of the curves and the formation of a H4 hysteresis loop between the desorption and adsorption curves suggest the presence of a mesoporous structure within CBC, consistent with SEM characterization results. Notably, the rapid rise in the adsorption curve at low relative pressure signifies a large specific surface area and well-developed microporous structure within CBC. As the relative pressure increases, the adsorption capacity gradually approaches a plateau, indicating the transition to the adsorption stage of the porous layer following micropore saturation.

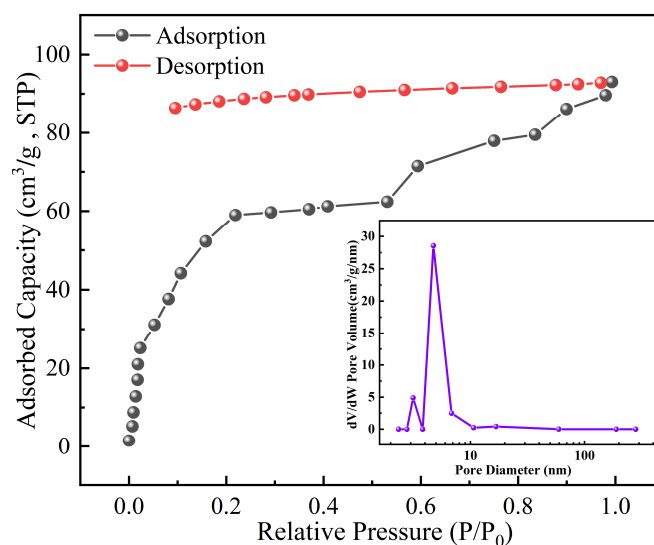


Figure 13. Nitrogen adsorption–desorption curves and pore size distribution of CBC.

The pore size distribution profile reveals a distinct peak within the 10 nm aperture range, indicating a concentrated distribution of pore sizes, possibly corresponding to micropores or small mesopores.

In summary, the observed characteristics of CBC, including its large specific surface area, concentrated pore size distribution, and mesoporous structure, underscore its potential as a porous material favorable for the adsorption of water pollutants such as Cr(VI).

(3) FTIR analysis before and after Cr(VI) adsorption.

Figure 14 illustrates the FTIR spectra acquired before and after the adsorption of Cr(VI) by CBC. Comparative analysis of the infrared spectra enables the qualitative assessment of functional groups present on the surface of CBC.

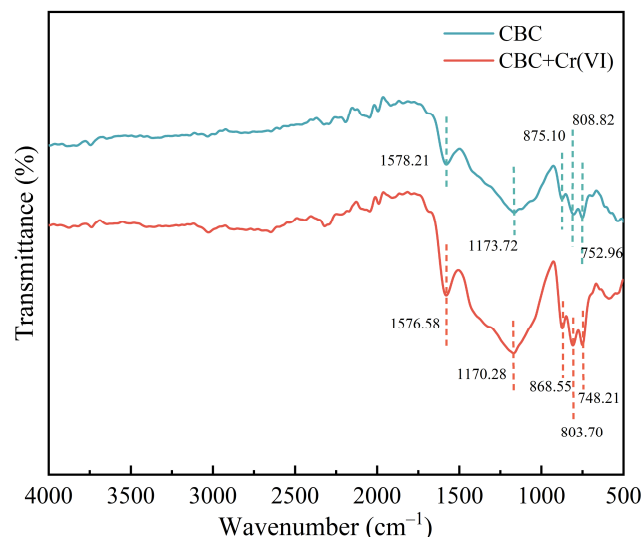


Figure 14. FTIR diagram of CBC before and after adsorption of Cr(VI).

As depicted in Figure 14, the absorption peaks observed at 1173.72 cm^{-1} and 1170.28 cm^{-1} before and after the adsorption of CBC represent the C-O-C tensile vibration. The peaks detected at 1576.58 cm^{-1} and 1578.21 cm^{-1} may arise from the stretching vibration of C=O bonds or partial stretching vibration of -COOH groups [37]. Additionally, the peaks at 875.10 cm^{-1} and 868.55 cm^{-1} correspond to the bending vibration of aromatic C-H planes [38]. The absorption peaks at 808.82 cm^{-1} and 803.70 cm^{-1} indicate condensation reactions, C-H bending vibrations, and aromatic ring formation during the preparation of CBC [39]. Furthermore, the peaks observed at 752.96 cm^{-1} and 748.21 cm^{-1} may also be associated with C-H bending vibrations, typically linked to substituted aromatic rings.

Figure 14 further reveals that upon Cr(VI) adsorption by CBC, slight shifts in peak positions and alterations in peak intensities are observed, suggesting chemical interactions between these functional groups and Cr(VI). Notably, the -COOH groups may undergo exchange with cations, enhancing CBC's adsorption capacity for Cr(VI). The presence of C=O and -COOH groups in the FTIR spectrum indicates their potential for complexation with chromium ions.

(4) XRD analysis before and after Cr(VI) adsorption.

XRD analysis was employed to examine the structural and phase composition changes in corncob biochar film pre- and post-Cr(VI) adsorption. Figure 15 illustrates a broad diffraction peak within the 2θ range of $20\text{--}25^\circ$, characteristic of carbon materials, which is indicative of corncob aromatization and graphitization during pyrolysis, thereby suggesting an amorphous structure for CBC.

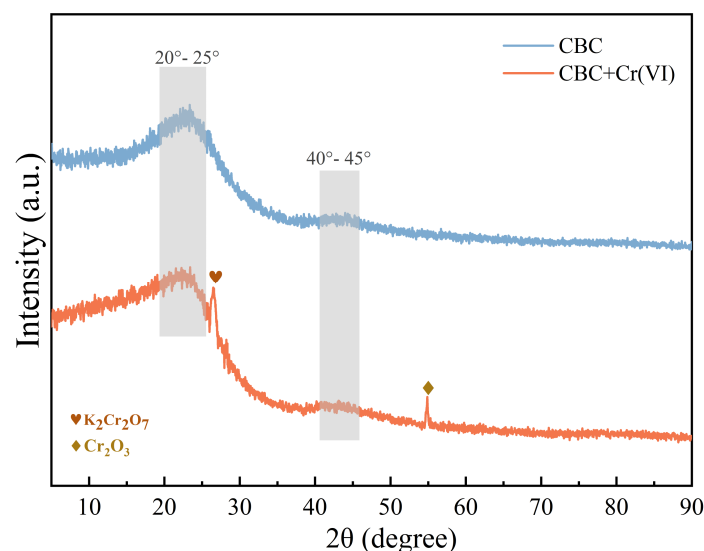


Figure 15. XRD of CBC before and after adsorption of Cr(VI).

Upon Cr(VI) adsorption, the XRD pattern of CBC exhibited diffraction peaks at $2\theta = 26.48^\circ$ and 54.85° . Comparison with standard card data revealed correspondence to crystal faces PDF#34-0756 (210) and PDF#38-1479 (116), respectively. This finding confirms the presence of $K_2Cr_2O_7$ and Cr_2O_3 on the CBC material following Cr(VI) adsorption, signifying successful adsorption of Cr(VI) by CBC.

(5) XPS analysis before and after Cr(VI) adsorption.

Figure 16a displays the total XPS spectra of corncob biochar film before and after Cr(VI) adsorption, revealing the emergence of the Cr2p peak value post-adsorption.

In Figure 16b, the C 1s and O 1s spectra before and after Cr(VI) adsorption by CBC are presented. In the C 1s region, the primary chemical states of carbon pre- and post-adsorption include C-C/C-H (around 284.8 eV), C=O (around 286 eV), and C-O/O-C=O (around 288.8 eV). After Cr(VI) adsorption, a slight decrease in the proportion of C-C/C-H (from 76.85% to 76.59%) and an increase in C=O (from 14.50% to 14.66%) suggest the involvement of more carbonyl groups in the adsorption process. Similarly, the proportion of C-O/O-C=O also increased (from 8.65% to 8.75%), potentially indicating the presence of more alcohol or carboxyl groups forming coordination bonds with Cr(VI).

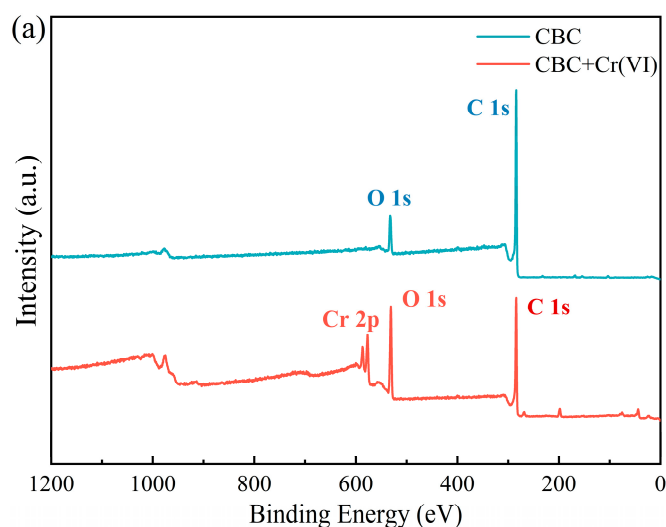


Figure 16. Cont.

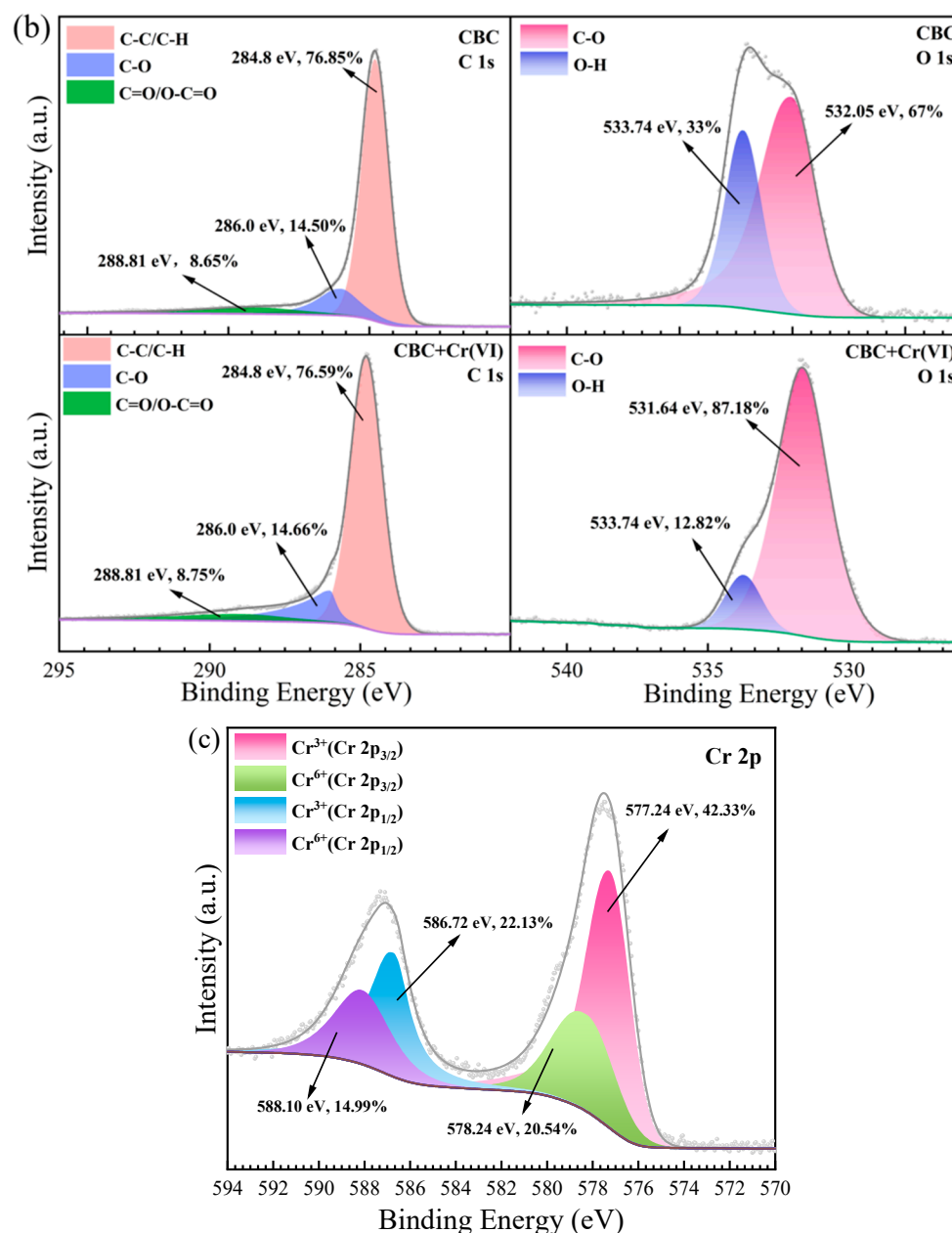


Figure 16. XPS spectra of CBC. (a) Full spectrogram; (b) C 1s, O 1s; and (c) Cr 2p.

In the fine O 1s spectrum, the main chemical states of oxygen pre- and post-adsorption include C-O (around 532.0 eV, 531.64 eV) and O-H (around 533.74 eV). Following adsorption, there was a notable increase in the proportion of C-O (from 67% to 87.18%) and a decrease in O-H (from 33% to 12.82%). This indicates that during the adsorption process, chemical bonds are formed between the adsorbent surface and the target molecule, resulting in an increase in the proportion of C-O bonds. This usually indicates that adsorbent molecules have reacted with active oxygen functional groups (such as O-H) on the surface of the material to form new C-O bonds [40,41]. The decrease in O-H ratio indicates that the hydroxyl group on the surface of the material is partially consumed, which may result in a dehydration reaction or covalent bond formation with adsorbent molecules. This further proves that the surface active site is involved in the adsorption reaction [42,43]. The increasing proportion of C-O and the decreasing proportion of O-H indicate that the hydroxyl group on the surface of the material participates in the chemical reaction during the adsorption process, leading to the formation of a C-O bond; this reflects an adsorption

mechanism dominated by chemisorption and accompanied by the transformation of surface functional groups and the consumption of active sites. This change indicates that there is a strong interaction between adsorbent and material [44,45]. Because a decline in O-H led to an increase in C-O and C=O, this conclusion is also reflected in the figure of C 1s, but because the C-C bond has absolute dominance, the increase in C-O and C=O content is not as significant as that in O 1s [46,47]. A 20% increase in the O 1s signal caused by C-O means that there is a 20% increase in the strength of the O 1s signal in the presence of C-O. This may be because the formation of the C-O bond increases the number of oxygen atoms on the surface of the material, resulting in an enhanced O 1s signal. O's C 1s signal increased by a total of only 0.26%, This difference may be due to differences in the chemical environment on the surface and inside of the sample. The C-O bond may be primarily present on the surface of the sample, while other oxygen-containing species may be present in different forms inside or on the surface of the sample. In addition, sample preparation and processing may also affect the measurement results of C 1s signals [48–50].

In Figure 16c, four distinct peaks are observed in the Cr2p orbit, representing different oxidation states of chromium. The Cr2p_{3/2} peaks at 577.24 eV and Cr2p_{1/2} peaks at 586.72 eV indicate the presence of Cr(III), while peaks at 578.24 eV and 588.10 eV indicate the presence of Cr(VI). Notably, the peak intensity of Cr(III) is relatively strong compared to Cr(VI), suggesting that a portion of Cr(VI) undergoes reduction to the less toxic Cr(III) during the adsorption process. This reduction mechanism may be attributed to the interaction between functional groups (e.g., hydroxyl, carbonyl, etc.) on the biochar film surface and Cr(VI), facilitating its reduction to Cr(III) [51].

4. Conclusions

This study investigated the preparation, characterization, and removal of Cr(VI) from water using corncob biochar film, revealing its efficiency through various characterization techniques such as FTIR, XPS, and SEM.

(1) The optimal preparation conditions for CBC were determined as follows: a heating rate of 5 °C/min, a pyrolysis temperature of 500 °C, and a pyrolysis time of 120 min, resulting in a removal rate of 73.55% and an adsorption capacity of 18.39 mg/g. Heating rate and pyrolysis temperature significantly influenced Cr(VI) removal by CBC, whereas pyrolysis time had minimal impact. In the experiment that tested Cr(VI) adsorption by CBC, the best initial concentration was 0.03 g/L, the best pH was 2, and the best adsorbent dosage was 8 g/L. The adsorption kinetics of Cr(VI) by CBC followed the quasi-second-order kinetic model, and the adsorption isotherm conformed to the Langmuir model.

(2) SEM analysis revealed tube bundle structures in CBC morphology, with pores partially closed and the surface becoming rougher after Cr(VI) adsorption. BET analysis confirmed CBC's porous nature, while XRD analysis indicated its amorphous structure. FTIR and XPS studies revealed diverse functional groups on the biochar film's surface, suggesting complex reactions facilitating effective Cr(VI) adsorption. The adsorption mechanism of Cr(VI) by biochar film primarily involves monolayer adsorption controlled by chemical reaction mechanisms, including electrostatic forces and complexation reactions of surface functional groups. Additionally, biochar film's surface polarity and hydrophilic properties significantly regulate its adsorption efficiency. However, the removal rate decreased to 20.01% after five cycles, indicating decreased efficiency upon reuse.

Author Contributions: Y.W. and J.Z. (Writing—review and editing): Preparation, creation and/or presentation of the published work by those from the original research group, specifically critical review, commentary or revision—including pre- or post-publication stages. S.J. (Formal analysis): Application of statistical, mathematical, computational, or other formal techniques to analyze or synthesize study data. Z.X. and J.L. (Conceptualization): Ideas; formulation or evolution of overarching

research goals and aims. T.Y. and C.T. (Resources): Provision of study materials, reagents, laboratory samples, instrumentation, computing resources, or other analysis tools. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by The Technological Project of Heilongjiang Province “the open competition mechanism to select the best candidates” (2022ZXJ05C02).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in this article.

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

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