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Study on the removal efficiency of Cr(VI) from corn cob biochar loaded with zero-valent iron on wastewater

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Abstract

In this study, the adsorption of Cr(VI) in wastewater by corncob biochar modified with zero-valent iron was evaluated. The results showed that zero-valent iron modification significantly improved the adsorption effect of Cr(VI) in wastewater. The main research contents and results were as follows: CBC-nZVI was successfully prepared by liquid-phase reduction method with grape seed extract as reducing agent under the optimal iron-carbon ratio of 1:1. The removal rate of Cr(VI) by CBC-nZVI was as high as 96.14%, and the adsorption capacity was increased to 24.04 mg/g, which was 22.59% higher than that of unmodified CBC. The results not only demonstrated the high efficiency of CBC-nZVI in treating wastewater containing Cr(VI), but also confirmed the potential application of grape seed extract as an environmentally friendly reducing agent in environmental treatment. The adsorption process of Cr(VI) by CBC and CBC-nZVI accords with pseudo-second order kinetic model and Langmuir adsorption isotherm model, and it is pointed out that the adsorption process is mainly monolayer chemisorption. In addition, after CBC-nZVI was recycled for 5 times, the removal rate of Cr(VI) remained at around 50%, demonstrating its good stability and reuse potential. The results of SEM, BET, FTIR, XPS and XRD show that CBC and CBC-nZVI have mixed microporous and mesoporous characteristics and amorphous structure, and CBC-nZVI reduces the problem of aggregation of nZVI. Meanwhile, abundant oxygen-containing functional groups endow CBC and CBC-nZVI with excellent adsorption performance, which mainly removes Cr(VI) through electrostatic action, coordination reaction and redox reaction. In addition, the water affinity and surface polarity of the adsorbent also affect the adsorption process.

Keywords: cob; biochar; zero-valent iron; Cr(VI)

1. Introduction

With the rapid development of science and technology and the continuous improvement of agricultural modernization level in China, the annual output of agricultural products continues to grow. As one of the main food crops in China, the annual output of corn has reached about 280 million tons.[1] In the process of corn processing, corn cobs are the main by-product, and the annual output exceeds 60 million tons.[2] Due to high output, corn cobs have long faced the problems of resource waste, carbon emission and soil degradation caused by incineration or waste.[3] However, corn cobs can be prepared into biochar after high temperature calcination. Biochar is a carbonaceous material prepared by pyrolysis of biomass resources. Because of its high specific surface area, rich pore structure and surface functional groups, it is widely used in the adsorption and removal of heavy metals in wastewater, which has become a research hotspot in the environmental field.[4][5][6] Biochar prepared from corncob can be converted to high value by pyrolysis. Its cellulose/hemicellulose content is higher than that of traditional wood materials. After pyrolysis, it is easier to form stable aromatic structure and has low ash content. It has significant potential in treating sewage pollution.[7][8]

However, Cr(VI) removal efficiency of conventional biochar is poor in some cases, which limits its further application in water treatment field.[9] Cr(VI), as a highly toxic heavy metal pollutant, is widely present in industrial wastewater, and its efficient removal has always been an important challenge in environmental treatment.[10][11][12] In order to improve the removal efficiency of biochar, modification technology is usually used to optimize it.[13][14][15] Among them, zero-valent iron (nZVI) can reduce toxic heavy metal ions due to its strong reducing ability.(e.g. Cr^{6+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , etc.) reduced to low or non-toxic forms, or fixed by coprecipitation.[16][17] nZVI modified biochar is a biochar treated by chemical reduction method, in which metallic iron is reduced to zero-valent iron particles by the action of reducing agent, and reacts with the surface of biochar to improve the performance of biochar.[18] It can effectively remove a variety of pollutants in water, especially heavy metal Cr(VI), so it is an ideal choice for modified biochar.[19][20][21] However, due to its remarkable magnetic and high surface energy characteristics, nZVI is prone to agglomeration when used alone, resulting in a reduction in its specific surface area and reactivity, thus weakening its removal

effect on pollutants.[22][23][24] In order to solve this problem, nZVI is loaded on the surface of biochar to form a composite material, which not only can effectively prevent the agglomeration of nZVI, but also can combine the dual purification mechanism of chemical reduction and physical adsorption to significantly improve the removal efficiency of heavy metals in water.[25]

Traditional methods for preparing nZVI include vapor deposition, liquid phase reduction, etc., but these methods are expensive and cause secondary pollution.[26] In recent years, a low-cost and environmentally friendly method for preparing nZVI has been successfully developed by extracting flavonoids or polyphenols from natural resources such as tea leaves and fruit wastes as reducing agents.[27][28] These natural reducing agents are not only widely available, but also avoid the use of toxic reducing agents (such as sodium borohydride) in traditional chemical synthesis methods, reducing the risk of secondary pollution and eliminating the potential harm of traditional chemical reducing agents to the environment.[29][30] Therefore, compounding this green synthetic nZVI with biochar not only reduces the cost of material preparation, but also reduces the dependence on chemical reagents, further reduces the negative impact on the environment, and promotes the recycling of natural resources.[31] In this chapter, grape seed extract is used as a natural reducing agent to prepare biochar-loaded zero-valent iron composites.[32]

Based on the above background, green synthesis of nZVI from grape seed extract and its application to modified biochar to remove pollutants has significant advantages and feasibility.[33] The removal efficiency of Cr(VI) was systematically studied by adjusting the experimental conditions such as Fe/C ratio, Cr(VI) initial concentration, material dosage and solution pH value.[34][35] In addition, through adsorption model fitting and material characterization analysis, the application potential of grape seed extract in material preparation and its adsorption mechanism for Cr(VI) were discussed in depth.[36][37] The green synthesis method adopted in this study has the advantages of simple operation, low cost and environmental friendliness. The preparation process of biochar usually involves pyrolysis of biomass, which can realize carbon fixation and reduce greenhouse gas emissions.[38][39][40] Combined with green synthesis nZVI, the environmental performance of the material is further improved. It provides more green solutions for environmental protection and pollution control.

1. Experimental Part

2.1 Experimental drugs

The main chemicals and reagents are shown in Table 1-1.

Table 1-1 Chemical reagents in experiment

Drug name	Chemical formula	purity	supplier
Dibenzoyl dihydrazine	$C_{13}H_{14}N_4O$	analysis pure	Fuchen (Tianjin) Chemical Reagent Co., LTD
Concentrated sulfuric acid	H_2SO_4	analysis pure	Tianjin Guangfu Fine Chemical Research Institute
Phosphoric acid	H_3PO_4	analysis pure	Tianjin Fuyu Fine Chemical Co., LTD
Potassium dichromate	$K_2Cr_2O_7$	analysis pure	Tianjin Fuchen chemical reagent factory
Acetone	C_3H_6O	analysis pure	Nanjing Chemical Reagent Co., LTD
HCL	HCL	analysis pure	Nanjing Chemical Reagent Co., LTD
Sodium hydroxide	NaOH	analysis pure	Tianjin Mainland chemical reagent factory
Anhydrous ethanol	CH_3CH_2OH	analysis pure	Tianjin Tianli Chemical Reagent Co., LTD
Ferrous sulfate heptahydrate	$FeSO_4 \cdot 7H_2O$	analysis pure	Tianjin Tianli Chemical Reagent Co., LTD
Grape seed OPC powder	-	98%	Shandong Jinsheng Biotechnology Co., LTD

2.2 Experimental instruments and equipment

The main instruments used in this paper are shown in Table 1-2.

Table 1-2 Instrument required in experiment

Instrument name	Model number	producer
Ultraviolet-visible spectrophotometer	UV-51	Shanghai Yuan Analysis Instrument Co., LTD
Infrared	Spectrum Two	Shanghai Perkinelmer Enterprise Management Co., LTD
Electronic balance	FA2004	Shanghai Yue Ping Scientific Instrument Co., LTD
Blast drying oven	DHG-9055A	China Shanghai Yiheng Scientific Instrument Co., LTD
pH meter	PHS-2F	Shanghai Yi Electrical Scientific Instruments Co., LTD
Water bath shaker	SHC-C	Shanghai Jingqi Instrument Co., LTD
Chinese herbal medicine crusher	1000C	Dongguan City Fangtai Electric Co., LTD
High temperature combustion tube furnace	SK-2-13	Beijing Yongguang Medical Instrument Co., LTD
Oxygen-free glove box	-	Henan Xingda Plastic Co., LTD

2.3 Preparation of zero-valent iron supported by biochar

2.3.1 Preparation of zero-valent iron

Zero-valent iron was prepared by liquid phase reduction. Grape seed OPC powder (proanthocyanidins $\geq 98\%$) 2g purchased from the Internet was dissolved in 100mL distilled water to obtain grape seed extract. Dissolve 1.39g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 100mL distilled water and stir in a beaker for 30min to obtain 0.5mol/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution. All solutions were put into an oxygen-free glove box, and 100mL grape seed extract was slowly added to the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution at room temperature

(25°C) under N₂ atmosphere, stirring continuously to promote the reaction until black solids appeared. After drip adding, continue to stir for 1h, then rapidly vacuum filter, and then wash with anhydrous ethanol and distilled water for 3 times each, and freeze vacuum drying at -56°C and -0.095MPa, to obtain zero-valent iron (nZVI).

2.3.2 Preparation of zero-valent iron supported by biochar

Preparation of biochar supported zero-valent iron by liquid phase reduction. According to the experimental method of Assirey Eman A et al.[41] The calcination conditions of 500°C, 2h, 5°C/min were selected for the preparation of biochar. Finally, the removal rate of corncob biochar (CBC) was 74.77%. Add into 100mL, 0.5mol/LFeSO₄•7H₂O solution and stir for 30min. The grape seed extract was slowly added to the iron-carbon mixture at room temperature (25°C) in a glove box under N₂ atmosphere, and stirred for 1h to make it fully react. After the end, the mixture was quickly vacuumized and filtered, then washed with anhydrous ethanol and distilled water for three times each, and frozen vacuum dried at -56°C and -0.095MPa to obtain biochar/zero-valent iron composite material, which was recorded as CBC-nZVI.

2.4 Characterization and principle of materials

2.4.1 Scanning electron microscope (SEM) determination

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

2.4.2 Specific surface area (BET) and aperture analysis

The specific surface area, total pore volume and average pore diameter of corncob biochar samples were measured by nitrogen adsorption-desorption method, and the pore structure was evaluated by analyzing the types of desorption curves.

2.4.3 X-ray diffraction (XRD) determination

In this experiment, the crystal structure of the material was determined by X-ray diffractometer. Test conditions: Scanning Angle is 5-90° , scanning speed is 5°/min.

2.4.4 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. All spectra are calibrated at C1s(C-C284.8eV).

2.4.5 Fourier Infrared Spectroscopy (FTIR) determination

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

2.5 Adsorption experiment

2.5.1 Cr(VI) standard curve drawing

The Cr(VI) standard curve is drawn according to the national standard GB7467-S7.

1. Preparation of reagents

Cr(VI) standard solution: Weigh potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, superior pure) $0.2829 \pm 0.001\text{g}$, dry and dissolve in water to make 100 mg/L chromium standard storage solution. Draw 5 mL from the reserve solution and dilute it to 500 mL to obtain 1 mg/L chromium standard solution.

Color developing agent: Weigh dibenzoyl dihydrazine ($\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$) 2 g , dissolve in 50 mL acetone and add distilled water to dilute to 100 mL , store in brown bottle at low temperature. Check the color before use, if the color becomes darker, it should not be used. Cr(VI) reacts with $\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$ to form a purple-red compound.

1. Cr(VI) determination

Take 50 mL distilled water in the colorimetric tube, add 0.5 mL sulfuric acid solution (sulfuric acid: distilled water =1:1) and 0.5 mL phosphoric acid solution (phosphoric acid: distilled water =1:1), shake well. Add 2 mL of color developer, shake well and leave for 5-10 minutes. The absorption value was measured at 540 nm wavelength and used as a blank test. The sample to be tested (Cr(VI) concentration $<0.05\text{mg}$) was diluted to 50 mL and absorbance was determined in the same way. By subtracting the absorbance value of blank test, the concentration of Cr(VI) is calculated using the standard curve.

1. Drawing of standard curves

Add Cr(VI) standard solution in different volumes (0 mL , 0.2 mL , 0.5 mL , 1 mL , 2 mL , 4 mL , 6 mL , 8 mL , 10 mL) into the 50 mL colorimetric tube, dilute it to the line, measure absorbance according to the established steps, and draw the concentration-absorbance curve accordingly. In order to subsequently determine the concentration of Cr(VI) by absorbance. Figure 1-1 shows the standard curve.

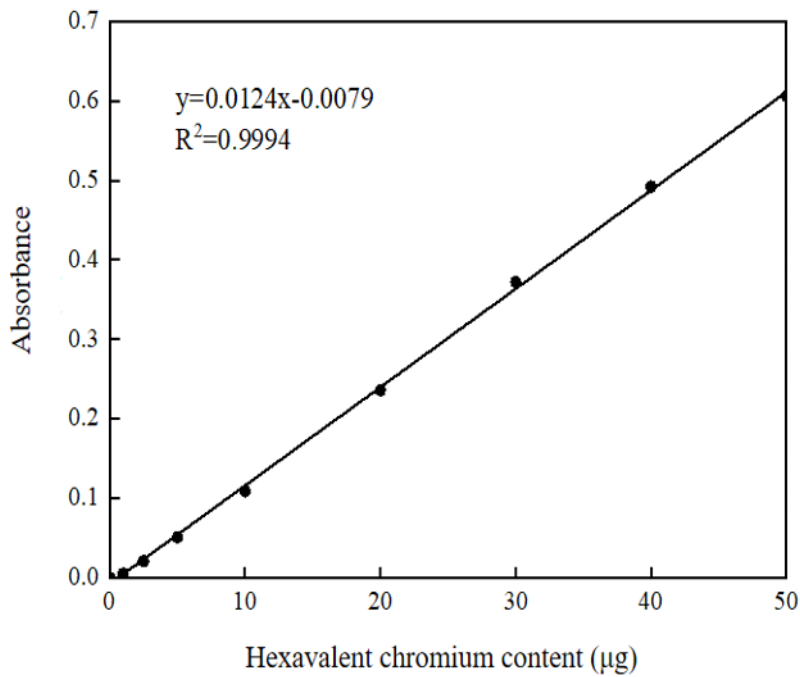


Fig.1-1 The standard curve of Cr(VI)

2.5.2 Adsorption experiment method

0.1g biochar and 50mLCr(VI) solution (50mg/L, pH=2) were oscillated in a water bath at 25°C and 130r/min for 24h for adsorption experiment. After the adsorption, 0.22μm filter membrane was used to filter and sample, and the remaining concentration of Cr(VI) was measured by standard curve to evaluate the adsorption performance of biochar. The adsorption capacity and removal rate were 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 (1.1) and (1.2) :

$$\dots\dots\dots (1.1)$$

$$\dots\dots\dots (1.2)$$

Formula:

Initial mass concentration of C_0 -- Cr(VI) (mg/L);

Mass concentration (mg/L) at time of C_t -- Cr(VI)t;

V -- solution volume (L);

t -- adsorption time (min);

m - Dosage of biochar.

2.6 Adsorption kinetics experiment

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

2.7 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, 100 mg/L (pH=2) were prepared, and 0.1g CBC-nZVI was added. The removal rate (r) and adsorption capacity (Q) were calculated by using 0.22µm filter membrane after 24 h oscillating in a constant temperature water bath oscillator at 25 °C and 130 r/min.

2.8 Adsorption cycle regeneration experiment

0.1gCBC-nZVI was added to 50mL Cr(VI) solution (50mg/L, pH=2) and oscillated in a constant temperature water bath oscillator at 25°C and 130r/min for 24h. After saturation adsorption, CBC-nZVI was placed in 50mL, 0.1mol/LNaOH, and shook under the same conditions to release Cr(VI). After that, the Cr(VI) removal experiment was carried out with recycled CBC-nZVI and its removal efficiency was measured.

1. Experimental results and discussion

3.1 Study on Cr(VI) removal performance of biochar/zero-valent iron

3.1.1 CBC-nZVI production and nZVI proportion estimation

Table 1-3 shows the output data of the composite CBC-nZVI. In this material, the amount of nZVI can be calculated by the total production of CBC-NZVI minus the amount of CBC added. Based on the tabular data, it was observed that nZVI yields were roughly the same for all materials, indicating that the conversion efficiency of Fe²⁺ to nZVI was not affected by the addition of biochar.

Table 1-3 Preparation of the CBC-nZVI composites and estimation of nZVI ratios.

CBC Dosage (g)	Fe ²⁺	Grape seed OPC powder content (g)	Total production (g)	nZVI Production (g)	Proportion of nZVI (%)
0.093	0.28	2	0.2694	0.1764	65.4789
0.14	0.28	2	0.2962	0.1562	52.7346
0.28	0.28	2	0.4714	0.1914	40.6024
0.56	0.28	2	0.6916	0.1316	19.0283

3.1.2 Factors affecting Cr(VI) removal efficiency

3.1.2.1 Influence of iron-carbon ratio on Cr(VI) removal by CBC-nZVI

0.093g, 0.14g, 0.28g, and 0.56gCBC were added into 100mL and 0.5mol/LFeSO₄•7H₂O solution respectively, and then an equal amount of grape seed extraction solution with a concentration of 0.02g/mL was slowly added into the iron carbon mixed solution in the glove box, and stirred in N₂ atmosphere for 1h to make it fully react. CBC-nZVI with iron to carbon ratio of 3:1, 2:1, 1:1 and 1:2 were obtained respectively.

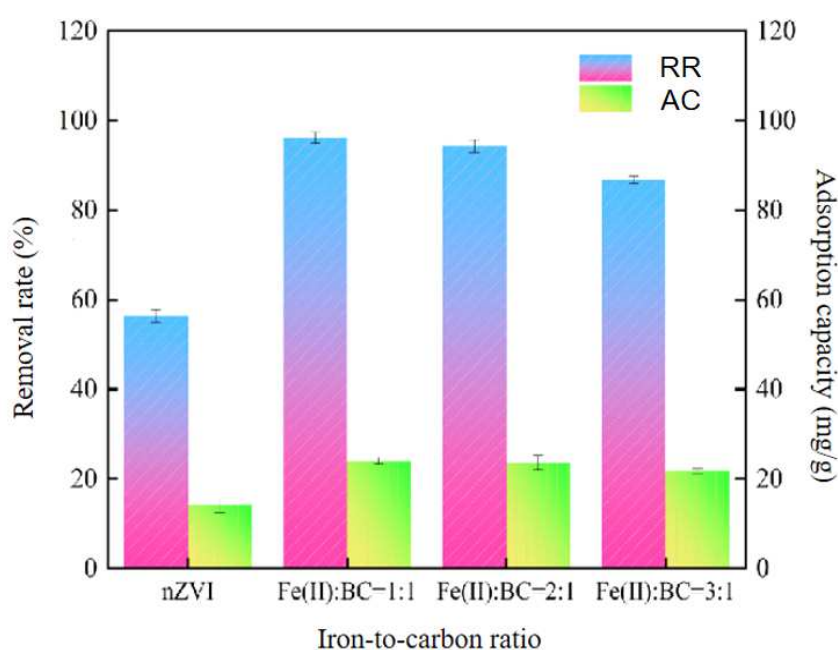


Fig.1-2 The impact of different iron-carbon ratios on the removal of Cr(VI) by CBC-nZVI

Figure 1-2 shows the effect of different iron-carbon ratios on the removal of Cr(VI) by CBC-nZVI. As can be seen from the figure, when the iron-carbon ratio increases from 1:1 to 3:1, the removal rate and adsorption capacity of Cr(VI) decrease significantly. This may be due to the accumulation of too much nZVI, resulting in a decrease in its effective surface area and a corresponding decrease in the active site of Cr(VI) reaction, thus reducing the removal rate. Secondly, excess nZVI may cause Cr(VI) to be over-reduced, producing some side reaction products, which may be re-dissolved into the solution, reducing the apparent removal efficiency. The removal rate of iron carbon ratio 1:1 is higher than 1:2, which may be due to the high adsorption capacity of CBC, which preferentially adsorbs Cr(VI),

prevents it from contacting nZVI, and reduces the chance of Cr(VI) reduction to Cr(III).

The removal rate of all CBC-nZVI materials was higher than that of biochar alone and nZVI alone. When the iron-carbon ratio was 1:1, the removal rate and adsorption capacity of Cr(VI) reached the highest, which were 96.14% and 24.04mg/g, respectively, higher than that of nZVI(R=56.39%, Q=14.1mg/g) and CBC(R=73.55%, Q=18.39mg/g), which indicated that the performance and removal efficiency of biochar could be effectively improved by loading zero-valent iron on biochar.

3.1.2.2 Influence of solution pH on Cr(VI) removal by CBC-nZVI

Take 50mL of Cr(VI) solution of 50mg/L and place it in a beaker, and adjust the pH of the solution with HCl and NaOH solution (pH gradient is set to 2, 3, 4, 5, 6, 7, 8, 9). Then the solution was transferred to a 100mL conical bottle, 0.1g of CBC-nZVI was added to it, and the reaction was carried out in a water bath oscillator for 24h at 25°C and 130r/min. After the shock, 0.22μm filter membrane was used to filter and sample the absorbance, and the removal rate R and adsorption amount Q were calculated.

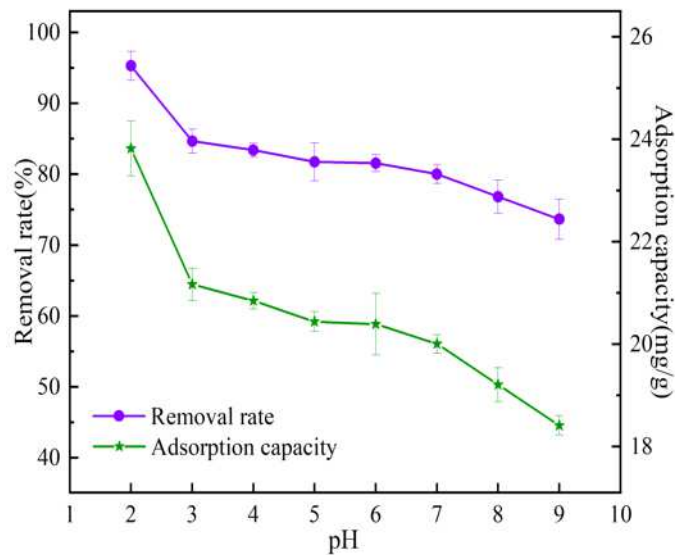
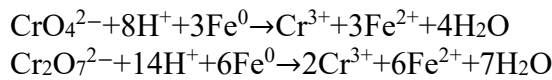


Fig.1-3 Effect of pH on Cr(VI) removal

Figure 1-3 shows the Cr(VI) removal efficiency and adsorption capacity of CBC-nZVI as the pH value of the solution changes. When pH value increased, the removal rate and adsorption capacity decreased significantly, and the decrease of adsorption capacity and removal rate changed sharply when pH=3. When pH=2, the removal rate and adsorption capacity reached the peak values, which were 95.27%

and 23.82mg/g, respectively, and the removal rate was higher than that of CBC33.91%. In the range of pH 3 to 9, the removal rate tends to be stable and the adsorption capacity decreases. When pH=9, the removal rate is 73.63% and the adsorption capacity is 18.41mg/g, which is higher than the removal rate (61.36%) and the adsorption capacity (15.34mg/g) when CBCpH=2. This suggests that lower pH is conducive to the removal of Cr(VI) from water by CBC-nZVI.

It can be seen from the figure that under alkaline conditions, the corrosion rate of nZVI is slow and the Fe^{2+} generated is less, thus reducing the reduction efficiency. Acidic conditions are more conducive to the removal of Cr(VI) by CBC-nZVI, because chromium solution contains HCrO_4^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ and other anions. When nZVI is added, a reduction reaction occurs with Cr(VI), reducing Cr(VI) to Cr(III), and the chemical reaction is:



3.1.2.3 Influence of Cr(VI) initial concentration on Cr(VI) removal by CBC-nZVI

50mL of Cr(VI) solution with a concentration of 10mg/L, 20mg/L, 30mg/L, 40mg/L, 75mg/L and 100mg/L pH of 2 was taken into a 100mL conical bottle, and then 0.1g of CBC-nZVI was added into the bottle. Reaction in a water bath oscillator for 24h. After the oscillation, the absorbance was measured, and the removal rate R and adsorption amount Q were calculated.

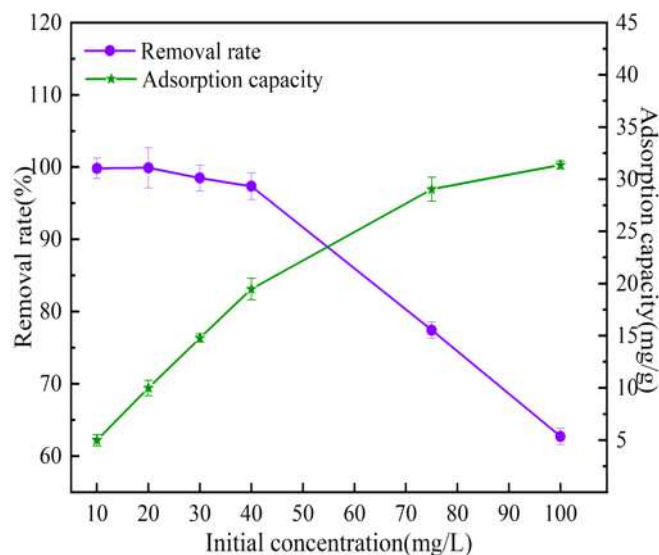


Fig.1-4 Effect of Initial concentration on Cr(VI) removal

As can be seen from Figure 1-4, when the initial concentration of Cr(VI) increased from 10mg/L to 100mg/L, the removal rate of Cr(VI) by CBC-nZVI decreased from 99.82% to 62.71%, and the adsorption capacity increased from

4.99mg/g to 31.35mg/g. CBC-nZVI was more efficient at removing Cr(VI) when the initial concentration was low, possibly because the relatively low contaminant concentration allowed the reaction to be unrestricted and the reaction site to be abundant. However, as the initial concentration increases, the sites available for reaction become insufficient to handle more Cr(VI) molecules, resulting in a decrease in removal rates. Since more Cr(VI) molecules are available for adsorption, the amount of CBC-nZVI adsorbed per gram increases with the initial concentration.

3.1.2.4 Influence of adsorbent dosage on Cr(VI) removal by CBC-nZVI

50mL, 50mg/L Cr(VI) solution with pH=2 was put into 100mL conical bottle, and 0.05g, 0.1g, 0.2g, 0.3g, 0.4g CBC-nZVI was added to the solution, and then reacted in a water bath oscillator for 24h at 25°C and 130r/min. After the oscillation, the absorbance was measured, and the removal rate R and adsorption amount Q were calculated.

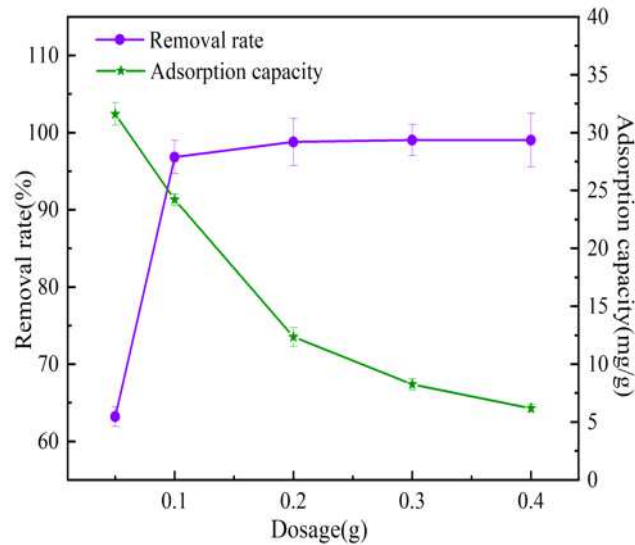


Fig.1-5 Effect of CBC-nZVI dosage on Cr(VI) removal

As can be seen from Figure 1-5, with the increase of the dosage of CBC-nZVI, the removal rate of Cr(VI) significantly increased, especially at a low dosage. This suggests that increasing the amount of CBC-nZVI can significantly improve the removal efficiency, possibly because more active sites are involved in the reaction. At the dosage of 0.1g, the removal rate increased sharply, indicating that this point may be the critical point at which the reaction began to proceed significantly. The adsorption capacity decreased gradually with the increase of the dosage of CBC-nZVI. This may be because as the dosage increases, the Cr(VI) available for adsorption per unit mass of CBC-nZVI decreases, indicating that the adsorption has

reached a saturated state. When the dosage exceeds a certain point (e.g. 0.2g), the removal rate stabilizes, which may mean that all available Cr(VI) has been effectively removed, or that the reaction has reached an equilibrium state. Therefore, the use of CBC-nZVI is more cost-effective at low doses.

3.1.3 Adsorption kinetics experiment

In order to further explore the rate control steps in the adsorption process of CBC-nZVI removing Cr(VI), quasi-first-order kinetics and quasi-second-order kinetics (as shown in formulas 1.3 and 1.4) were used to fit the kinetic data, and the intra-particle diffusion model (as shown in formula 1.5) was used to analyze the intra-particle diffusion process of Cr(VI).

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

$$\dots\dots\dots (1.3)$$

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 equations:

$$\dots\dots\dots (1.4)$$

Formula:

k_s ——Rate constants for quasi-second-order kinetic models, min^{-1} 。

(3) Equation of diffusion within particles:

$$\dots\dots\dots (1.5)$$

Formula:

k_j ——The rate constant of the diffusion reaction within the particle, $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$;

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-nZVI adsorbing Cr(VI) are shown in Figure 1-5, and the fitting parameters are shown in Table 1-4.

Table 1-4 Kinetic fitting parameters of Cr(VI) adsorption by CBC-nZVI

	$Q_e(\text{mg/g})$	Quasi-first-order dynamics			Quasi-second-order dynamics		
		$Q_t(\text{mg/g})$	$k_c(\text{min}^{-1})$	R^2	$Q_t(\text{mg/g})$	$k_s(\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1})$	R^2
CBC-nZVI	23.05981	21.76871	0.0218	0.95993	23.3704	0.0015	0.99258

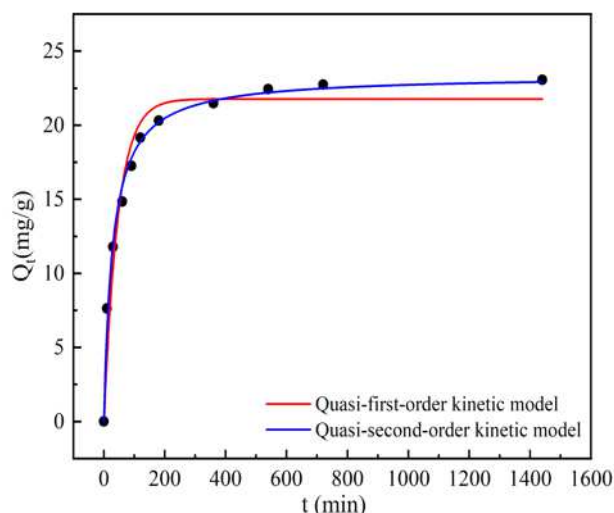


Fig. 1-6 Kinetic fitting curve of Cr(VI) adsorption by CBC-nZVI

According to Table 1-4, the adsorption of Cr(VI) by CBC-nZVI is more consistent with the quasi-second-order kinetic model. The fitting R^2 of CBC-nZVI using the quasi-second-order kinetic model is 0.99258, and the fitting degree is extremely high, higher than that of the quasi-first-order kinetic model. The equilibrium adsorption capacity of 23.3704mg/g fitted by the model is also basically consistent with the experimental result of 23.05981mg/g.

Therefore, the quasi-second-order kinetic model can more accurately describe the dynamic change of Cr(VI) adsorption capacity over time after the addition of CBC-nZVI. According to this model, the adsorption process of Cr(VI) by CBC-nZVI is mainly dominated by chemisorption, and this process is affected by the square of the number of available adsorption sites on the surface of CBC-nZVI. With the increase of time, the adsorption capacity of Cr(VI) increased rapidly within the first 180min. There are may be due to the beginning a large number of unused functional groups and a large specific surface area on the surface of CBC-nZVI. As time progressed to 360min, the adsorption rate began to slow down due to the reduction of available adsorption sites, and reached an equilibrium state around 1440min. In addition, the rate constant $k_s < 1$ indicates that the reaction is rapid.

Table 1-5 Adsorption particle diffusion fitting parameters for CBC-nZVI on Cr(VI)

	Phase I			Phase II		
	R^2	$k_j(\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2})$	$C(\text{mg/g})$	R^2	$k_j(\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2})$	$C(\text{mg/g})$
CBC-nZVI	0.96786	1.26697	4.55347	0.83767	0.0837	20.2449

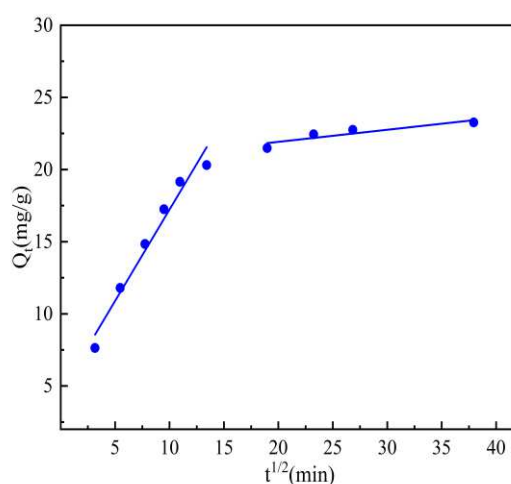


Fig. 1-7 Particle diffusion fitting curves of CBC-nZVI adsorption Cr(VI)

As shown in Table 1-5 and Figure 1-7, the adsorption behavior of Cr(VI) by CBC-nZVI presents two main stages according to the in-particle diffusion model: The rapid adsorption in the initial stage is attributed to the extramembrane diffusion, that is, Cr(VI) quickly passes through the solution interface to the surface of the adsorbents; The subsequent second attachment stage is due to the slow migration and adsorption of Cr(VI) in the channels inside the adsorbent. Because the fitted curve does not pass through the coordinate origin, this indicates that in addition to intra diffusion, surface adsorption also plays an important role in the adsorption rate, and the two together determine the overall adsorption rate. In addition, the adsorption line slope of CBC-NZVI is larger than that of CBC, indicating that the liquid film diffusion of Cr(VI) on CBC-NZVI is smoother.

3.1.4 Isothermal adsorption experiment

In order to better evaluate the adsorption capacity of CBC-nZVI on Cr(VI) and understand the adsorption mechanism between CBC-nZVI and Cr(VI), Langmuir model and Freundlich model were used for fitting. Figure 1-7 shows the fitting curve, and Table 1-6 describes the model parameters.

Table 1-6 Isotherm model parameters

	Langmuir model			Freundlich model		
	Q_m (mg/g)	K_l (L/mg)	R^2	K_f (L/mg)		R^2
CBC-	50.20174	0.01476	0.96679	1.86887	0.61009	0.92411

nZVI						
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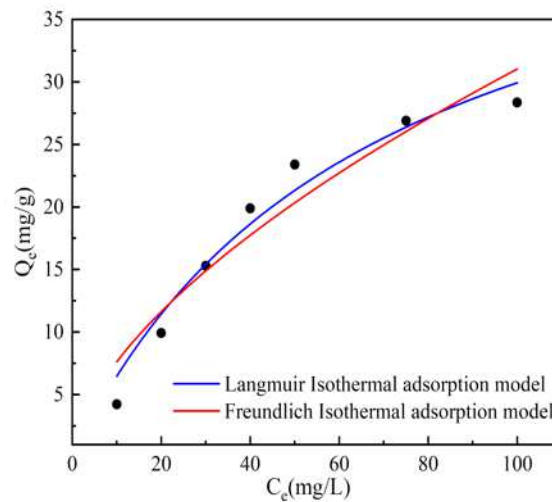


Fig.1-8 Isothermal adsorption fitting curve of Cr(VI) by CBC-nZVI

As shown in Table 1-6 and Figure 1-8, the correlation coefficient R^2 obtained by the Langmuir model is more significant than that obtained by the Freundlich model, indicating that the adsorption process of Cr(VI) by CBC-nZVI mainly complies with the Langmuir model, indicating that there are uniformly distributed and fixed number of adsorption sites on the surface of CBC-nZVI. The adsorption of Cr(VI) on its surface showed monolayer adsorption characteristics. K_l in Langmuir model is less than 1, indicating that the adsorption process is easier to carry out. This result emphasizes that CBC-nZVI can adsorb Cr(VI) more efficiently.

3.1.5 Adsorption cycle regeneration experiment

As shown in Figure 1-9, by observing the removal efficiency, it can be found that after five cycles of adsorption-resolution cycles, the removal performance of Cr(VI) by CBC-nZVI gradually decreases. The removal rate of Cr(VI) was reduced by 46.27% (from 96.83% to 50.56%) under the adsorption of CBC-nZVI. However, the Cr(VI) removal rate of CBC-NZVI remained above 50%, which still had good adsorption performance compared with the original corncob biochar CBC. Therefore, in the actual application process, the selection of CBC-nZVI as the adsorbent is not only economical and applicable, but also can efficiently remove pollutants.

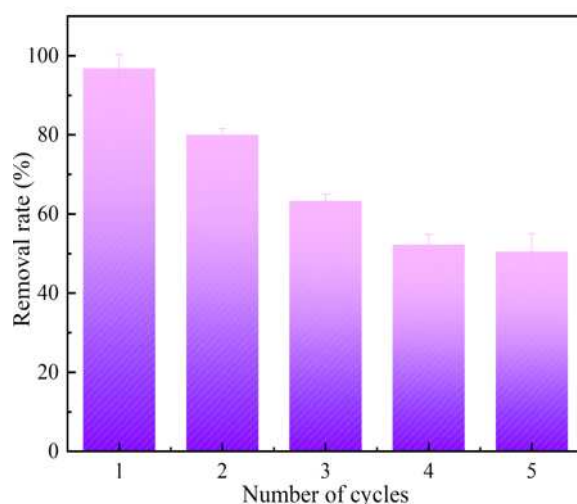


Fig.1-9 The ability of CBC-nZVI recycling to adsorb Cr(VI)

3.2 Material characterization and removal mechanism

3.2.1 SEM analysis before and after adsorption of CBC-nZVI

Figure 1-10 shows the SEM images of green zero-valent iron (nZVI) and biochar/zero-valent iron (CBC-nZVI) before and after adsorption of Cr(VI).

Figure 1-10(a) is nZVI, from which it can be seen that nZVI presents a characteristic spherical structure when prepared by liquid phase reduction method. These particles attract each other due to their significant surface effects and the presence of magnetic interactions, forming spherical particles and clumping together. Figure 1-10(b) and (c) are CBC-NZVI. It can be found that after loading nZVI, the surface of CBC becomes slightly rough, and there are spherical particles embedded in the skeleton of CBC or dispersed on the surface of CBC. The carbon skeleton of CBC separated nZVI, thus reducing the agglomeration of nZVI. nZVI prepared from grape seed extract was successfully loaded on CBC. As can be seen in Figure 1-10(d), after CBC-NZVI adsorbed Cr(VI), the surface particles of CBC became larger, indicating that nZVI participated in the process of Cr(VI) removal.

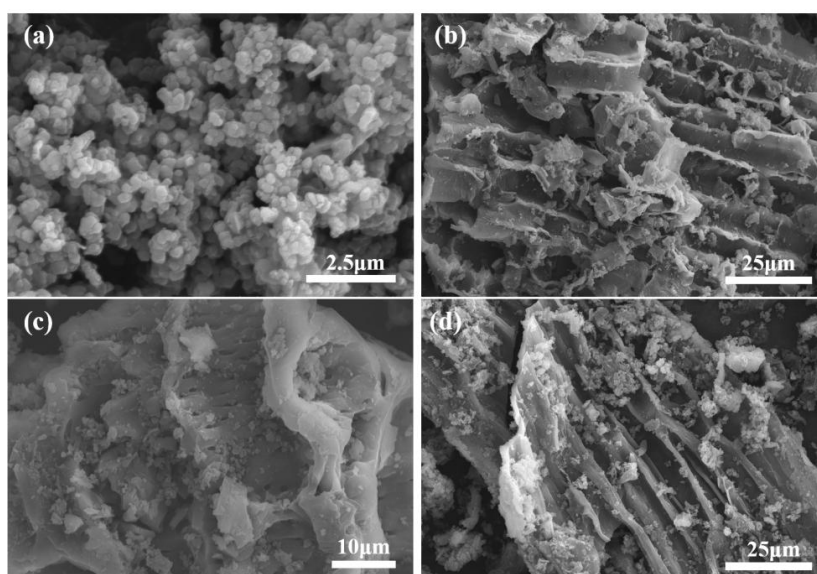


Fig.1-10 SEM images of CBC-nZVI before and after adsorption and nZVI: (a) nZVI (b) (c) CBC-nZVI before adsorption; (d) CBC-nZVI after adsorption

3.2.2 BET analysis of CBC-nZVI

Table 1-7 Parameters of specific surface area and pore structure of CBC-nZVI

Sample	BET surface area (m ² /g)	V _{Mesopores} (cm ³ /g)	V _{Micropores} (cm ³ /g)	Average pore size(nm)
CBC-nZVI	2.568305	0.015208	0.015424	14.442866

As can be seen from Table 1-7, BET's surface area is 2.568305m²/g, which is smaller than the specific surface area of CBC. This may be because iron particles blocked the channels of CBC-NZVI, resulting in smaller loss of CBC-NZVI specific surface area. The mesoporous volume is 0.015208cm³/g, and the micropore volume is 0.015424cm³/g, indicating that there are both micropores and mesoporous in CBC-nZVI. The average pore size is 14.442866nm, which belongs to the range of mesoporous, which can promote the adsorption and diffusion of larger molecules, and is effective for the removal of Cr(VI).

As can be seen from Figure 1-11, the N₂ adsorption-desorption isotherm of CBC-nZVI follows the Type IV isotherm. The curve forms a hysteresis ring between the desorption curve and the adsorption curve, which belongs to the H3 hysteresis ring, which may indicate the presence of mesoporous structure in CBC-nZVI. The embedded pore size distribution map shows two prominent peaks within the pore size range of 10nm, indicating that the pore size distribution of CBC-nZVI is

relatively concentrated, and the prominent peaks correspond to the presence of micropores and mesoporous pores, which may contribute to the adsorption of Cr(VI).

In summary, CBC-nZVI is porous and can provide multiple adsorption points for Cr(VI), which is beneficial for its adsorption performance.

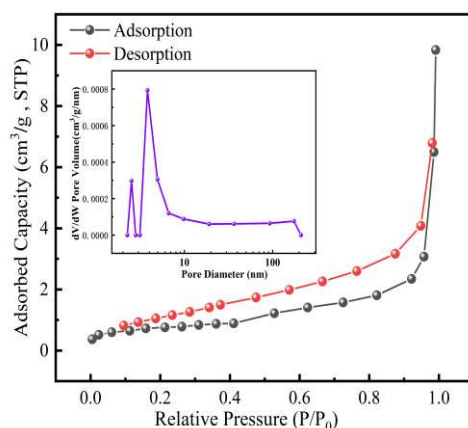


Fig.1-11 Nitrogen adsorption-desorption curves and pore size distribution of CBC-nZVI

3.2.3 FTIR analysis before and after Cr(VI) adsorption by CBC-nZVI

FIG. 1-12 shows the Fourier infrared spectra of nZVI and CBC-nZVI adsorbing Cr(VI). By comparing with the infrared spectra, the functional groups on its surface can be qualitatively analyzed. The peak of CBC-nZVI at 3365.59cm⁻¹ may be caused by the stretching and bending vibration of O-H functional groups. nZVI showed a strong -OH vibration peak at 3365.59cm⁻¹, which may be due to the -OH bond contained in polyphenols (proanthocyanidins) in grape seed extract. The absorption peak at 1608.41cm⁻¹ can be attributed to the tensile vibration of C=C, which usually corresponds to the skeleton vibration band of the aromatic ring. The absorption peak at 1440.83cm⁻¹ may be caused by the bending vibration of C-H. The vibration peak of olefin double bond = C-H appeared at the absorption peak at 1270.06cm⁻¹, which may be due to the influence of anhydrous ethanol group during the preparation of nZVI, or due to the attachment of Fe₃O₄, Fe₂O₃ and FeOOH formed by the oxidation of Fe(0) to the surface of the material. The absorption peak at 1113.87cm⁻¹ may be related to C-O tensile vibration. The absorption peaks at 875.05cm⁻¹ and 813.63cm⁻¹ may be related to C-H bending vibration or heterocyclic structure. The vibration of the absorption peak at 616.32cm⁻¹ represents Fe-OH and Fe-O, and this peak exists in both nZVI and CBC-nZVI, indicating that

nZVI is successfully loaded on CBC, and nZVI is successfully reduced by preparing nZVI with grape seed extract.

It can be seen from the figure that after CBC-nZVI adsorbed Cr(VI), the absorption peak shifted and the strength changed, and these functional groups had chemical interaction with Cr(VI). The absorption peak value decreased from 3365.59 cm^{-1} to 3358.02 cm^{-1} , 1608.41 cm^{-1} to 1604.24 cm^{-1} , 1440.83 cm^{-1} to 1438.92. 1270.06 cm^{-1} becomes 1267.80 cm^{-1} , 1113.87 cm^{-1} becomes 1103.44 cm^{-1} , 875.05 cm^{-1} becomes 869.01 cm^{-1} , 813.63 cm^{-1} becomes 809.15 cm^{-1} , The peak value at 616.32 disappeared after adsorption of Cr(VI), indicating that nZVI and Cr(VI) had a reduction reaction, and CBC-nZVI successfully removed Cr(VI).

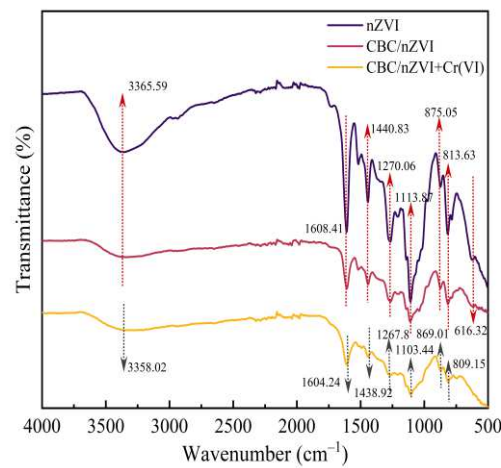


Fig.1-12 FTIR diagram of CBC-nZVI before and after adsorption of Cr(VI) and nZVI

3.2.4 XRD analysis before and after Cr(VI) adsorption by CBC-nZVI

XRD was used to analyze the structure and phase composition of nZVI and CBC-nZVI before and after adsorption of Cr(VI). Figure 1-11 shows that there is a broadband diffraction peak of CBC-nZVI in the $2\theta=20^{\circ}$ - 25° range, which is the characteristic peak of carbon, indicating that CBC-nZVI has amorphous structural characteristics. nZVI and CBC-nZVI have Fe0 characteristic peaks at $2\theta=44.72^{\circ}$, corresponding to the (110) crystal plane of standard card PDF#06-0696, indicating that grape seed extract has strong reducing property and nZVI has been successfully prepared. For CBC-nZVI, the peak at $2\theta=35.624^{\circ}$ is attributed to the Fe₂O₃(110) crystal plane (PDF#33-0664), indicating successful loading of nZVI on the CBC-nZVI surface.

After the adsorption of Cr(VI) by CBC-nZVI, the characteristic peak of Fe 0 disappeared obviously. The diffraction peaks of $K_2Cr_2O_7$ and Cr_2O_3 appear at $2\theta=27.629^\circ$ and 54.838° , corresponding to the crystal surfaces of PDF#34-0756(121) and PDF#38-1479(116). The characteristic peaks of $FeCr_2O_4$ appear at $2\theta=37.864^\circ$, 43.232° and 62.582° , corresponding to the (222), (400) and (440) crystal faces of standard card PDF#34-0140. The diffraction peak of $Fe(OH)_2$, PDF#13-0089(101), appears at $2\theta=37.393^\circ$. At $2\theta=48.164^\circ$, the $FeO(OH)$ diffusive peak appears and corresponds to the crystal face of the standard card PDF#46-1315(005).

The presence of Cr(III), Fe(III), and Fe(II) detected after the CBC-nZVI reaction is evidence of a REDOX interaction between Cr(VI) and nZVI. It mainly includes the reduction of Cr(VI) to Cr(III) in the form of Cr_2O_3 and $FeCr_2O_4$, and the conversion of Fe 0 to $Fe(OH)_2$, $FeO(OH)$ and Fe_2O_3 . The results of XRD show that CBC-nZVI is involved in the adsorption and reduction of Cr(VI).

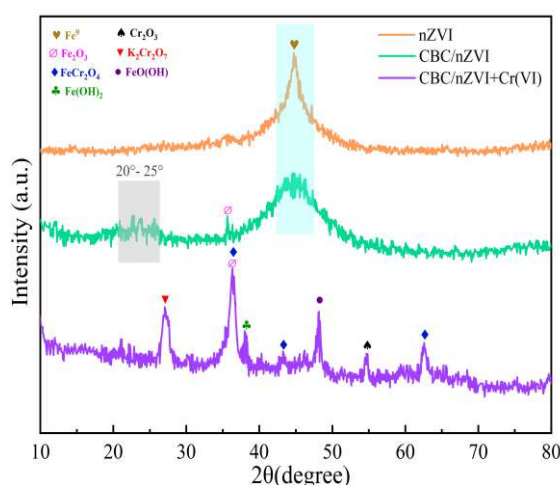


Fig.1-13 XRD of CBC-nZVI before and after adsorption Cr(VI)、nZVI

3.2.5 XPS analysis before and after Cr(VI) adsorption by CBC-nZVI

In this experiment, CBC-nZVI basically removed Cr(VI) in water. The surface of CBC-nZVI before and after adsorption was analyzed by XPS, and the mechanism of Cr(VI) removal was studied by detecting the valence change and content of elements on the surface.

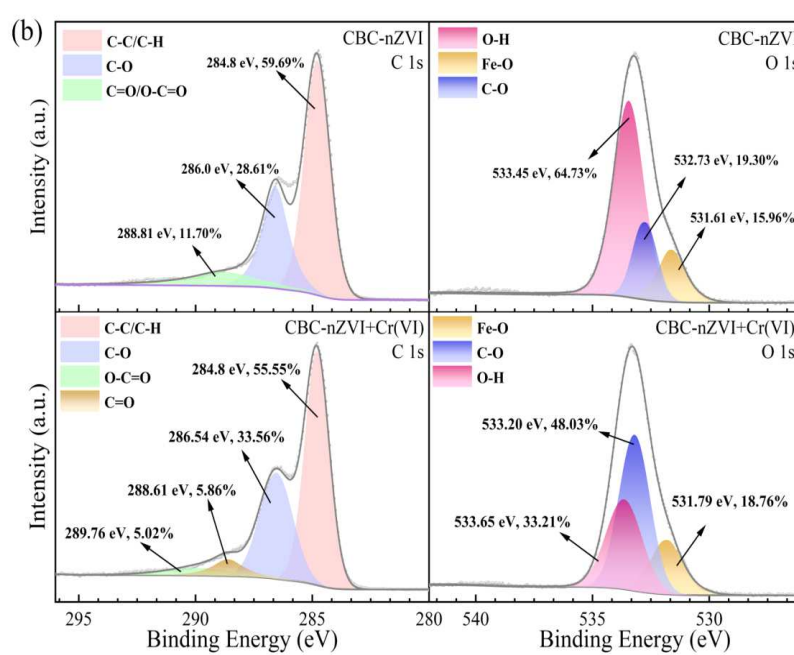
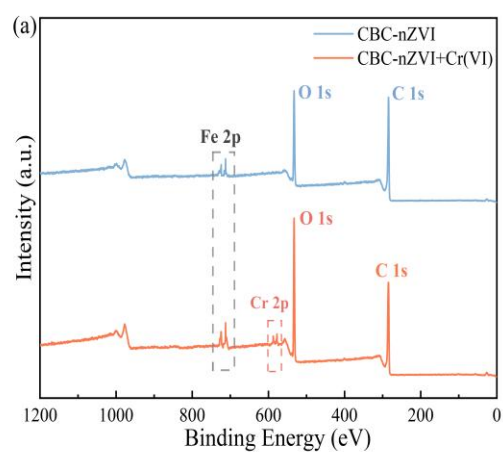
Figure 1-14(a) shows the changes of surface elements before and after the reaction between CBC-nZVI and Cr(VI). It is found that after CBC-nZVI adsorbs Cr(VI), a new Cr2p peak appears and the Fe2p peak becomes smaller. At the same time, the peak value of C1s decreased, indicating that CBC-nZVI played a certain

role in the process of removing Cr(VI), and reduction and complexation reactions may occur.

Compared with the adsorption of Cr(VI) by CBC-nZVI, the binding energy contents of C-C, O-C=O, C-O, C=O and O-H in the spectra of C1s and O1s shown in Figure 1-14(b) changed, and the positions were slightly shifted, indicating that functional groups such as C=O and C-O participated in the removal process of Cr(VI). Other studies have also shown that functional groups such as hydroxyl and carbon-based skeleton in biochar can reduce Cr(VI) to a certain extent. In addition, Fe-O peaks exist at 533.25eV. After the reaction with Cr(VI), C-O bond decreases from 532.73eV to 531.79eV, O-H bond decreases from 533.45eV to 533.20eV, and Fe-O bond increases from 531.61eV to 531.79eV, indicating that iron oxides are formed during the reaction process.

FIG. 1-14(c) shows the Fe2p spectra before and after Cr(VI) adsorption by CBC-NZVI. It can be found that the characteristic peak of Fe0 exists on the CBC-NZVI spectrum, indicating that the reducing component (proanthocyanidins) in grape seed extract can reduce Fe(II) to Fe0 and successfully load on CBC. The peak disappears after adsorption because Fe0 is oxidized by Cr(VI) during the reaction. Binding energy at 710.69eV, 712.25eV, 714.66eV and 727.52eV corresponds to the peak of Fe2p_{3/2} in FeO, which may be due to the oxidation of Fe(II) during the preparation of CBC-nZVI. In addition, Fe(II) content decreased by 8.12%, while Fe(III) content increased by 7.83%, which proved that Fe(II) participated in the reaction and oxidized to produce Fe(III). REDOX reaction is one of the mechanisms of Cr(VI) adsorption.

FIG. 1-14(d) is a fine spectral diagram of Cr 2p. Cr on CBC-nZVI exists in two valence states: Cr(III) and Cr(VI). The peaks of 577.43 eV and 587.03 eV can be attributed to Cr(III) in Cr 2p orbit, while the peaks of 578.39 eV and 588.10 eV can be attributed to Cr(VI) in Cr 2p orbit. It can be found that the area proportion of Cr(III) and Cr(VI) is 51.42% and 48.57%. The effect of CBC-nZVI on Cr(VI) removal is a combination of adsorption and reduction, and the reduction is the main effect. The peaks at 577.55 eV and 587.20 eV correspond to Cr 2p_{3/2} and Cr 2p_{1/2}, respectively. The binding energy at 577.43eV and 588.10eV corresponds to the characteristic peak of Cr(III), indicating that CBC-nZVI can reduce Cr(VI) to Cr(III) with lower toxicity.



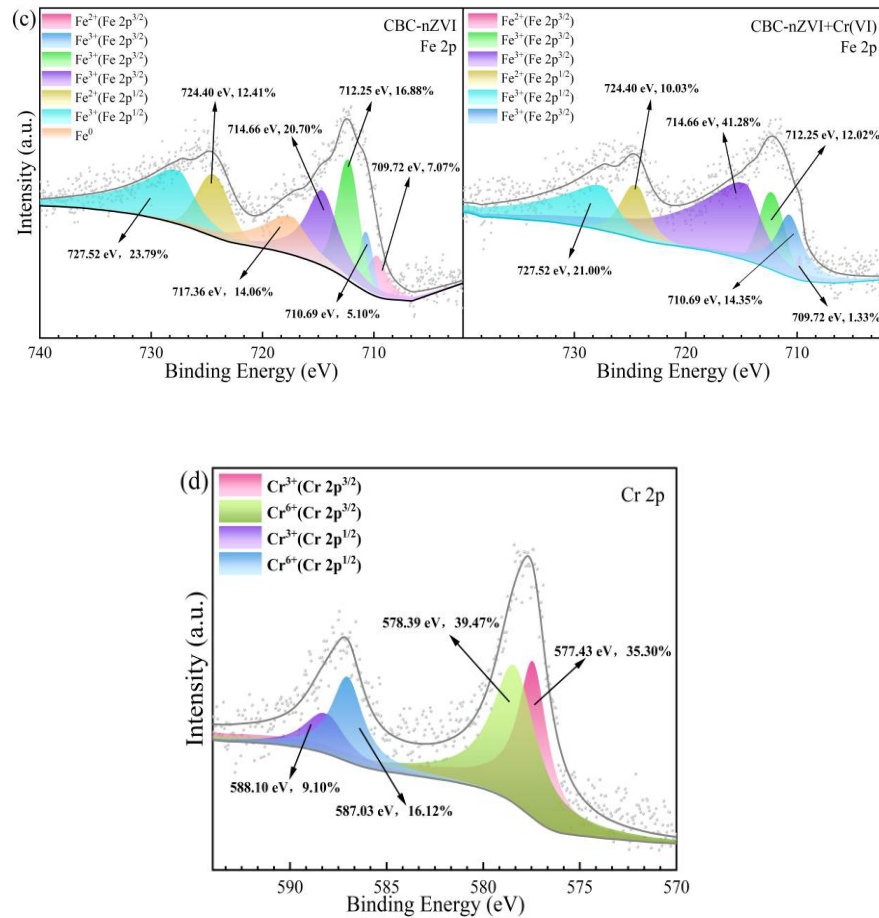


Fig.1-14 XPS spectrums of CBC-nZVI. (a) Full spectrogram; (b) C 1s、O 1s; (c) Fe 2p; (d) Cr 2p

1. Conclusion

In this study, the preparation and characterization of CBC-nZVI and the test of Cr(VI) removal in water were studied, and the removal efficiency was revealed by FTIR, XPS and other characterization techniques.

1. The CBC-nZVI composite was successfully prepared with grape seed extract by liquid phase reduction method. The effect of CBC-nZVI prepared with different iron-carbon ratio on Cr(VI) removal rate was studied. The results showed that when the ratio of iron to carbon was 1:1, the removal efficiency was 96.14% and the adsorption capacity was 24.04mg/g, which was much higher than that of nZVI(R=56.39%, Q=14.1mg/g) and CBC(R=73.55%, Q=18.39mg/g). The results showed that the removal efficiency of biochar was improved by loading zero-valent iron on biochar.

2. The removal of Cr(VI) by CBC-nZVI under different physicochemical conditions was studied, including pH value of solution, initial concentration of Cr(VI) and dosage of CBC-nZVI. The results showed that the removal rate decreased with the increase of pH value, and decreased with the increase of initial concentration of Cr(VI), and reached saturation at 0.1g.

3. The adsorption process of Cr(VI) by CBC-nZVI conforms to the quasi-second-order kinetic model and the Langmuir adsorption isothermal model. This means that the removal of Cr(VI) by CBC-nZVI is mainly achieved through a

chemically controlled monolayer adsorption mechanism, involving electrostatic interaction, coordination reaction of surface functional groups and reduction reaction.

4. SEM characterization showed that nZVI agglomeration on CBC-nZVI was reduced, and many spherical particles were attached to the surface of CBC-nZVI, indicating that nZVI was successfully loaded. BET analysis results show that CBC-nZVI has porous properties, while XRD, FTIR and XPS studies show that the particles loaded on the surface of CBC-nZVI are nZVI, which effectively improves the removal efficiency of Cr(VI).

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