

Study on the adsorption of heavy metals by biochar modified with different modifiers under room temperature

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Abstract. In order to obtain an environment-friendly biochar adsorption material with excellent adsorption performance, the biochar made from corn straw was modified with FeCl₃, Na₂S and KMnO₄ as modifiers, and the adsorption effect of biochar on several heavy metal ions in water before and after modification was studied. The properties of biochar before and after modification were characterized by SEM, XRD, FTIR and BET, and the adsorption mechanism was discussed. The results showed that the three modified reagents could effectively improve the adsorption capacity of biochar for three heavy metal ions in water, and the adsorption effect was still good at room temperature. The adsorption difference is related to the specific surface area, pore structure, aromatic structure and SiO₂ content of biochar. The adsorption mechanism mainly includes the complexation reaction between physical adsorption and surface functional groups. This study is beneficial to promote the resource utilization of agricultural and forestry waste biomass, and provides a certain reference basis for related research.

1 Introduction

Rapid economic and social development has brought about a large number of heavy metal pollutants, which seriously harm the ecological environment and biological health^[1]. Biochar (BC) is a kind of porous carbon material with wide sources, environmental protection and low cost^[2]. Due to its unique high aromatic and heterocyclic structure, complex pore structure, large specific surface area, stable structural capacity and abundant surface functional groups, it has good adsorption capacity and can effectively repair heavy metal pollution^[3]. However, the current heavy metal pollution, especially the heavy metal pollution in the soil is complex and diverse, and the original BC cannot achieve the ideal adsorption effect. The adsorption performance of BC can be improved by modification treatment, such as increasing specific surface area, pore complexity or changing the functional group substance category on the surface, so as to achieve better treatment effect of heavy metals. The chemical modification methods are widely used, including acid modification, alkali modification, oxidant modification, metal oxide modification and carbonaceous material modification^[4]. For example, acid modification can remove metals and other impurities on the surface of BC, and introduce acidic functional group substances^[5]. Alkaline modification can increase the surface area of BC and introduce oxygen-containing functional groups^[6-7]. Oxidants can also introduce oxygen-containing functional groups, activate the surface functional groups of BC and increase their active sites^[8]. In this study, ferric chloride

(FeCl₃), sodium sulfide (Na₂S) and potassium permanganate (KMnO₄) were selected as modifiers to study the adsorption of three heavy metals by biochar before and after modification under room temperature. The purpose of this study is to compare the modification effect and mechanism of different kinds of modified reagents on biochar at room temperature, so as to provide a basis for subsequent practical application. Although the specific surface area of biochar from corn straw is not the optimal choice, as agricultural waste, it has a large yield and is of great significance for its comprehensive utilization.

2 Materials and methods

2.1 Biochar modification

Corn stalk biochar was purchased from Suzhou City, Jiangsu Province. It was pre-dried to a constant weight and then screened with a diameter of 0.425mm before utilization. The modified biochar with the best adsorption effect on the three kinds of heavy metal ions was screened out at room temperature (20°C) through the pre-experiment, and the optimal modification concentration of the corresponding modified reagent was obtained. The optimal concentration of the selected modifier was 0.4mol/L of FeCl₃ solution, 0.4mol/L of Na₂S solution and 0.2 mol/L of KMnO₄ solution. The original biochar is marked as BC, the modification of FeCl₃ is marked as BC-F, the modification of Na₂S is marked as BC-S, and the modification of KMnO₄ is marked as BC-P. The above

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three kinds of modified biochar and BC were used as raw materials for subsequent adsorption experiments.

2.2 Characterizations

Scanning electron microscope (SEM) images of biochar before and after modification were obtained with a JSM-6701F Scanning Microscope. Their X-ray diffraction (XRD) measurements were performed within the angle range $2\theta = 5\text{--}90^\circ$ using a Shimadzu X-ray diffractometer XRD-6100 type. Fourier transform infrared spectra (FT-IR) for the samples were generated by a PerkinElmer spectrum 3 FT-IR Spectrometer ($400\text{--}4,000\text{ cm}^{-1}$). The BET surface area, pore surface, and pore volume of these samples were performed on the Feldman ASAP 2020 physical adsorption instrument.

2.3 Adsorption experiment

The adsorption properties of three kinds of modified biochar on Cr^{6+} , Pb^{2+} and Cu^{2+} were determined by batch experiments. Every result came from at least three parallel samples. The initial concentration of heavy metal solution was 50 mg/L , with the vibration rate was 120 r/min . All tests were carried out at room temperature (20°C). The three influencing factors of solution pH, adsorption time and biochar dosage were studied. The concentrations of Cr^{6+} , Pb^{2+} and Cu^{2+} in water samples were determined by spectrophotometry. The Langmuir adsorption model^[9] and Freundlich adsorption model^[10-11], were used to simulate the experimental data.

3 Results and discussion

3.1 Initial assessment

Table 1. Adsorption capacity of three kinds of heavy metals before and after modification of biochar.

The adsorption quantity (mg/g)	Cr^{6+}	Pb^{2+}	Cu^{2+}
BC	11.58	20.55	16.25
BC-F	29.76	24.39	23.92
BC-S	29.57	24.47	23.49
BC-P	29.57	24.86	23.66

As is shown in **Table 1**, the modified biochar still has a good adsorption effect at room temperature. When the biochar is modified by FeCl_3 or Na_2S , the optimal concentration of the modifier is 0.4 mol/L . the optimal concentration of KMnO_4 modification is 0.2 mol/L , which may be because the adsorption promotion effect of oxidation on biochar can only be realized at relatively low concentration. The modified biochar with the best adsorption effect on Cr^{6+} and Cu^{2+} was BC-F, and the best adsorption effect on Pb^{2+} was BC-P.

3.2 SEM analysis

As can be seen from the SEM image in **Fig.1.**, BC has a relatively smooth surface, which is in the shape of sheets of different sizes, and the pores are not obvious. After modification, its surface has undergone significant changes. The apparent characteristics of the three kinds of modified biochar are not exactly the same. Generally speaking, the surface pores increase significantly, and tend to be regular, and the specific surface area was enlarged by the pore broadening effect, which strengthens the adsorption site on the surface of biochar itself and improves the adsorption capacity^[12]. The pore structure of BC-F is the most regular, and the size of the flake particles of BC-S is uniform. The surface of BC-P is the roughest, which may be the result of oxidation.

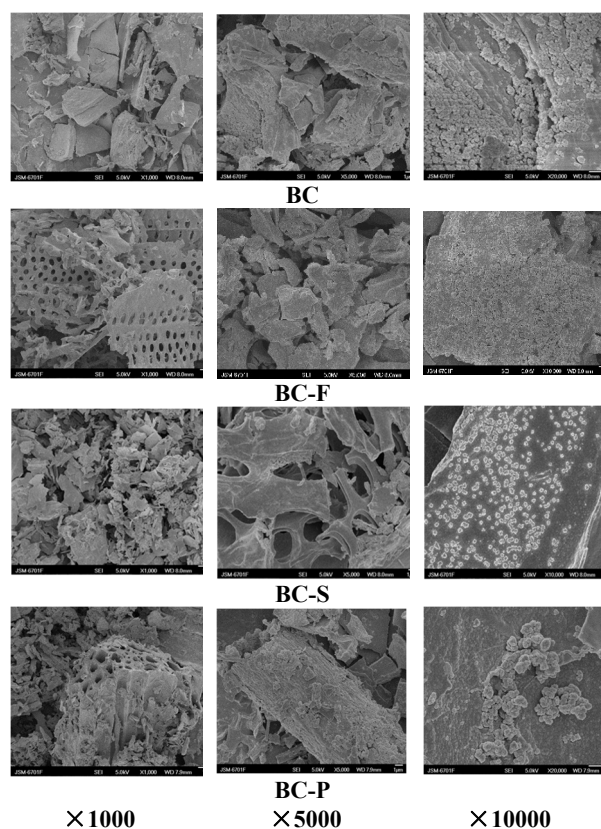


Figure 1. SEM images of biochar before and after modification

3.3 XRD analysis

As shown in **Fig.2.**, compared with BC, the crystal phase structure of BC-F and BC-S did not change greatly, indicating that the use of FeCl_3 and Na_2S to modify biochar did not affect the crystal structure. The crystal structure of BC-P is destroyed due to the strong oxidation of KMnO_4 . The crystal surface diffraction peaks of the modified biochar at $2\theta=26^\circ$ and 40° are obviously weakened. BC-F and BC-S showed new characteristic peaks at 16.6° and 76.6° , indicating that the corresponding groups were introduced.

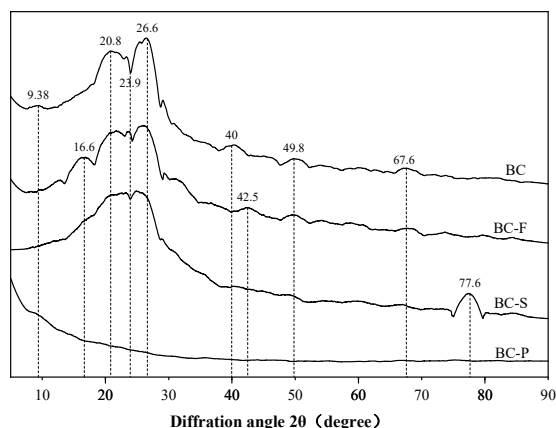


Figure 2. XRD analysis of biochar before and after modification

3.4 FT-IR spectra analysis

As can be seen from the FTIR spectra in **Fig.3.**, the wide peak at 3391~3405 cm^{-1} was the stretching vibration of hydroxyl O-H. The absorption peak at 2915~2921 cm^{-1} is methylene asymmetric stretching vibration. The carbonyl (C=O) had a peak at around 1585~1597 cm^{-1} [11,13]. The carbon oxygen bonds (C-O, C-O-C) had a peak at around 1059~1076 cm^{-1} , and carboxyl (-COOH) had a peak near 1378 cm^{-1} [11,14]. The peak at 1378 cm^{-1} was markedly increased in BC-S spectra after adsorption, this peak was the result of metal carboxylate (-COO)^[11,15], which proved that metal ions interacted with organic functional groups during adsorption process. The absorption peaks at

1434 and 1075 cm^{-1} are C-O stretching vibration and O-H in-plane bending vibration absorption peaks, and the peak at 875 cm^{-1} is C-H in-plane bending vibration in the aromatic ring. Compared with the BC, the position of absorption peak and the intensity change in the infrared absorption spectrum did not obvious.

3.5 BET analysis

After modification, the specific surface area and pore volume of biomass carbon increased significantly, while the average pore size decreased. The larger the specific surface area was, the more adsorption sites could be provided, so that the adsorption effect was significantly improved (**Table 1**). The porous structures of biochar before and after modification were quantitatively characterized by N_2 adsorption method. According to the adsorption-desorption isotherm (**Fig.4.**), it can be seen that the modification process has a great influence on the formation of biomass carbon pore structure. The original biochar samples were close to II type isotherm, but not typical, indicating that the pore size structure was large and the distribution was irregular. The modified biochar samples showed a typical IV isotherm, which indicated that the samples were mesoporous structure, and the modification reagent led to the coalescence of pores, leading to the formation of mesoporous structure. The hysteresis loop in the isotherm is between HL type and H3 type, indicating that although the modified biochar still belongs to the slit pore characteristics formed by polymer sheet particles, the pore structure tends to be evenly distributed, and the adsorption capacity is significantly improved.

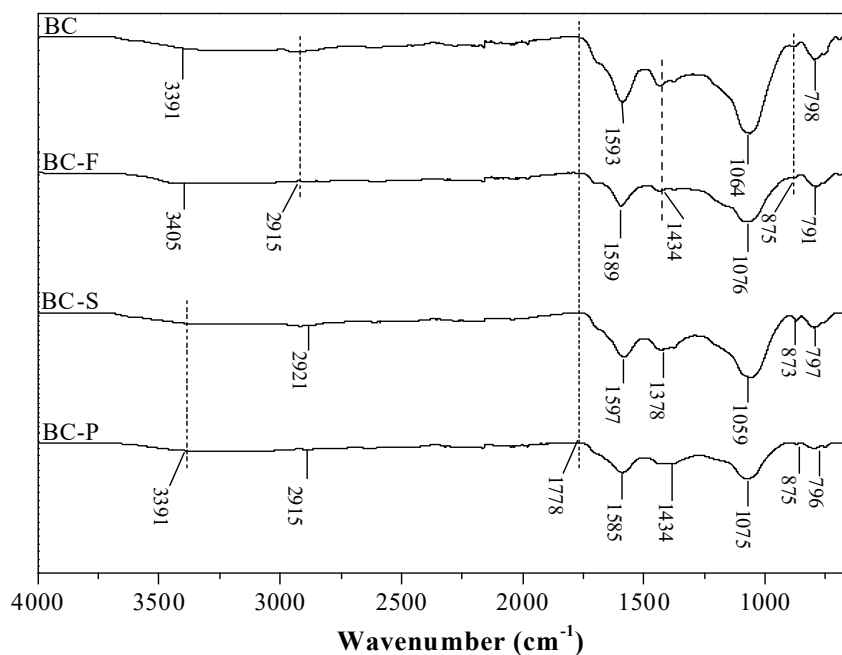


Figure 3. FT-IR spectra of biochar before and after modification

Table 2. Surface area and pore volume of biochar before and after modification

Product ID	BET specific surface (m ³ /g)	Micropore surface areas (m ³ /g)	External specific surface areas (m ² /g)	Total pore volume (cm ³ /g)	Micropore volumes (cm ³ /g)	Average pore width (nm)
BC	0.1760	5.5563	-5.3803	0.0048	0.0027	101.9823
BC-F	5.4575	1.3405	4.1170	0.0115	0.0008	10.0261
BC-S	11.0621	0.8222	10.2400	0.0214	0.0005	8.1276
BC-P	3.9397	-	4.9679	0.0131	-0.0151	16.1592

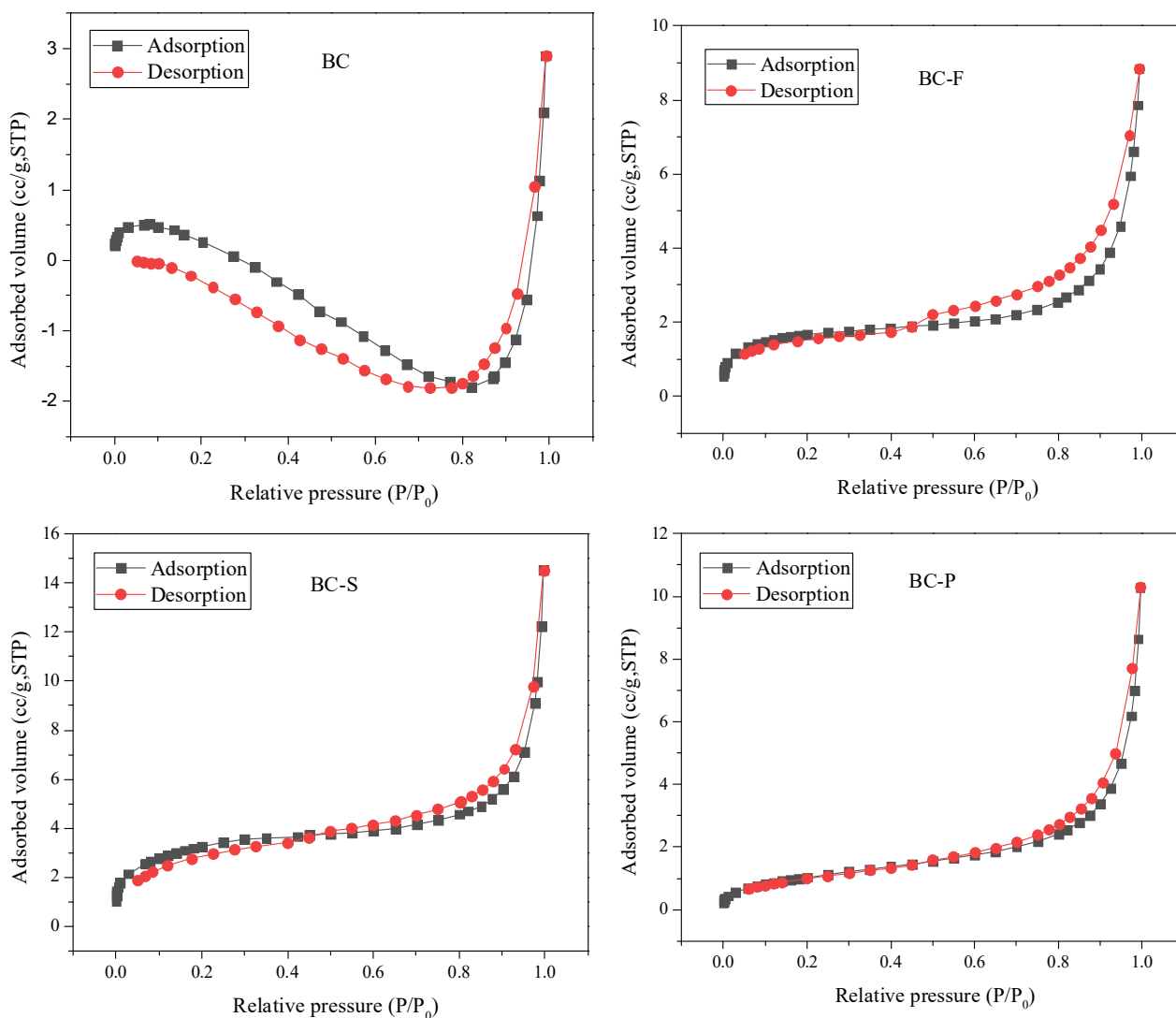


Figure 4. BET analysis of biochar before and after modification

4 Conclusions and perspectives

The results show that the biochar modified by FeCl₃, Na₂S and KMnO₄ has a good adsorption effect on heavy metals of Cd, Pb and Cu at room temperature. As an oxidizing modifier, KMnO₄ can only promote the adsorption of

biochar at a relatively low modified concentration. The modified biochar with the best adsorption effect on Cr⁶⁺ and Cu²⁺ was BC-F, and the best adsorption effect on Pb²⁺ was BC-P. At room temperature, the pH of the solution is the main factor affecting the adsorption, and the optimal removal pH of each metal is different.

After modification, surface pores of the biochar increase significantly, and tend to be regular, and the specific surface area was enlarged by the pore broadening effect. There are still some differences in the apparent morphology of the three different modified biochar. The XRD analysis showed that the content of SiO₂ decreased after modification, and among the three modifiers, only KMnO₄ would cause the destruction of the crystal structure of biochar. The infrared spectrum analysis showed that the surface functional groups of the prepared biochar had no significant change before and after modification, mainly containing hydrophilic functional groups such as carboxyl group and hydroxyl group as well as aromatic ring structure. The difference of adsorption effect of biochar before and after biochar comes from the difference of specific surface area, pore structure, aromatic structure and SiO₂ content. That is, the larger the specific surface area, the richer the pore structure, the more adsorption sites provided, and the stronger the electrostatic adsorption capacity of heavy metals. The higher the degree of aromatization, the stronger the cationic π bond. In order to further explore the mechanism, more experimental studies and analysis are needed.

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