RESEARCH ARTICLE

Effect and mechanism of changes in physical structure and chemical composition of new biochar on Cu(II) adsorption in an aqueous solution

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HIGHLIGHTS

- The adsorption capacity of Cu(II) by C-O-Fe structure biochar is 98.039 mg g^{-1} .
- The biochar skeleton can produce Fe-O-Cu complex with Cu(II).
- About 49.5% of Cu(II) is immobilized through ion exchange.

GRAPHICAL ABSTRACT

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ABSTRACT

To improve the adsorption effect of biochar on heavy metal Cu(II), we prepared new biochar and explored its modification process influence on original biochar's physical structure and chemical composition as well as its adsorption mechanism for Cu(II) in an aqueous solution. Through research work, we have reached some significant conclusions: (1) The modified biochar (M_{2-800}) can adsorb Cu(II) at the rate of 98.039 mg g^{-1} , 38.8 times higher than that of the original biochar C800 (2.525 mg g^{-1}); (2) The biochar modification process boosts its etching and pore expansion, helping Cu(II) enter the inner surface of the adsorbent, but chemical adsorption is still the most essential fixation method for Cu(II); (3) The alkaline modification process promotes the formation of oxygen-containing functional groups, in which -OH/-COOH and iron ions would form C-O-Fe structures such as hydroxyl bridges (Fe-O-) and carboxy bridges (Fe-OOC-); (4) Carboxyl is the primary site of Cu(II) fixation in M_{2-800} , and M_{2-800} has higher electronegativity (-47.8 mV) and larger pH (11.61), so that Cu(II) can be removed by electrostatic attraction and precipitation.

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1 Introduction

With the development of modern industry, the pollution caused by heavy-metals-bearing water and industrial wastes

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has become increasingly prominent. Because heavy metal ions can be accumulated in food chain, have strong toxicity, and are not readily degradable by microorganisms (Huang et al., 2018), their pollution control has attracted broad attention of scholars at home and abroad (Wang et al., 2012). Current studies have found that removing heavy metal ions in aquatic environment involves ion exchange, membrane separation, solvent extraction, chemical precipitation, electrochemical treatment, and so on. Nevertheless, these methods suffered one or more drawbacks, such as poor removal capacity at low concentrations, susceptible contamination of the membrane, difficulty in handling residual solvents, high energy consumption, and low adsorption efficiency (Zhou et al., 2020). Moreover, the adsorption method is widely used for its simple equipment, easy operation, stable effect and low cost (Luo et al., 2020a). Adsorbents play a key role in the process of heavy metal removal. Among them, the equilibrium adsorption capacity and pollutant removal efficiency are significant evaluation indicators that should be considered (Luo et al., 2020b). At present, there are many adsorbents for removing heavy metals, such as biopolymers, biochar, clay, plants, metal oxides, and so on.

Biochar (BC) is a carbon-rich product obtained by pyrolysis of biomass at high temperatures under anaerobic or anoxic conditions (Gao et al., 2012), the adsorption mechanism of biochar for heavy metals is similar to the physical adsorption of activated carbon. The specific surface area, pore structure and surface functional groups of activated carbon will all affect the adsorption capacity of activated carbon on heavy metals (Sun et al., 2018). However, the original biochar prepared by direct pyrolysis has insufficient specific surface area and few functional groups, compromising the removal efficiency of heavy metals. Therefore, it is necessary to modify the primitive biochar to improve its adsorption capacity (Yang et al., 2018). The addition of iron-based materials can combine the advantages of biochar and iron components to achieve the result of synergistic removing of heavy metals (Ahmed et al., 2017). Magnetic nano-zero-valent iron biochar can remove Cd^{2+} , Pb^{2+} , Cu^{2+} , Cr^{6+} , Zn^{2+} , and Ni^{2+} in water effectively (Zhu et al., 2017). Lin et al. (2018) found that the maximum removal rate of Cd by iron oxide nanoparticles prepared from plant leaves was 98.50% under the condition of pH = 8.07. Zhu et al. (2019) concluded that the adsorption capacities of Cd by nano-zero-valent iron biochar (nZVI) and nano- α -hydroxyferric oxide biochar (nHIO) were 22.37 mg g^{-1} and 26.43 mg g^{-1} , respectively, which were three times that of the original biochar (7.02 mg g^{-1}). Xu et al. (2019) synthesized magnetic chlorinated biochar (Fe-Cl/BC) and suggested that the Fe_3O_4 in mixed material would provide active sites for Hg^0 . Xiao et al. (2019) proved that the adsorption capacities of Cr(VI) and Cu(II) by the complex of chitosan and magnetic Luffa Biochar (CMLB) were higher than that of the original biochar. Zhou et al. (2014) prepared zero-valent iron (ZVI) biochar and found that the removal of As(V) and P was attributed to anionic and composite surfaces of ZVI biochar.

Yang et al. (2020) found that nZVI-BC (1:1) had a high removal efficiency in a wide pH range of 5.0–8.0 for Cd (II). Zhou et al. (2018a) successfully loaded Fe_3O_4 nano-particles on the surface of palm fiber biochar (MBCI), and the characterization results showed that carboxyl groups of MBCI were obviously more than that of the pristine BC. Liu et al. (2017) prepared mesoporous activated carbonized poplar catkins (ACPCs) and found that ACPCs had a higher specific surface area, and the maximum adsorption capacity for inorganic U(VI) and Co (II) was 71.85 and 110.17 mg g^{-1} , respectively.

The modified biochar has many advantages. First, the incorporation of iron-based materials has the advantages of low cost and strong adsorption capacity (Yang et al., 2018). Secondly, in the preparation of the biochar, iron ions generated Fe-O-/Fe-OOC- group with -OH/-COOH on the surface of biochar, which can form Fe-O-Cu complex with heavy metal Cu(II) in an aqueous solution. In addition, the alkaline modification can also increase the number of oxygen-containing functional groups (-OH, -COOH), promote the development of pore structure, and thus significantly improve the removal efficiency of Cu(II). However, the application of alkaline-modified iron-based biochar in the removal of heavy metals still needs to be improved, primarily including: (1) after the addition of iron ions, particles are easier to agglomerate due to the smaller particle size, resulting in low specific surface area of biochar; (2) modification will affect the development of pore structure of biochar, damaging the pore structure in varying degrees (Wang et al., 2017; Yin et al., 2018). Moreover, most of the iron-modified material has not changed the carbon skeleton structure of the original biochar, and the adsorption mechanism on heavy metals is still unclear. In this study, the biochar with the special C-O-Fe structure was prepared. This specifically modified biochar could constantly adsorb heavy metals and be easily recycled and reused. The contribution of physical adsorption and chemical adsorption (especially for iron-containing functional groups) in the new material to the Cu(II) was also studied in detail, which improved the adsorption mechanism of biochar for heavy metals.

2 Materials and methods

2.1 The preparation of modified biochar

Wash rice straws with deionized water and make them air-dry naturally, cut straws into spare parts for subsequent use. 5 g FeSO_4 and 5 g $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ are added into 200 mL deionized water to be mixed uniformly and labeled as M_1 , while 15 g FeSO_4 and 15 g $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ in 200 mL deionized water are labeled as M_2 . 10.00 g treated straws are added to the mixed solution M_1 and M_2 , respectively. The mixtures are treated by ultrasound for 2 h and impregnated for 24 h. And then, we use 5 mol L^{-1} NaOH solution to adjust the mixture's pH value to 10+. Next, the pH-adjusted mixtures

are performed ultrasonic operation for 2 h, remove the excess solution by the vacuum suction filter, and dry the separated straws at 80°C.

Put the straws into pyrolysis furnace, and parameters are set for preparing biochar (The preparation atmosphere is CO_2 , the heating rate is $20^\circ\text{C min}^{-1}$, the pyrolysis temperature is set to 400°C and 800°C , the residence time is 20 min). Among them, the original biochar prepared at 400°C is marked as C400, while the original biochar prepared at 800°C is labeled as C800. The modified biochar is represented by M_{X-Y} , in which X represents the type of iron solution (1 or 2) and Y represents the pyrolysis temperature (400 or 800°C).

2.2 Experiment on the removal of Cu(II) by modified biochar

Weigh 0.1 g biochar (C400, C800, M_{1-400} , M_{2-400} , M_{1-800} , and M_{2-800}) in a 250 mL Erlenmeyer flask and add 100 mL Cu(II) solution with the concentration of 100 mg L^{-1} , and 0.01 mol L^{-1} . NaNO_3 is added in the mixed solution as the background electrolyte. Seal the bottle mouth with plastic wrap, and shake it for 48 h under the conditions of 298.15 K and 200 r min^{-1} to achieve complete equilibrium of Cu(II) adsorption. Next, the mixed solutions are passed through the $0.22 \mu\text{m}$ aqueous filter, and the Cu(II) concentration of the filtrate is determined by flame atomic absorption spectrometry.

2.3 Composition and properties of biochar before and after modification

Specific surface area and pore size analysis: JW-BK132F specific surface area and a pore size analyzer determined biochar's specific surface area and pore distribution size. Their samples were subjected to isothermal nitrogen adsorption and desorption measurement by a static volume method. The specific surface area of the sample was calculated by the BET equation, and the pore size distribution was calculated by the BJH model.

Morphological analysis of biochar: The sample was scanned using a TM3030 Scanning Electron Microscope (SEM) (Hitachi, Japan); the surface element was distributed using a Quantax 70 Energy Dispersive X-ray Spectrometer (EDS) equipped with a scanning electron microscope (Brook, Germany) to scan.

Determination and analysis of oxygen-containing functional groups: ① Infrared spectroscopy (FTIR): The sample was prepared by mixing the biochar and KBr at a mass ratio of 1:100, uniformly mixed in an agate mortar and fully ground, and placed in a tableting machine to form a sheet. The infrared spectrum of biochar was measured by FTIR infrared spectrometer model Nicolet iS 50. The OMNIC 9 software was used to collect the map. The scanning parameters were: scan range $400\text{--}4000 \text{ cm}^{-1}$, resolution 4.0 cm^{-1} , scan accumulation 16 times. ② X-ray diffraction (XRD): The X-ray spectrum was measured and analyzed using a D8 advance A25 X-ray (Bruker, Germany). The source was Cu $\text{K}\alpha$ ($1.5418 \text{ \AA}$), the measurement range (2θ) was 5 to 80, the step was 0.01, and

Fig. 1 Adsorption isotherm of M_{2-800} in Cu(II) solution.

the scanning speed was 10 s/step. ③ X-ray photoelectron spectroscopy (XPS): Biochar samples were measured by XPS, and the results were fitted with C, O, and Fe elemental morphology using INSTALLATION Advantage v 5,945,0,6174 software. Correction of the charge displacement was performed using C1s (284.6 eV) before fitting.

The determination of ion exchange: 0.1 g M_{2-800} was mixed with 100 mL Cu(II) solution with the concentration of 100 mg L^{-1} , and the released amount of light metals (including Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) from M_{2-800} during the adsorption process was measured (Al-Asheh and Duvnjak, 1998; Li et al., 2017). As a control, the released amount of cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) after continuous washing with deionized water at the same pH was also determined. The value of the release cations (meq L^{-1}) during the Cu(II) adsorption process was calculated as the difference between the release of cations in the control group and the measured cations in the supernatant after the adsorption of Cu(II). The concentrations of these cations were determined by inductively coupled plasma emission spectrometry (ICP-OES).

Determination of zero-point potential of modified biochar: The zeta potential was used to characterize the surface charge change of the sample. The zeta potential of the material was determined by a nano-particle size ZETA potential analyzer (Malvern ZEN 3600 Zetasizer Nano). Add 0.05 g of M_{2-800} into 50 mL deionized water to prepare the biochar suspension with a concentration of 1 g L^{-1} adsorbent, adjust the mixture's pH value (2.0–12.0) used 0.1 M NaOH/0.1 M HCl, and then determine the zeta potential of the solutions.

2.4 Data processing

The adsorption amount q_t (mg g^{-1}) of Cu(II) by the modified biochar is calculated by follows:

$$q_t = (C_0 - C_t) V / m$$

where V (L) represents the volume of the Cu(II) solution, C_0 (mg L^{-1}) and C_t (mg L^{-1}) represent the concentration of the Cu(II) solution before and after adsorption, respectively, and m (g) represents the quality of added biochar.

The mapping software Origin 8.6 was used to analyze the various data and maps measured in the experiments.

3 Results and discussion

3.1 The adsorption capacity of Cu(II) by different biochar

The adsorption isotherm of M_{2-800} to Cu(II) is shown in Fig. 1. It can be seen from Fig. 1 that the adsorption capacity of M_{2-800} for Cu(II) gradually decreases with the increase of temperature, suggesting that increasing temperature is not conducive to the Cu(II) adsorption, so the most suitable adsorption temperature is 298 K. To investigate the thermodynamic behavior in the adsorption process, the Langmuir and Freundlich thermodynamic model formulas (Formula 1–2) were used to fit the Fig. 1, and the fitting results are shown in Table 1 and Table 2, respectively.

$$\frac{C_e}{Q_e} = \frac{1}{K_L \cdot Q_m} + \frac{C_e}{Q_m} \quad (1)$$

$$\lg Q_e = n \lg C_e + \lg K_F \quad (2)$$

where C_e is the equilibrium concentration of Cu(II) in the sample solution, mg L^{-1} ; Q_e is the equilibrium adsorption capacity of Cu(II), mg g^{-1} ; K_L is the Langmuir constant, L mg^{-1} ; Q_m is the maximum adsorption capacity of Cu(II), mg g^{-1} ; n is the Freundlich empirical constant; K_F is the Freundlich constant, $\text{mg}^{1-n} \text{L}^n \text{g}^{-1}$.

Comparing the correlation between the two models (Tables 1 and 2), one can see that the R^2 fitted by the Langmuir isotherm equation is greater than that of the Freundlich equation at any temperatures, indicating that the adsorption behavior of M_{2-800} on Cu(II) more closely follows the Langmuir isotherm equation. The adsorption reaction is single-layer adsorption only on the surface of the adsorbent. The

theoretical maximum adsorption capacity of M_{2-800} for Cu(II) is calculated to be 98.039 mg g^{-1} according to the Langmuir model, consistent with the actual adsorption capacity of 96.517 mg g^{-1} measured in the experiment.

Figure 2 exhibits the adsorption isotherms of original biochar (C400 and C800) and modified biochar (M_{1-400} , M_{2-400} , M_{1-800} , and M_{2-800}) for Cu(II). The Langmuir and Freundlich models were used to fit the adsorption data, and the corresponding results are shown in Table 3. It can be seen from Table 3 that the adsorption amount of Cu(II) by biochar will increase with the increasing preparation temperature ($400^\circ\text{C} \rightarrow 800^\circ\text{C}$), and the adsorption capacities of modified biochar are significantly higher than that of the original biochar. M_{2-800} have the highest adsorption capacity for Cu(II), followed by M_{1-800} . The adsorption amount of Cu(II) by M_{2-800} is 98.039 mg g^{-1} , which is about 38.8 times that of C800 and 14.9 of M_{2-400} , suggesting that the modified biochar has more adsorption sites than the original biochar. To better illustrate the outstanding advantages of modified biochar in Cu(II) adsorption, we have studied a large number of literatures, and the results are shown in Table 4. From Table 4, it can be seen that during the adsorption process of heavy metal Cu(II), the lowest adsorption amount is the original soft-(pine) biochar (1.47 mg g^{-1}), and the highest adsorption amount is the sewage sludge derived biochar (SSDB) modified by $\text{NH}_3 \cdot \text{H}_2\text{O}$ (74.51 mg g^{-1}), and the adsorption amount of most materials for Cu(II) is between 30 and 60 mg g^{-1} .

3.2 The effect of physical structure change of biochar on Cu(II) adsorption

3.2.1 The changes of specific surface area and pore structure of modified biochar

As can be seen from Table 5 that C800 is mainly composed of micro-pores (with an average pore diameter of 2.03 nm), as well as M_{1-800} and M_{2-800} are primarily in the form of mesopores (pore diameter are 3.89 and 6.81 nm, respectively), revealing that the modification can catalyze the

Table 1 Fitting results of Langmuir isothermal equation of M_{2-800} on Cu(II).

T (K)	Regression equation	R^2	Q_m	K_L
298	$C_e/Q_e = 0.0102C_e + 0.0186$	0.9994	98.0392	0.5484
308	$C_e/Q_e = 0.0105C_e + 0.0398$	0.9992	95.2381	0.2638
318	$C_e/Q_e = 0.0107C_e + 0.071$	0.9941	93.4579	0.1507

Table 2 Fitting results of Freundlich isothermal equation of M_{2-800} on Cu(II).

T (K)	Regression equation	R^2	n	K_F
298	$\lg Q_e = 0.2411 \lg C_e + 1.5883$	0.9298	0.2411	38.7525
308	$\lg Q_e = 2.4711 \lg C_e - 3.2495$	0.8298	2.4711	0.0006
318	$\lg Q_e = 1.8897 \lg C_e - 2.0574$	0.7231	1.8897	0.0088

generation of more volatile substances and play the role in etching and pore enlargement. The change in pore structure will help more contaminants enter the adsorbents' void, increase the contraction probability of heavy metals with the inner surface of the adsorbent and promote the removal of contaminants (Ma et al., 2016). Through alkaline modification, the biochar's specific surface area and pore volume are all reduced to some extent. The specific surface area of M_{2-800} ($1.35 \text{ m}^2 \text{ g}^{-1}$) is less than 0.6% of C800, due to the increasing content of Fe and the decomposition of the carbon skeleton at higher temperatures (Chen et al., 2019). Yang et al. (2018) have also proved that with the increasing content of α -FeOOH, the biochar's specific surface area and pore volume

would decrease significantly due to the greater collapse and destruction. According to the scanning electron micrograph of biochar (Fig. 3), C800 (Fig. 3A) has a relatively flat surface, a compact structures and irregular long strip pores. The surface of modified biochar M_{1-400} (Fig. 3B), M_{2-400} (Fig. 3C), M_{1-800} (Fig. 3D), and M_{2-800} (Fig. 3E) are relatively rough and the pore structures are damaged in varying degrees, spherical polymers or irregular crystals can be observed, indicating that there are Fe containing substances formed on the surface of biochar. Compared with M_{2-800} , there are a lot of fine particles on the surface of $M_{2-800-\text{Cu}}$ (Fig. 3F), which are Cu(II) adsorbed by the material. The pore structure of M_{2-800} will be partially blocked after adsorption of the heavy metals, but the overall

Fig. 2 Adsorption isotherms for Cu(II) by different biochars, all the experiments were done in triplicate.

Table 3 Langmuir and Freundlich isotherm parameters for Cu(II) adsorption on different biochar.

Adsorbents	Langmuir model			Freundlich model		
	$Q_{\max}$ (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F ($\text{mg}^{1-n} \text{ L}^n/\text{g}$)	n	R^2
C400	1.147	0.019	0.9566	0.046	0.622	0.9541
C800	2.525	0.029	0.9667	0.255	0.440	0.9745
M_{1-400}	5.426	0.120	0.9862	2.468	0.153	0.9188
M_{1-800}	17.123	0.803	0.9982	12.909	0.065	0.9552
M_{2-400}	6.570	0.132	0.9894	3.079	0.149	0.9532
M_{2-800}	98.039	0.548	0.9994	38.752	0.241	0.9298

structure is relatively complete, and there is no serious collapse of pore, indicating that the modified biochar has a relatively stable structure.

3.2.2 The analysis of adsorption-desorption characteristics of modified biochar

It can be seen from the adsorption-desorption isotherm of biochar (Fig. 4) that C800 is biased to the Y-axis at the lower relative pressure and achieves adsorption equilibrium when the relative pressure is less than 0.2, usually considered as a microporous or monolayer adsorption, belonging to I-type isotherm. The adsorption-desorption isotherm of M₁₋₈₀₀ is relatively gentle at the lower relative pressure ($P/P_0 = 0-0.1$); and then, the adsorption amount of N₂ will gradually increase with the increasing relative pressure until it is close to the vapor pressure (Fig. 4C), explaining that the material M₁₋₈₀₀ primarily occurs in the multi-layer adsorption dominated by the medium and large pores, which is in line with the trend of

IV-type isotherms. In the adsorption-desorption isotherm of M₂₋₈₀₀, the adsorption capacity of N₂ will increase continuously with the increasing relative pressure, it is presumed that the material belongs to the non-porous adsorption of II-type isotherm. The separation phenomenon of the adsorption isotherm from desorption isotherm is more pronounced (Fig. 4D), caused by the irreversible pore deformation of the biochar.

Through comprehensive analysis according to Table 5, Fig. 3, and Fig. 4, we have known that the physical adsorption based on micro-pores is the primary channel to fix Cu(II) by C800. Alkaline modification can enlarge the pores of biochar, but it also causes the collapse and fracture of carbon skeleton structure. The modified biochar primarily occurs in non-porous adsorption (chemical adsorption) to absorb Cu(II). Usually, the microporous property of biochar is significant for gas adsorption, but little importance for heavy metal ions adsorption in aqueous systems (Issabayeva et al., 2010). Moreover, the surface activity of M₁₋₈₀₀ and M₂₋₈₀₀ will be enhanced through

Table 4 Comparison of adsorption capacity of different biochars on Cu(II).

Biochar feedstock	Modification condition	Heavy metal	Adsorption capacity	Reference
Gingko (<i>Spiraea blumei</i>) leaf biochar (GB)	-	Cu(II)	$Q_{\max} = 59.9 \text{ mg g}^{-1}$	Lee et al. (2019)
Palm oil mill sludge biochar (POSB)	-	Cu(II)	$Q_{\max} = 48.8 \text{ mg g}^{-1}$	Goh et al. (2019)
Miscanthus giganteus biochar	H ₂ O ₂	Cu(II)	$Q_{\max} = 15.7 \text{ mg g}^{-1}$	Cibati et al. (2017)
Hickory wood biochar	KMnO ₄	Cu(II)	$Q_{\max} = 34.2 \text{ mg g}^{-1}$	Wang et al. (2015)
Cymbopogon schoenanthus L. Spreng (HLG) biochar	H ₂ O ₂	Cu(II)	$Q_{\max} = 53.8 \text{ mg g}^{-1}$	Zuo et al. (2016)
Farmyard manure biochar (DBC-FYM)	-	Cu(II)	$Q_{\max} = 44.5 \text{ mg g}^{-1}$	Batool et al. (2017)
Poultry manure biochar (DBC-PM)	-	Cu(II)	$Q_{\max} = 43.68 \text{ mg g}^{-1}$	Batool et al. (2017)
Date-seed biochar	-	Cu(II)	$Q_{\max} = 0.42 \text{ mmol g}^{-1}$	Mahdi et al. (2018)
Sewage sludge derived biochar (SSDB)	NH ₃ ·H ₂ O	Cu(II)	$Q_{\max} = 74.51 \text{ mg g}^{-1}$	Tang et al. (2019)
Biochar/MnAl-layered double hydroxides (LDH) composites(MnAl-LDH)	MnSO ₄ and Al(NO ₃) ₃	Cu(II)	$Q_{\max} = 74.07 \text{ mg g}^{-1}$	Wang et al. (2018)
Ferromanganese binary oxide-biochar composites (FMBC)	KMnO ₄ and Fe(NO ₃) ₃	Cu(II)	$Q_{\max} = 64.9 \text{ mg g}^{-1}$	Zhou et al. (2018b)
Soft- (pine) biochar	-	Cu(II)	$Q_{\max} = 1.47 \text{ mg g}^{-1}$	Jiang et al. (2016)
Hard-wood (jarrah) biochar	-	Cu(II)	$Q_{\max} = 4.39 \text{ mg g}^{-1}$	Jiang et al. (2016)
Rice straw (<i>Oryza sativa</i> L.) biochar	-	Cu(II)	$Q_{\max} = 0.37 \text{ mol kg}^{-1}$	Jiang et al. (2015)
Pristine biochar (UBC) from earthworm manure	-	Cu(II)	$Q_{\max} = 36.56 \text{ mg g}^{-1}$	Wang et al. (2017b)
Earthworm manure biochar treated by HCl (WBC)	HCl	Cu(II)	$Q_{\max} = 8.64 \text{ mg g}^{-1}$	Wang et al. (2017b)
Modified biochar (M ₂₋₈₀₀)	Fe ²⁺ /Fe ³⁺	Cu(II)	$Q_{\max} = 98.039 \text{ mg g}^{-1}$	This work

Fig. 3 Scanning electron micrograph of biochars before and after modification: (A) Scanning electron micrograph of C800 (*1000), (B) Scanning electron micrograph of M₁₋₄₀₀ (*1000), (C) Scanning electron micrograph of M₂₋₄₀₀ (*8000), (D) Scanning electron micrograph of M₁₋₈₀₀ (*8000), (E) Scanning electron micrograph of M₂₋₈₀₀ (*4000), (F) Scanning electron micrograph of M_{2-800-Cu} (*4000), Note: M_{2-800-Cu} represents the sample after adsorption of Cu(II) by M₂₋₈₀₀.

modification, which has stronger adsorption capacity and promotes the removal of heavy metals (Liu et al., 2015). The enhanced surface activity of the modified biochar can be explained from the following. Part of the irons was oxidized into iron oxides in the pores of biochar, and some were converted into hydroxides. These iron oxides and hydroxides have the high specific surface area and -OH functional

groups, which have obvious chemisorption characteristics. They can react with metals and other cations/ anions and can purify heavy metal pollution. The presence of Fe²⁺/Fe³⁺ can promote the evolution of the chemical structure of biochar (Zhu et al., 2017), and the results of Yang et al. (2016b) showed that with the activation of FeCl₃, more oxygen-rich groups were formed on the modified biochar, especially C = O.

Some of the introduced $\text{Fe}^{2+}/\text{Fe}^{3+}$ were converted into zero-valent iron, which makes the composite material have a certain reduction ability and stronger adsorption capacity.

3.3 The effect of chemical composition changes of biochar on Cu(II) adsorption

3.3.1 The formation of C-O-Fe structure in modified biochar

The special C-O-Fe structure ($\text{R-O-Fe}_x\text{O}_y$, $\text{R-COO-Fe}_x\text{O}_y$) can be formed by co-pyrolysis of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and straws in alkaline solution (Formulas 3–8) (Mak et al., 2011; Yang et al., 2016a;

Lin et al., 2018). The functions of alkaline solution are as follows: (1) The addition of NaOH can swell the straw fibers and increase the intermediate cavity (Li et al., 2014), facilitating the contact of the contaminant with the inner surface; (2) NaOH-modification can increase the surface activity and oxygen-containing functional groups, as well as introduce hydroxyl and carboxyl groups (Wang and Wang, 2019); (3) Fe(OH)_2 , Fe(OH)_3 , FeOOH , Fe_3O_4 , and other substances can be produced by co-pyrolysis of alkaline and straws (Formulas 9–14) (Wu et al., 2018), which can further promote the formation of iron-containing functional groups such as Fe-R-COOH , Fe-R-OH and so on. Research has

Fig. 4 N_2 Adsorption-desorption isotherms of biochar before and after modification: (A) N_2 adsorption-desorption isotherms of C800, M_{1-800} , and M_{2-800} in the range of $P/P_0 = 0-1.0$, (B) (C) (D) represent the local enlarged maps of C800, M_{1-800} , and M_{2-800} , respectively, Note: $\text{M}_{2-800}\text{-Cu}$ represents the sample after adsorption of Cu(II) by M_{2-800} .

Table 5 The analysis of specific surface area and pore diameter of modified biochar.

Sample	BET specific surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	t-plot micropore volume ($\text{cm}^3 \text{g}^{-1}$)	BJH mesopore volume ($\text{cm}^3 \text{g}^{-1}$)	Average aperture (nm)
C800	241.9328	0.122767	0.068921	0.073571	2.02977
M_{1-400}	28.6780	0.102836	—	0.174658	14.34354
M_{1-800}	67.4032	0.065531	0.015739	0.083292	3.88890
M_{2-800}	1.3520	0.002301	0.000277	0.008863	6.80898

testified that Fe^{3+} can enter the interior of the biochar skeleton by electrostatic interaction and generate the hydroxyl bridge (Fe-O-) and carboxyl bridge (Fe-OOC-) with oxygen-containing functional groups (e.g., $-\text{OH}$ and $-\text{COOH}$) (Yang et al., 2018). In addition, the C-O-Fe structure can also be produced on biochar's surface by ligand exchange, chelation, bridging, or C- π -cation interaction (Joseph et al., 2010). Figure 5 shows the formation process of C-O-Fe structure of alkaline modified biochar.

To analyze the contribution of C-O-Fe structure in modified biochar to Cu(II) adsorption, we compared the adsorption difference of C800, M_{2-800} and $\text{M}_{2-800\text{-ash}}$ (the remaining ash portion of M_{2-800} after burning) on Cu(II) (Table 6). It can be seen from Table 6 that the adsorption efficiency of M_{2-800} is much greater than the total adsorption amount of C800 and $\text{M}_{2-800\text{-ash}}$ ($98.039 \text{ mg g}^{-1} > 12.415 \text{ mg g}^{-1}$). It can be seen from Table 7 that C800 is primarily composed of C (44.82%), while $\text{M}_{2-800\text{-ash}}$ is primarily composed of Fe (82.5%). This indicates that it is the synergistic effect of C, O, and Fe in M_{2-800} that improves the removal of Cu(II) rather than a single element. The study of Yang et al. (2018) has also obtained the same conclusion as ours that the removal efficiency of Cu(II) in the composite material was significantly improved (71.9%) compared with the separate corn straw biochar (42.3%) and $\alpha\text{-FeOOH}$ (6.7%).

Figure 6 shows the change in C-O-Fe structure before and after adsorption of Cu(II) by modified biochar. It can be seen from Fig. 6A that the band between 900 cm^{-1} – 600 cm^{-1} can be assigned to the bending vibration of Fe-O and Fe-OH (Zhang et al., 2012; Andjelkovic et al., 2015), and the peak of 600 cm^{-1} is attributed to the Fe-C stretching of iron carbide (Gutierrez-Becerra et al., 2012). The C-O bonds in C-O-Fe structure can be destroyed during the process of electron transfer to generate $\text{C}=\text{O}/\text{C}=\text{C}$ or iron oxides (Huang et al., 2017). The five peaks of M_{2-800} in XRD diagram (Fig. 6B) are 30.122° , 35.511° , 43.138° , 56.984° and 62.705° , corresponding to (220), (311), (400), (511) and (440) crystal planes of Fe_3O_4 cubic crystals, the diffraction peaks $2\theta = 44.7^\circ$ and $2\theta = 65.22^\circ$ match well with the (110) and (200) crystal planes of

Fig. 5 Effects of $\text{Fe}^{2+}/\text{Fe}^{3+}$ modification on the structure of biochar and the formation of C-O-Fe.

the a-Fe⁰ crystal. From Fig. 6A, we can also find that the modification has caused a slight shift of the peak and increased the vibration frequency of the surface functional groups, such as -OH (3446 cm⁻¹-3450 cm⁻¹-3462 cm⁻¹) and -COOH (1384 cm⁻¹-1394 cm⁻¹-1401 cm⁻¹), indicating that Fe³⁺ was immobilized on the biochar's surface by the interaction with these functional groups (Zhang et al., 2017). Compared with M₂₋₈₀₀, the content of functional groups in M_{2-800-Cu} such as -OH, -C=O and -COOH decreased significantly, suggesting that the above groups have participated in the binding of Cu(II), which complexed with the target metals by coordination (Wang et al., 2013). Liu et al. (2020) used piggery sludge and thiourea to produce modified biochar (MBC), the FTIR and XPS analysis suggested that C-O, C=O, and other functional groups can adsorb heavy metals by coordination and ion exchange. Moreover, the formation of Fe-O-Cu complex (Fu et al., 2017) such as CuFe₂O₄ through the interaction of iron-containing functional groups and copper ions also promote the removal of Cu(II).

3.3.2 The change of oxygen-containing functional groups in modified biochar

To analyze the type of organic functional groups combined with Cu(II), we performed narrow-band analyses of C 1s, O 1s and Fe 2p orbitals, the results are shown in Fig. 7 and Table 8, respectively. In Fig. 7 C 1s, the characteristic peaks at 284.4, 286.0, 286.7, 287.8 and 288.7 eV can be assigned to aromatic C, hydroxyl C, ketone C, carbonyl C, and carboxyl C (Chen et al., 2017; Guo et al., 2017; Doskočil et al., 2018). The percentage of aromatic C, ketone C and carboxyl C decreased by 8.01%, 61.14% and 66.87% respectively after the Cu(II) adsorption (Table 8), explaining that they have participated in the Cu(II) fixation. In Fig. 7 O 1s, the peaks at 530.1, 531.9, 532.9, and 536.2 eV are assigned to lattice oxygen, carbonyl oxygen, hydroxyl oxygen and carboxyl oxygen, respectively (Guo et al., 2017). The percentage of carboxyl oxygen decreased by 96.45% after Cu(II) adsorption, explained that Cu(II) is primarily adsorbed to the carboxyl functional group on the surface of M₂₋₈₀₀, consistent with the

Fig. 6 The infrared spectra and X-ray diffraction patterns of the biochars before and after modification: (A) The infrared spectra of C800, M₁₋₄₀₀, M₂₋₄₀₀, M₁₋₈₀₀, M₂₋₈₀₀ and M_{2-800-Cu}, (B) The X-ray diffraction patterns of C800, M₁₋₄₀₀, M₂₋₄₀₀, M₂₋₈₀₀ and M_{2-800-Cu}. Note: M_{2-800-Cu} represents the sample after adsorption of Cu(II) by M₂₋₈₀₀.

Table 6 The analysis of adsorption capacity of Cu(II) by modified biochar.

Materials	M ₂₋₈₀₀	C800	M _{2-800-ash}
The adsorption amount of Cu(II) (mg g ⁻¹)	98.039	2.525	9.890

Note: M_{2-800-ash} —the remaining ash portion of M₂₋₈₀₀ after burning.

Table 7 The composition of C800 and M_{2-800-ash}.

	N (%)	P (%)	K (%)	S (%)	C (%)	H (%)	Fe (%)
C800	0.94	0.66	6.91	0.42	44.82	0.52	0
M _{2-800-ash}	-	-	0.43	-	-	-	82.5

Note: M_{2-800-ash} —the remaining ash portion of M₂₋₈₀₀ after burning.

result of FTIR (Fig. 6A). Loukia Hadjittofi et al. (2014) prepared cactus fiber modified biochar and proved that the carboxyl group is the primary binding site of Cu(II). Huang et al. (2018) reached the same conclusion that carboxyl groups are also responsible for the Cu(II) adsorption in an aqueous solution. Xu and Xue proposed that -COOH on biochar's surface can react with metals to form complex (Formula 15) (Xue et al., 2012; Xu et al., 2013), surface complexation is an essential mechanism of Cu(II) adsorption process (Sun et al., 2014). From Table 8, we can also find that Fe(II) accounts for 12.95%

of total iron before Cu(II) adsorption while decreasing to 6.28% after adsorption. At the same time, the content of Fe(0) will also decrease from 1.25% to 0.6%. These phenomena above have proved that Fe(II) and Fe(0) in an aqueous solution are primarily responsible for reducing Cu(II) to Cu(0) (Wang et al., 2019) (Formula 16–17). A part of $\text{Fe}^{2+}/\text{Fe}^{3+}/\text{Fe}^0$ in biochar will react with residual OH^- to convert into hydroxides such as $[\text{Fe}(\text{OH})]^+$, $[\text{Fe}(\text{OH})_3]^{2-}$ and $\text{Fe}(\text{OH})_2$ (Fig. 6A). These iron oxides and iron hydroxides have obvious chemical adsorption characteristics and a certain redox

Fig. 7 X-ray photoelectron spectra of M_{2-800} and $\text{M}_{2-800-\text{Cu}}$: (A) C 1s narrow scan spectra of M_{2-800} , (B) C 1s narrow scan spectra of $\text{M}_{2-800-\text{Cu}}$, (C) O 1s narrow scan spectra of M_{2-800} , (D) O 1s narrow scan spectra of $\text{M}_{2-800-\text{Cu}}$, (E) Fe 2p narrow scan spectra of M_{2-800} , (F) Fe 2p narrow scan spectra of $\text{M}_{2-800-\text{Cu}}$. Note: $\text{M}_{2-800-\text{Cu}}$ represents the sample after adsorption of Cu(II) by M_{2-800} .

capacity, can participate in the fixation of metal ions, and purify heavy metal pollution.

3.3.3 The effect of ion exchange in modified biochar on Cu(II) adsorption

Ion exchange is one of the most critical mechanisms for the adsorption of heavy metals in an aqueous solution (Li et al., 2017). Luo et al. (2020b) prepared the biochar-mineral composite (BMC) to remove Pb(II) from the coagulation sludge of swine wastewater and found that Pb(II) adsorption onto BMC occurred predominantly via ion exchange, via the electrostatic interaction, and via coordination with C–H and C–OH bonds in the biochar. As shown in Table 9, the amount of Cu(II) adsorbed by M₂₋₈₀₀ is 3.0725 meq L⁻¹, while the amount of Na⁺, K⁺, Ca²⁺ and Mg²⁺ released at the same time was 1.5224 meq L⁻¹, suggesting that the contribution rate of ion exchange to Cu(II) adsorption is about 49.55%. However, the contribution rate of ion exchange to Cu(II) adsorption in C800 is 75.90%. The two above phenomena display that the contribution of ion exchange to Cu(II) adsorption in M₂₋₈₀₀ is reduced compared with the C800. It is speculated that there are two reasons for the happening: first, some cationic sites are replaced by newly added Fe during the co-pyrolysis process of Fe²⁺/Fe³⁺ and straws; secondly, the catalysis action of alkaline promotes the development of oxygen-containing functional groups in biochar, increasing the immobilization of Cu(II) by the complexation of oxygen-

containing functional groups and iron-containing substance, while the contribution of ion exchange is correspondingly reduced. In addition, some functional groups (–COOM, –R–O–M, etc.) on the surface of modified biochar can also adsorb Cu(II) through an ion exchange mechanism.

3.3.4 The effect of static point gravity in modified biochar on Cu(II) adsorption

The electrostatic attraction depends on the solution's pH and the biochar's zero-point charge (pH_{pzc}). This is because that pH can affect the existence speciation of Cu (Zhang et al., 2015), Zeta potential determines the electrical property of surface charge in adsorbent particles. Figure 8 exhibits the zeta potential curve of M₂₋₈₀₀, the isoelectric point pH_{zpc} of M₂₋₈₀₀ can be obtained as 6.35. When the solution's pH is less than pH_{pzc} (pH < pH_{pzc}), Cu only exists as the positive substance and the surface of M₂₋₈₀₀ also has the positive charge, competitive adsorption will occur between high concentrations of H₃O⁺ and Cu(II) that will limit the binding of metal ions to adsorption sites (González et al., 2007); When the pH is closer to the adsorbent's isoelectric point, the electrostatic repulsion between metal ions and adsorbed molecules becomes smaller and the adsorbed molecules have higher stability (Amini et al., 2008; Özer et al., 2009), that the Cu(II) in solution slowly turns to [Cu(OH)]⁺; With the continuous increase of pH (pH > pH_{pzc}), the dissociation of functional groups (such as carboxyl) on adsorbent's surface is gradually enhanced (Yan et al., 2018), which increases the electronegativity of the material, and provides a great potential for the electrostatic adsorption of Cu(II) on M₂₋₈₀₀. The pH value of M₂₋₈₀₀ is 11.61 and the zeta potential is –47.8 mV as we measured, it is speculated that electrostatic interaction is one of the critical adsorption mechanisms of Cu(II) in an

Table 8 Distribution of carbon, oxygen and iron functional groups on the surface of modified biochar before and after Cu(II) adsorption.

Element	Binding energy /eV	Types of functional groups	The content before adsorption (%)	The content after adsorption (%)
C 1s	284.4	Aromatic carbon	75.30	69.27
	286.0	Hydroxyl carbon	3.84	20.65
	288.7	Carboxyl carbon	15.83	5.33
	286.7	Ketone carbon	2.11	0.82
	287.8	Carbonyl carbon	2.92	3.93
O 1s	531.9	Carbonyl oxygen	76.73	1.10
	532.9	Hydroxyl oxygen	6.90	98.31
	536.2	Carboxyl oxygen	15.76	0.56
	530.1	Lattice oxygen of metal oxide	0.61	0.03
Fe 2p	709.1	Fe ³⁺ (Octahedral coordination)	62.85	57.29
	711.3	Fe ²⁺ (Octahedral coordination)	12.95	6.28
	717.2	Fe ³⁺ (Tetrahedral coordination)	22.95	35.74
	706.1	Fe (0)	1.25	0.6

aqueous solution. Higher pH also impacts the hydrolysis equilibrium of copper ions, so that heavy metals can be fixed by precipitation (Cheng et al., 2007; Uchimiya et al., 2012). P in biomass is largely retained during pyrolysis, mostly insoluble form (Angst and Sohi, 2013). Romanyà and Rovira (2009) found that some of the P in biochar can be activated by high temperatures to become available during the preparation process. Inorganic P species can form at 350°C, and as the pyrolysis temperature increased, inorganic orthophosphate (PO_4^{3-}) became the only form existing in the biochar at 500°C (Uchimiya et al., 2014; Uchimiya et al., 2015). PO_4^{3-} in biochar can combine with heavy metal ions to form phosphate precipitation. The relevant precipitation reactions are shown in Formulas 18–20.

3.3.5 The effect of recycling times on the stability of biochar materials

The modified biochar and silicate binder were mixed in the ratio of 1:5 to prepare granular fertilizer, and the cycle stability of the new material was determined through multiple adsorp-

Fig. 8 The zeta potential of M_{2-800} and the species of Cu in the solution under different pH conditions.

Table 9 Cations release amount of biochar in adsorbing Cu(II) process.

System		Cu^{2+} adsorption (meq L^{-1})	Amount of cation released (meq L^{-1})				R(%)
			K^+	Ca^{2+}	Na^+	Mg^{2+}	
C800	Control group ^b	—	1.7033	0.3528	0.1488	0.2674	—
	Test group ^a	0.0614	0.0189	0.0102	0.0013	0.0162	75.90
M_{2-800}	Control group ^b	—	0.2148	0.0195	6.2180	0.0165	—
	Test group ^a	3.0725	0.0402	0.0653	1.3840	0.0329	49.55

^a Different between metal released by system and that by the control. ^b Biochar and deionized water. R, Contribution rate of ion exchange to Cu(II) adsorption.

tion-desorption experiments. As shown in Table 10, the quality of biochar particles was decreased slightly after each cycle. When the three cycles were over, the recovery rate of M_{2-400} and M_{2-800} after magnetic separation were 95.4% and 93.1%, respectively. After three cycles in the Cu adsorption experiment, the adsorption regeneration rate of M_{2-400} and M_{2-800} was as high as 77.5% and 79.4%, respectively, indicating that the prepared modified biochar has high reusability.

3.4 Adsorption mechanism of Cu(II) by modified biochar

Figure 9 shows the adsorption mechanism of Cu(II) by modified biochar. The alkaline modification has significantly changed the biochar's physical structure and chemical composition. First of all, from the physical point of view, alkaline solution enhances biochar etching and pore expansion in the pyrolysis process, which makes the biochar primarily in the form of macropores and mesopores, increasing the contact probability between pollutants and the inner surface of pores. Secondly, the special C-O-Fe structure has emerged during the co-pyrolysis process of Fe^{2+}/Fe^{3+} and

original straws in alkaline conditions, the Fe-O-/Fe-OOC-groups in the structure can generate Fe-O-Cu complex with Cu(II) in an aqueous solution, thus significantly improving the removal efficiency of Cu(II). The iron oxides and iron hydroxides ($Fe(OH)_2$, $Fe(OH)_3$, $FeOOH$ and Fe_3O_4 , etc.) in the products also have obvious chemical adsorption characteristics. The addition of alkaline will promote the development of oxygen-containing functional groups ($-OH$, $-COOH$). Carboxyl group is the primary binding site of contaminant Cu(II) and can form $(C-COO)_2Cu$ complex with Cu(II) in an aqueous solution. The Alkaline environment can promote the dissociation of carboxyl group and increase the electronegativity of the material, providing a large potential for the electrostatic adsorption of Cu(II) on the biochar's surface. Moreover, ion exchange, precipitation, and zero-valent iron ions will also accelerate the removal of Cu(II).

4 Conclusion

(1) The adsorption capacity of Cu(II) by M_{2-800} is

Fig. 9 Adsorption and removal mechanism of Cu(II) in solution by modified biochar M_{2-800} .

Table 10 The influence of cycle times on the recovery rate of biochar particles and Cu adsorption regeneration.

Samples	Particles recovery rate (%)			Regeneration rate of Cu adsorption (%)		
	1	2	3	1	2	3
M_{2-400}	97.1	96.6	95.4	91.2	83.7	77.5
M_{2-800}	96.5	94.7	93.1	97.6	88.9	79.4

98.039 mg g⁻¹, about 38.8 times that of the C800 (2.525 mg g⁻¹) and 14.9 of M₂₋₄₀₀ (6.570 mg g⁻¹). Through linear fitting, it is found that the Langmuir isotherm has a higher linear coefficient R^2 .

(2) The adsorption amount of Cu(II) by M₂₋₈₀₀ is much greater than the total adsorption capacity of C800 and M_{2-800-ash} (98.039 mg g⁻¹ > 12.415 mg g⁻¹), suggesting that it is the synergistic effect of C, O, and Fe in M₂₋₈₀₀ that improves the removal of Cu(II).

(3) The average pore diameter of M₂₋₈₀₀ is 6.81 nm with the majority of mesopore, which increases the contact probability between pollutants and the adsorbent. However, the specific surface area of M₂₋₈₀₀ is less than 0.6% of C800, due to the decomposition of carbon the skeleton with the increasing content of Fe at the higher temperature.

(4) Chemical adsorption is the primary channel to immobilize Cu(II) by M₂₋₈₀₀. About 49.5% of Cu(II) is fixed through ion exchange. The Fe-O-/Fe-OOC- groups can produce a Fe-O-Cu complex with Cu(II) in the aqueous solution, promoting the removal of Cu(II).

(5) Carboxyl group is the primary binding site of Cu(II). After Cu(II) adsorption, carboxyl carbon and carboxyl oxygen decrease by 66.87% and 96.45%, respectively. Because of the higher electronegativity (-47.8 mV) and larger pH value (11.61) of M₂₋₈₀₀, Cu(II) can also be fixed by electrostatic attraction and precipitation.

Conflicts of interest

The authors declare no competing financial interests.

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