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RESEARCH ARTICLE

Study of the mechanism of remediation of Cd-contaminated soil by novel biochars

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Abstract This article used novel non-magnetized and magnetized biochars prepared under a CO_2 atmosphere returned to Cd-contaminated soil and compared these to the effects of conventional biochars prepared under a N_2 atmosphere with regard to Cd-contaminated soil remediation. A pot experiment with lettuce (*Lactuca sativa*) was conducted to investigate the relative soil remediation effects of these biochars. The soil used for the pot experiment was spiked with 20 mg kg^{-1} Cd and amended with 5% of a biochar before sowing. Through these research works, some important results were obtained as follows: (1) applying biochar treated by pyrolysis under a CO_2 atmosphere can obtain the best remediation effect of Cd-contaminated soil that the content of cadmium in the lettuce roots, stems, and leaves was reduced 67, 62, and 63%, respectively; (2) the magnetic biochar aggregation for the soil is weak, so the heavy metal cadmium in the soil could not be immobilized well by the magnetic biochar; (3) The remediation mechanism of novel biochars is that biochar includes a large number of organic functional groups (−C–OH, −C=O, COO−) that can act in a complexing reaction with heavy metal Cd(II) and the inorganic salt ions (Si, S, Cl, etc.) that can combine with cadmium and generate a stable combination.

Keywords Biochar of CO_2 atmosphere · Magnetic biochar · Soil remediation · Cadmium

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Introduction

Farmland security is a worldwide problem, directly related to food safety, poverty alleviation and rural development (Edward 2000; Ingram et al. 2008). Agriculture in most developing countries is facing some critical problems and challenges. Due to population growth, urbanization, rapid industrialization, and serious water pollution (Lu et al. 2011; Muyanga and Jayne 2014; Singh 2014), the phenomenon of heavy metal pollution is appearing in crop fields. Among all of the heavy metal problems, cadmium (Cd) pollution has attracted increasing attention because Cd is a heavy metal with ecological toxicity that has an adverse effect on soil biological activity and also does harm to biodiversity, plant metabolism, and human health (Sebastia et al. 2007; Wang et al. 2013). Biochar has many features which can fix heavy metals, including microporous structure, oxygen-containing functional groups, high pH, and cation exchange capacity (CEC) (Chen and Lin 2001; Jiang et al. 2012a, b). Biochar derives from plant residues, and related studies indicate that biochar is suitable for fixing heavy metals in polluted soil (Chun et al. 2004; Mohan et al. 2007).

At present, the research on the remediation of Cd-contaminated soil by biochar focusses mainly on the comparison of the remediation effect caused by applying different quantities of biochar to Cd-contaminated soil to confirm the most suitable amount of biochar to add. Research on the mechanism for soil remediation merely stays at the macro level. Many reports discuss the influence on the physical and chemical properties of soil after applying biochar: applying biochar can make yellow-brown soil pH, organic carbon (OC), and CEC increase (Gao et al. 2016; Yousaf et al. 2016). The studies on the remediation effect have also explored the morphology of Cd(II) in the soil because adding biochar can increase the pH of the yellow-brown soil and

transform Cd from weak acid extraction into Cd in the form of oxidation (Gao et al. 2016; Woldetsadik et al. 2016). In addition, Cd can be adsorbed by the irregular surface structure and oxygen functional groups of biochar (Li et al. 2016; Qian et al. 2016). Therefore, the mechanism of remediation of soil contaminated by Cd using biochar and the exploration of the mechanism of fixing cadmium on the surface of the biochar at the micro level are relatively lacking.

In this paper, rice straw was used as the raw material and the in situ remediation mechanism for soil contaminated by Cd was studied using four types of biochars. Among these biochars, two types were prepared in an atmosphere of N_2 and CO_2 (name: BN and BC). No other researchers used CO_2 to prepare the biochar, so BC is a novel biochar product. In addition, two types of magnetic biochars were made from the modification of BC and BN (named MC and MN in this paper). The study includes analysis of the changes in the microscopic structure of biochar after the four types of biochars were applied to Cd-contaminated soil using scanning electron microscopy with energy-dispersive X-ray (SEM-EDX) analysis of the elemental Cd fixed on the biochar, as well as further exploration of the mechanism of fixation of Cd on the surface of the biochar at the micro level using x-ray photoelectron spectroscopy (XPS) to provide a theoretical guide for the use of biochar in the in situ remediation of soil contaminated by Cd.

Materials and methods

Experimental materials

All chemicals, including ferric sulfate (> 96%), ferrous sulfate (99.5%), cadmium nitrate, concentrated nitric acid (65–68%), and sodium hydroxide, used in this research were of analytical grade, while solutions were prepared using deionized (DI) water (18.2 MX) (Nanopure Water, Barnstead).

Soil samples were collected from the surface layer (0–20 cm) at an experimental field station at Huazhong Agricultural University, Wuhan City, Hubei Province. Collected soil was cleared of plant roots, stones, and other debris. The soil was air-dried and sieved through a 10-mm mesh screen. The soil was identified as red clay (ultisol) and pH; content of macronutrients (N, P, K); as well as Cd and Fe concentrations were determined. The soil analyses that were obtained are listed in Table 1.

Table 1 Physiochemical characteristics of the soil

pH	Total N, g kg^{-1}	Total P, g kg^{-1}	Total K, g kg^{-1}	Total Cd, mg kg^{-1}	Total Fe, mg kg^{-1}
6.86	2.0	0.644	3.3	0.08	30.2

The rice straw used for biochar production for this experiment was collected from an experimental field station at Huazhong Agricultural University in Hubei province. In general, rice straw is a common agricultural waste in China. Rice straw was chopped into approximately 3-cm-long pieces and placed in a biological carbon fluidized bed. Biochars were produced through pyrolysis using different atmospheres (CO_2 and N_2); both processes were carried out at 400 °C. The rate of temperature rise was set at 20 °C min^{-1} and maintained at the target temperature for 40 min. The biochars that were produced were sieved through a 5-mm sieve before the pot experiment. Biochar produced under CO_2 was labeled as BC, while the BN abbreviation was used for biochar obtained from the N_2 atmosphere.

Magnetic biochars were prepared by magnetizing rice straw. Dry rice straw was cut into pieces that were 1–2-cm-long using scissors. Aliquots of 10 g of rice straw were added to a Fe^{2+}/Fe^{3+} solution and this Fe^{2+}/Fe^{3+} solution was a ferric sulfate solution (0.4 mol/L) combined with a ferrous sulfate solution (0.06 mol/L). These solutions were mixed and stirred vigorously for 30 min at room temperature. A 10-M NaOH solution was added dropwise to the biochar Fe^{2+}/Fe^{3+} suspension until the pH reached 10–11, and the suspension was stirred for 30 min. Excess solution was removed by vacuum filtration. The pre-treated rice straw was pyrolysed in a furnace at the temperature of 400 °C in a N_2/CO_2 environment for 40 min, and the heating rate was maintained at 20 °C min^{-1}. The magnetic biochars produced using the same temperature in CO_2/N_2 environments were labeled as MC and MN, respectively.

We first used a CO_2 atmosphere to produce biochar for soil remediation and improvement. No other researcher had produced the biochar in a CO_2 reaction atmosphere. Therefore, we prepared these types of biochars in a CO_2 atmosphere which are some novel biochars.

Preparation of Cd-contaminated soil

Each pot was filled with 400 g of red clay soil. Cadmium as $Cd(NO_3)_2$ was added into the soil. The total concentration of Cd in the prepared soil was 20 mg kg^{-1}. Freshly contaminated soil was left for 1 week at room temperature to reach equilibrium, followed by separately adding 5% (of dry soil weight) of four different biochars (BC, BN, MC, MN) with thorough mixing. Each treatment was repeated two times, and pots with a prepared soil-Cd-biochar mixture were placed on a tray to prevent heavy metal leaching. The soil moisture content was maintained at 18–22% using deionized water.

Analysis of the content of cadmium in lettuce and biochar near the plant rhizosphere

Analysis of the content of cadmium in lettuce was performed using atomic absorption spectrometer (AAS). Firstly, the lettuce was dried, and then the root, stem, and leaf of dried lettuce were weighed; secondly, the root, stem, and leaf of dried lettuce were fully digested into the three solutions, respectively. At last, the cadmium concentrations of three solutions were detected by AAS, so the content of cadmium in root, stem, and leaf can be known.

Analysis of the content of cadmium in biochar near a lettuce rhizosphere and determination of the changes in the morphology of biochar after the application into soil was performed using a JMS-6390 LV SEM-EDX produced in Japan NTC. The biochar particles were screened out of the soil near the plant rhizosphere, which was under four different treatments (BC, BN, MC, MN), with forceps, and small soil particles on biochar surface were carefully removed to clean by the tweezers. The sample of biochar was heated in the oven at the temperature of 75 °C and then the moderate sample was dispersed into the surface of a copper column containing conductive adhesive. Gold was sprayed on the surface of the sample. Through combinated analysis by electron microscopic scanning and plane sweep, the content of heavy metal cadmium and the changes in the Cd morphology in the biochar could be obtained after soil remediation by the four different biochars.

Analysis of biochar by the attenuated total reflectance Fourier transform infrared spectroscopy

The attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectra were collected using a Tensor 27 FTIR spectrometer (Bruker Corporation). It is worthy to point out that the wave number accuracy of the FTIR instrument used in this study is better than 0.01 cm^{-1} measured at 2000 cm^{-1} (Bruker Optics TENSOR 27 FTIR). The scan range was 4000–400 cm^{-1} with an average of 64 scans and a spectral resolution of 2 cm^{-1}. The lipid solution was dropped onto a Zn–Se crystal surface (Pike Technologies, USA). All samples were scanned at least four times until identical spectra were acquired. The FTIR measurements were conducted at room temperature (25 °C).

Analysis of the species of cadmium in the biochar

The soil near the plant rhizosphere, which is under four different treatments (BC, BN, MC, MN), was taken out; the biochar particles were screened out with forceps; and small soil particles on biochar surface were carefully removed to clean by the tweezers. The sample of biochar was heated in an oven at the temperature of 75 °C, and the species of cadmium in the biochar was determined by (XPS, a MULT1LAB2000. The species of cadmium was measured by the INSTALLATION Avantage software. C1s (284.6 eV) was used to rectify the charge displacement before measuring to correct the effect of the nuclear power of the insulated samples.

Results and discussion

Comparison of remediation of the soil by four types of biochar

The study uses four types of biochar (BC, BN, MC, MN) prepared from the agricultural waste (rice straw) with the treatment of limited oxygen pyrolysis at the temperature of 400 °C as the remediation agent for Cd-contaminated soil. The content of cadmium in the soil is 20 mg/kg in this experiment, far more than the range that lettuce can withstand. Figures 1 and 2 shows the overall growth of lettuce in cadmium-contaminated soil. The toxic action on the plants by cadmium will be weakened when the concentration of Cd in the soil is reduced, and the overall growth of the plants will also present a different state. As a result, we can indirectly determine the effect of remediation of cadmium-contaminated soil by four types of different biochar according to the overall growth of the lettuce. From Figs. 1 and 2, we can conclude that the survival rate of lettuce (CK) is zero without biochar. For the other four treatments of biochar, heavy metal cadmium is all fixed in situ to some extent. Through comparing the four treatments, we find that the overall growth and germination rate of lettuce are as follows: BC > BN > MN > MC, demonstrating that the remediation effect of cadmium-contaminated soil by biochar is ranked as: BC > BN > MN > MC.

To present the in situ remediation effect of cadmium-contaminated soil by four biochars more directly, we chose the representative plants under four different types of treatments and measured the changes in cadmium content in their roots, stems, and leaves. Figure 3 shows the changes in the cadmium content in the different parts of the lettuce under the treatments by diverse passivators. As shown in Fig. 3, compared with the blank CK without biochar, applying biochar can prevent lettuce from observably absorbing and accumulating the heavy metal cadmium in the soil. The decrement in the cadmium content of the various parts of the lettuce will achieve the optimal effect on the whole after applying biochar BC (produced under the pyrolysis treatment in the CO_2 atmosphere), and the remediation effect of the other biochars are in the order BN > MN > MC. The decrease in the cadmium content in the different parts of the lettuce is in accordance with the growth of the lettuce in Figs. 1 and 2. Comparing the decrease of the cadmium content in the different parts of the lettuce after

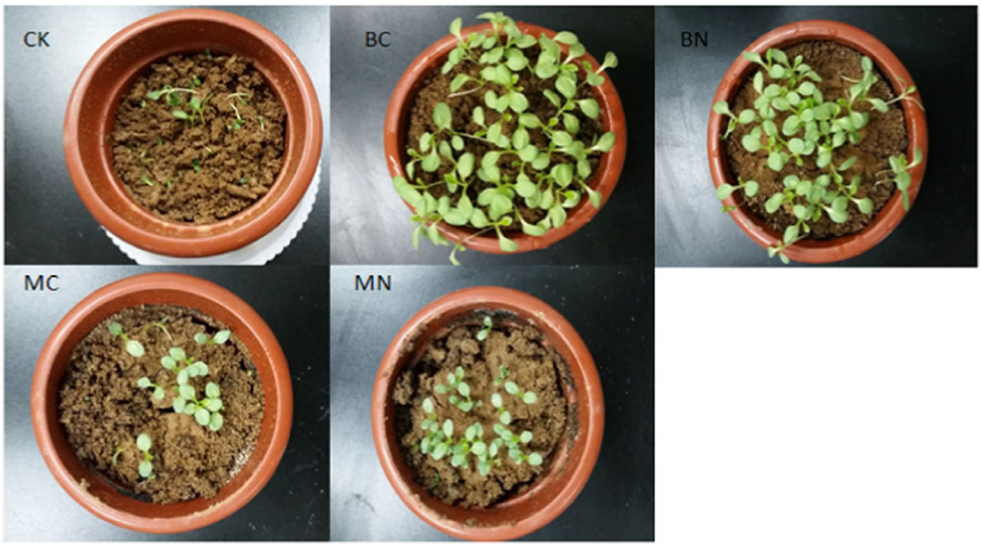

Fig. 1 The overall growth of lettuce with different treatments with biochar

the treatment with biochar BC shows that the content of cadmium in the lettuce roots, stems, and leaves was reduced 67, 62, and 63%, respectively. There is such a small difference in the cadmium decrease among the different parts of the lettuce, and the content of cadmium in the different parts of the lettuce is in the following order: root > stem > leaf. The appearance mentioned above illustrates that biochar can prevent plants from absorbing heavy metals such as Cd first from the root and prevent plants from transporting cadmium from the root to the ground part at the same time. To sum up, biochar has a good effect on the remediation of cadmium-contaminated soil in situ. Compared with the blank sample (CK), the content of cadmium in plants using biochar is reduced significantly. Moreover, applying biochar BC (prepared by the pyrolysis treatment in the CO_2 atmosphere) can produce the best remediation effect.

Effect on the morphology structure of biochar after the in situ remediation of cadmium-contaminated soil

Morphology structure is one of the most important physical characteristics of biochar. We can observe the changes in the biochar structure directly through the superficial characteristics of the morphology structure after applying the biochar to cadmium-contaminated soil. Figure 4 is an SEM photo of the in situ remediation of cadmium-contaminated soil under four different treatments (BC, BN, MC, MN). The top-left corner of each picture is the new morphology structure of the four biochars before in situ remediation. We can explore the specific remediation mechanism of the biochars in cadmium-contaminated soil through a comparison of the changes in the biochar morphology structure before and after remediating the soil.

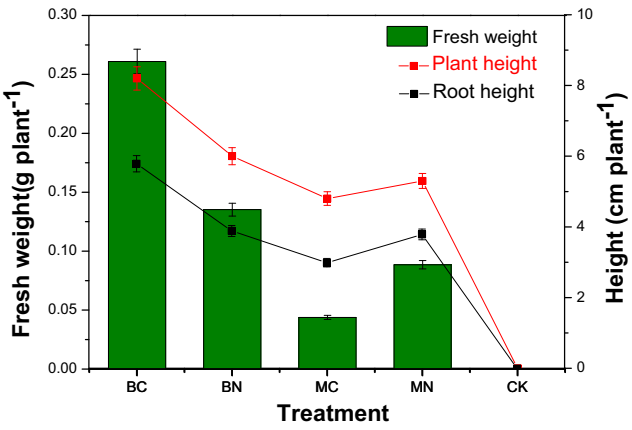

Fig. 2 Comparison of fresh weight and plant height of lettuces with different treatments

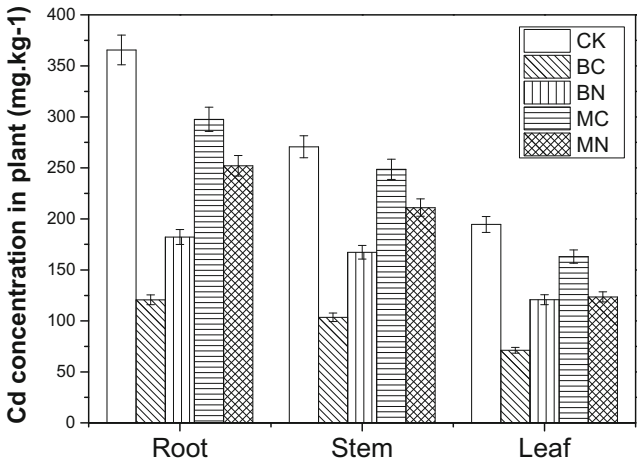

Fig. 3 Changes in the Cd concentrations in root, stem, and leaf under different treatments (BC, BN, MC, MN)

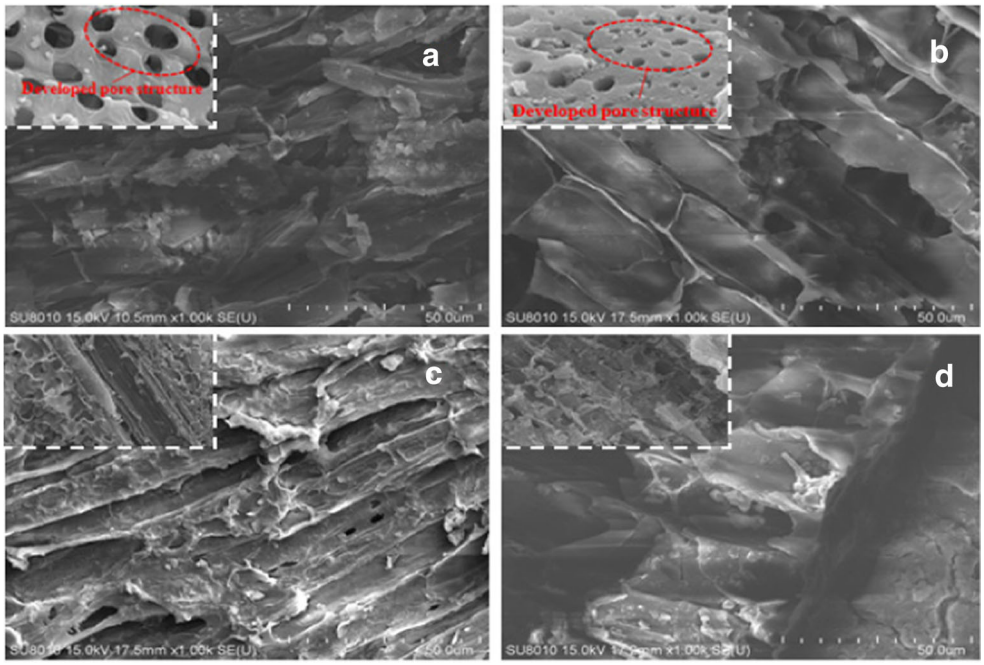

Fig. 4 Scanning electron microscope (SEM) images of the surfaces of the biochars after remediation. **a** SEM image of BC (×1000). **b** SEM image of BN (×1000). **c** SEM image of MC (×1000). **d** SEM image of MN (×1000)

Figure 4 shows that the unconsolidated porous structure of the four biochars is broken to a certain degree compared with the previous clear pore structure after application to the complex soil ecosystem. A part of the biochar is easy to decompose into a carbon source and a nitrogen source that can provide microorganisms for room and promote the growth and reproduction because that biochar has the characteristics of a loose multihole and large specific surface area. As a result, the structure of biochar is partly destroyed after the biochar is added to the complex soil environment for a long time. Figure 4a, b shows the morphology of the soil remediation by biochar prepared under the pyrolysis treatment in the carbon dioxide atmosphere and the nitrogen atmosphere. Clearly, the morphology of BC is more badly damaged than the morphology of BN, which illustrates that biochar BC can fuse tightly with soil and will be easy to touch with the heavy metal cadmium, absorbing and fixing it, blocking cadmium, achieving the purpose of in situ remediation in soil. At the same time, the heavy metals in the soil may be taken to the loose interstitial surface of the biochar to a large extent under the action of the water flow. The heavy metals on the biochar will go through a series of physical and chemical adsorptions and will be fixed tightly by the biochar in situ. Figure 4c, d shows the microstructure variation of the modified biochars MC and MN. We find that although there is a change in the morphology, the biochar carbon pore structure can be clearly distinguished. Because the surface of the modified magnetic biochar is covered with iron oxide, the microorganisms cannot breed on it. As a result, the pore structure of the magnetic biochar is not damaged. Moreover, a good ecological system between the soil system and the biochar system is difficult to form—the magnetic biochar aggregation for the soil is weak—so heavy metal cadmium in soil could not be fixed well by the magnetic biochar.

Changes in the cadmium content of the biochar after in situ remediation of cadmium-contaminated soil

To test whether the biochar applied to cadmium-contaminated soil does play a role in fixing the cadmium in situ, the study performed EDX spectral analysis of the biochar particles taken near the plant rhizosphere. Figure 5 shows the EDX spectral analysis results of the primitive biochars BC and BN. Figure 6 shows the EDX spectral analysis results for the magnetic biochars MC and MN.

Performing an energy spectrum elemental analysis at an arbitrary point of the biochar BC prepared in the carbon dioxide atmosphere in a cadmium-contaminated soil, we will find the peak of the cadmium in the sweep. The peak figure is shown in Fig. 5c. At the same time, performing an energy spectrum elemental analysis on an arbitrary point of biochar BN prepared in the nitrogen dioxide atmosphere, we will also seek out the peak of cadmium in the sweep of the peak figure in Fig. 5d. BC and BN originally contained no elemental cadmium, which suggests that the cadmium element comes from the heavy metal cadmium absorbed and fixed by the biochar in the cadmium-contaminated soil; so, BC and BN can fix heavy metal cadmium in situ through a series of complex physical and chemical adsorptions in soil. Through observing the density of the green points on the EXD surface scan, we can determine that the biochar BC is more intense than BN, the content of cadmium in the BC is 0.12 and 0.11%

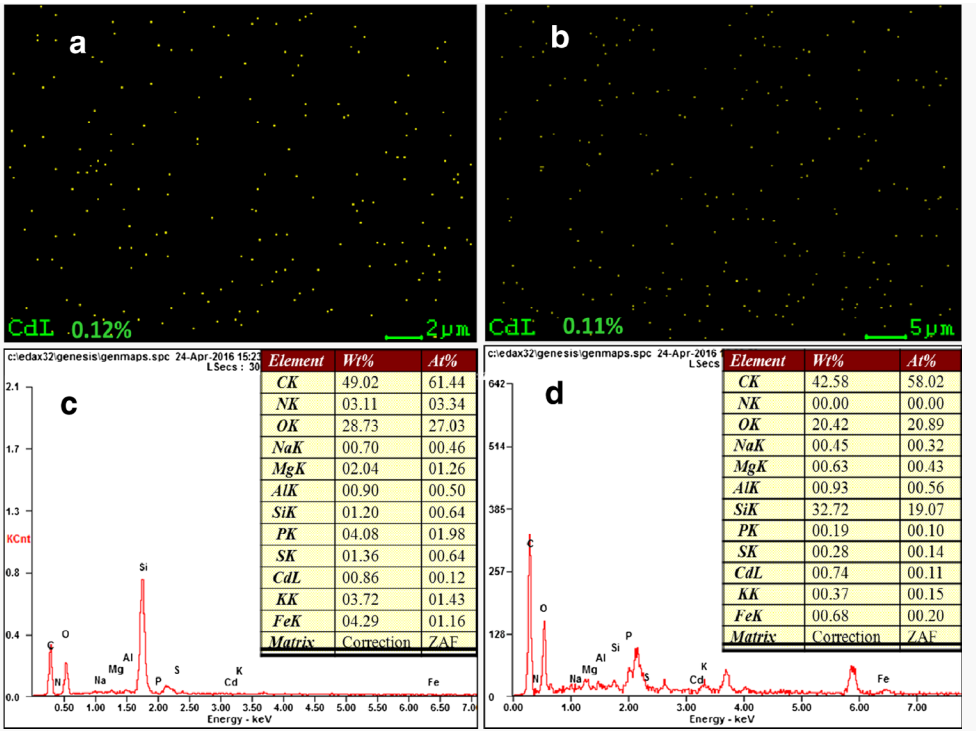

Fig. 5 EDX results for biochars after remediation. **a** Color-coded EDX dot maps of BC. **b** Color-coded EDX dot maps of BN. **c** EDX results for BC. **d** EDX results of BN

in BN, which is consistent with the morphology changes in the original biochar.

Performing an energy spectrum elemental analysis on an arbitrary point of the magnetic biochar MC from cadmium-contaminated soil, we found the peak of cadmium in the sweep peak figure as shown in Fig. 6c. Meanwhile, performing an energy spectrum elemental analysis on an arbitrary point of magnetic biochar MN, we also sought out the peak of cadmium in the sweep peak in Fig. 6d. Analyzing the fixing effect of the magnetic biochar on cadmium according to the EDX sweep surface result for MC in Fig. 6a, we can clearly find green points that represent of elemental cadmium, so the magnetic biochar MC also fixes a small part of the cadmium in situ. Compared with MC, the magnetic biochar MN fixes cadmium much more,

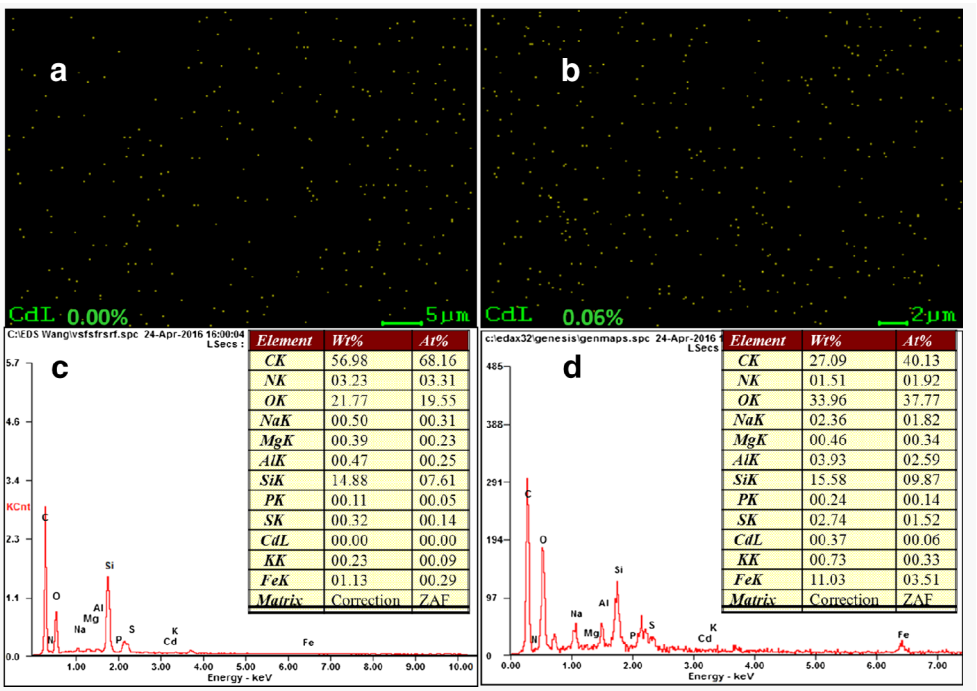

Fig. 6 EDX results of biochars after remediation. **a** Color-coded EDX dot maps of MC. **b** Color-coded EDX dot maps of MN. **c** EDX results for MC. **d** EDX results for MN

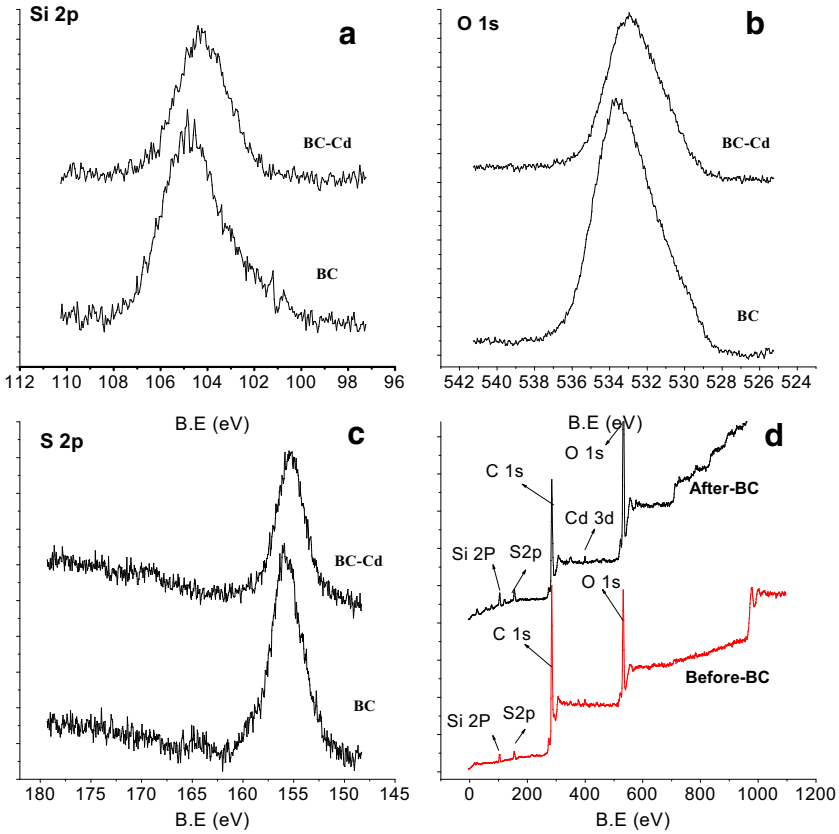

Fig. 7 XPS spectra of biochar BC before and after returning. **a** Si2p spectra of Cd(II) before and after returning BC. **b** O1s spectra of Cd(II) before and after returning BC. **c** S2p spectra of Cd(II) before and after returning BC. **d** the full spectra of Cd(II) before and after returning BC

with the relative content of Cd reaching to 0.06%. Through comparing the results of field emission in Figs. 5 and 6, the fixed absorption effect on cadmium by the original biochar is much better than the magnetic biochar in Cd-contaminated soil, consistent with the changes in the biochar morphology mentioned above. The phenomenon suggests that the characteristics of the pore structure of the original biochars (BC and BN) can fuse more tightly with the soil and touch the heavy metal cadmium more easily in the soil, thereby absorbing and fixing cadmium, blocking cadmium, and achieving the purpose of in situ remediation of the soil.

Analysis on the bound form of cadmium in BC after in situ remediation

Through the analysis of the changes in the morphology structure of the soil before and after in situ remediation by biochar in cadmium-contaminated soil and the variation of the cadmium content in the biochar, we can determine that biochar can absorb and polymerize heavy metal cadmium because of its unique pore structure. Moreover, EDX spectral analysis shows that heavy metal cadmium has been fixed very well on biochar in situ. To perform further to explore the fixing mechanism of cadmium onto the surface of the biochar from the micro level and provide a theoretical foundation for remediating heavy metal cadmium-contaminated soil in situ by biochar, we used the x-ray photoelectron spectroscopy to analyze the bound form of the cadmium irons. Figure 7 shows the changes in the Si2p, O1s, S2p, and integral binding energy before and after in situ remediation in cadmium-contaminated soil by the original biochar BC. Figure 8 shows the schematic diagram for charge transfer. Figure 9 is the Cd XPS spectrogram and variation in oxygen binding energy after in situ remediation by biochar BC. Table 2 is the relative content of cadmium in different species after in situ remediation by biochar BC.

Through the overall XPS results for biochar BC before and after remediation in Fig. 7d, we can determine that the biochar BC not applied to the cadmium-contaminated soil does not have the binding energy peak of cadmium in the previous example, while biochar BC shows the peak of cadmium at 405.2 eV after in situ remediation. The appearance suggests that biochar BC has already fixed Cd(II) in situ, consistent with the result from the EDX spectral diagram of biochar BC. From the XPS raw spectrum figure of biochar BC Si2p in Fig. 7a, we can see that the energy of Si2p is reduced from 104.893 to 104.195 eV. The reduction of the binding energy illustrates that Si increases the negative charge, and the negative charge moves from the outer electrons of Si to the inner layer after fixing Cd(II). Silicon gains the electrons involved in the remediation. From the XPS spectrum diagram in Fig. 7b, c, we can also conclude that the XPS peak binding energy of the biochar BC O1s reduced from 533.708 to 532.905 eV as well as S2p reducing from 156.065 to

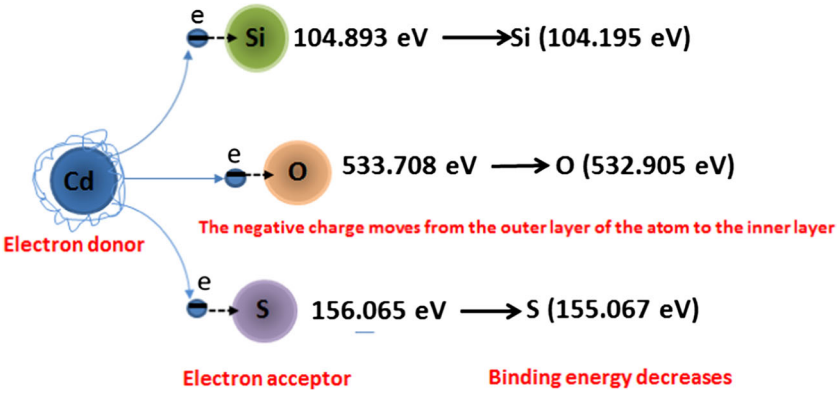

Fig. 8 Schematic diagram for charge transfer

155.067 eV, suggesting that the binding energy of the electrons in the O and S inner layers can decrease after fixing the cadmium ions. That O and S gain electrons can cause us to presume that electrons can transfer from cadmium ions to Si, O, and S atoms during the process of fixing Cd ions with biochar BC.

By comparing the XPS spectral diagram of C1s before and after fixing the heavy metal cadmium by biochar BC in Fig. 9b, c, we can determine that there is a characteristic peak of the C1s narrow-area spectrum near 284.6 eV, which consists of C atoms of carbon groups in C–H, C–C, or C=C. The binding energy does not change significantly after in situ remediation, as shown in Fig. 9c, which illustrates that the C atoms in the form of C–H, C–C, or C=C are not involved directly in the adsorption of Cd(II). The characteristic peak of the electronic binding energy appearing at 286.45 eV shows the existence of hydroxyl carbon (−C–OH). Likewise, the peak at 287.5 eV accounts for the existence of carbonyl carbon (−C=O) and 288.5 eV for carboxyl carbon (−COO−). After fixing cadmium in situ by the biochar, the electronic binding energy of −C–OH falls from 286.45 to 286 eV, the electronic binding energy of −C=O falls from 287.5 to 287 eV, and the electronic binding energy of −COO− increases from 288.5 to 288.85 eV. Therefore, C atoms with hydroxyl, carbonyl, and carboxyl groups all play a part in fixing Cd(II) in situ with biochar BC, consistent with the analytical result obtained by FTIR in Fig. 10. By analyzing the shift of the wavelength and the change of the crest in the FTIR spectrogram in biochar BC, we can determine that the characteristic peak of the oxygen-containing functional groups in BC obviously change, mainly because of the variation in the wavenumber, the decrease in the amplitude, and the reduction in peak intensities. The absorption peak at 3413 cm^{-1} is obviously reduced and migrates to 3481 cm^{-1} in the left, which suggests that the hydrogen bonding force of intramolecular −OH decreases because −OH is occupied by Cd(II) after absorption. Clearly, ion exchange action can occur during the process of absorption. At the same time, the absorption peak at 1118 cm^{-1} is obviously decreased and moves to 1102 cm^{-1} on the right. The phenomenon mentioned above suggests that the C–OH of the phenol and the ether is occupied by Cd(II), while H is replaced by Cd(II) after absorption. The absorption peak of C=O in carboxyl at 1599 cm^{-1} becomes weak, as well as the absorption peak of C–H in the aromatic hydrocarbon at 805 cm^{-1}, Cd(II)

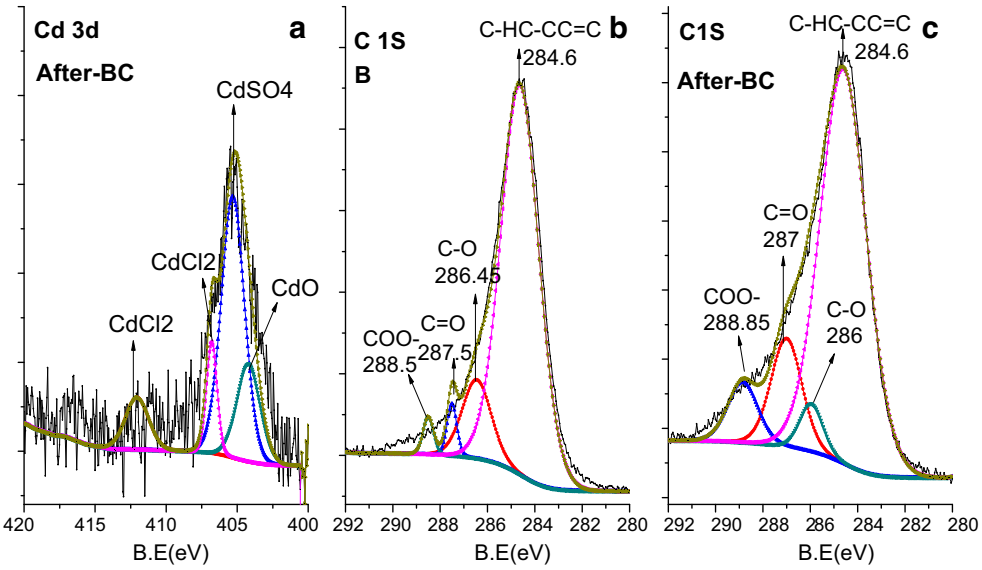

Fig. 9 Curve-fitted XPS spectra for Cd and the variation of the binding energy of the oxygen atom in BC

Table 2 Relative contents of different forms of Cd(II) in different biochars after remediation

Sample	CdO	Cd SO_4	$CdCl_2$
BC	21.20	56.62	22.17
BN	20.40	58.12	21.48
MC	13.64	45.20	41.16
MN	12.41	46.70	40.89

may be related to the ion exchange of −OH's H^+ in BC, and the complexation reaction of carbonyl (C=O) occurs. The shift of the peak at 1599 cm^{-1} will provide evidences for complexation between −COOH and Cd(II). Through comprehensive analysis of the XPS and the FTIR, we can determine that the reason why biochar can remediate Cd-contaminated soil in situ is that the functional groups of hydroxyl, carbonyl, and carboxyl can act as a complexation reaction with Cd(II).

From the XPS fitting curve of Cd3d in Fig. 9a, we know that the Cd in the original biochar BC includes three main forms—CdO, $CdSO_4$, and $CdCl_2$. The analysis of the changes in the binding energy in Fig. 7 verifies that O and S obtain electrons, while Cd has a tendency to lose electrons. According to the law of electronic conservation in the process of chemical reaction, Cd will combine with O, S, and Cl, then generate a combined state. From the area ratio of the photoelectron peak, we can determine that the proportion of the three types of combination state are as follows, respectively: $CdSO_4$ is 56.62%, $CdCl_2$ is 22.17%, and CdO is 21.2%. In summary, the original biochar BC can remediate cadmium-contaminated soil in situ in two ways: one way is that the biochar contains a large number of organic functional groups (−C–OH, −C=O, COO−) that can act in a complexation reaction with the heavy metal Cd(II). The other way is that the inorganic salt ions (e.g., Si, S, and Cl) in biochar BC can combine with cadmium and generate stable combinations.

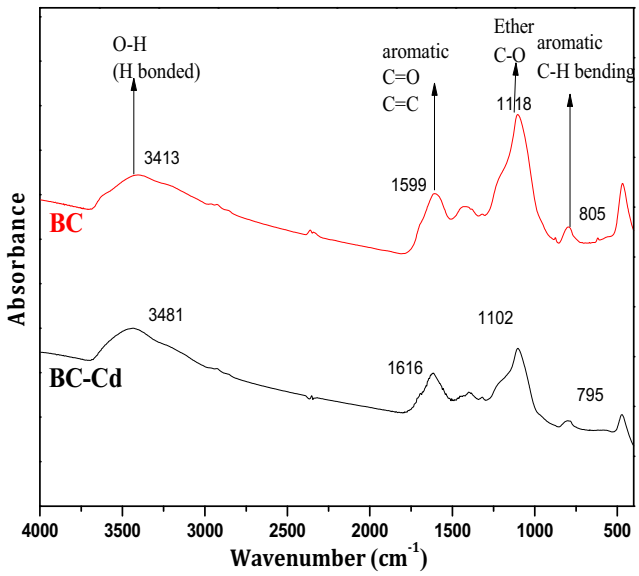

Fig. 10 FTIR spectra of BC and BC-Cd

Analysis of the bound form of cadmium ion after in situ remediation by magnetic biochar

This paper mainly explores the in situ remediation mechanism of cadmium-contaminated soil by the original and the magnetic biochar, according to the morphological structure analysis of the original biochar BC and the magnetic biochar. In Fig. 4, we can determine that the magnetic biochar surface is coated with iron oxide film; therefore, this section explores the solidification mechanism of cadmium on the surface of the magnetic biochar at the micro level. We used x-ray photoelectron spectroscopy not only to analyze the bound form of cadmium ions but also to explore the binding status of Fe in the magnetic biochar. Through comparing the morphological changes of Fe and Cd in the magnetic biochar before and after returning, we try to analyze the probable remediation mechanism. Figure 11 portrays the changes of Fe2p, O1s, S2p, and the overall binding energy before and after in situ remediation by the magnetic biochar MN. Figure 12 fits the XPS spectral graph about Cd and Fe after in situ remediation by the magnetic biochar MN. Table 2 shows the relative contents (%) of Cd(II) in different forms of the magnetic biochar MN after remediation as well as Table 3 about Fe in MN.

Through the overall XPS results from the magnetic biochar MN before and after returning in Fig. 11d, we can determine that the magnetic biochar MN not added into the cadmium-contaminated soil does not have the binding energy peak of cadmium in the previous spectrum, where it appears that the peak of cadmium has the binding energy of 405.2 eV. The appearance suggests that the magnetic biochar MN has already fixed Cd(II) in situ, consistent with the result from the EDX spectral diagram of biochar MN mentioned above. Moreover, relative to the overall XPS figure for the original biochar BC, there is a binding energy peak of Fe in MN. The binding energy of Fe2p1/2 in the magnetic biochar MN is decreased from 725.103 to 724.511 eV. Likewise, Fe2p3/2 is reduced from 711.589 to 711.137 eV, which suggests that the binding energy of the electrons in the inner layers of the magnetic biochar after in situ remediation decreases, and the negative charges of the Fe covering the surface of the magnetic biochar increases. Fe obtains electrons involved in the reaction during the process of fixing cadmium in situ by the magnetic biochar. From the XPS spectral diagram in Fig. 11b, c, we can also conclude that the XPS peak binding energy of the magnetic biochar MN O1s reduced from 532.838 to 532.205 eV as well as S2p reducing from 163 to 161.5 eV, which suggests that the binding energy of electrons in the O and S inner layers can decrease after fixing cadmium ions and the O and S gain electrons. The appearance also can cause us to presume that electrons can transfer from cadmium ion to Si, O, and S atoms during the process of fixing Cd ions by MN. The binding energy migration phenomenon for each element before and after returning by magnetic biochar MN is basically similar

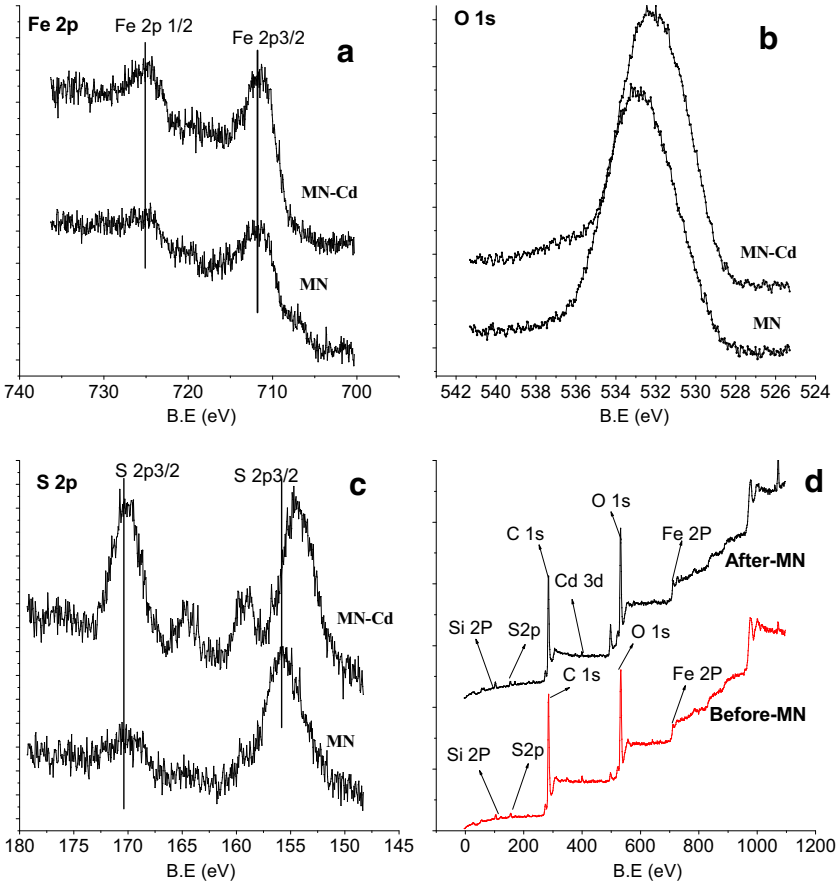

Fig. 11 XPS spectra of magnetic biochar MN before and after returning. **a** Fe2p spectra of MN before and after returning. **b** O1s spectra of MN before and after returning. **c** S2p spectra of MN before and after returning. **d** The full spectra of MN before and after returning

to the original biochar BC, but Fe takes part in the reaction in the magnetic biochar.

From the XPS fitting curve of Cd3d in Fig. 12a, we can determine that the Cd in the magnetic biochar MN includes three main forms—CdO, $CdSO_4$, and $CdCl_2$. The analysis of the binding energy changes in the magnetic biochar in Fig. 11 above verifies that O, S, and Fe act to obtain electrons, and Cd has a tendency to lose electrons. According to the law of electronic conservation in the process of chemical reaction, Cd will combine with O, S, and Cl, then generate a combined state. From the area ratio of the photoelectron peak, we know that the proportion of the three types of combination state are $CdSO_4$ is 46.7%, $CdCl_2$ is 40.89%, and CdO is 12.41%. From the XPS fitting curve of Fe2p in Fig. 12b, we can determine that Fe in the magnetic biochar MN includes four main forms—Fe_3O_4, $Fe_2(SO_4)_3$, $FeCl_3$, and FeX_n (unknown chemical form). From the photoelectron peak area ratio of Fe, we can know that the proportion of the four types of combining

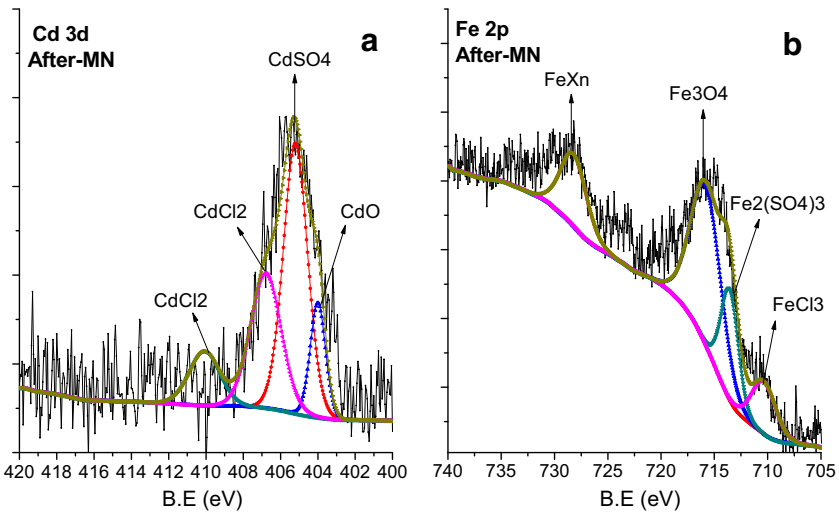

Fig. 12 Curve-fitted XPS spectra for Cd and Fe in MN

Table 3 Relative contents of different forms of Fe in magnetic biochar MN after remediation

The Sample	FeXn	Fe_3O_4	$Fe_2(SO_4)_3$	$FeCl_3$
MN	18.95	48.93	19.32	12.79

states are as follows: FeX_n is 18.95%, Fe_3O_4 is 48.93%, $Fe_2(SO_4)_3$ is 19.32%, and $FeCl_3$ is 12.79%. Comparing the content of Cd in each form in the magnetic biochar MN to the original biochar BC, we find that the relative content of $CdSO_4$ in the original biochar BC (56.62%) is higher than the relative content of $CdSO_4$ in MN (46.7%). Analyzing various chemical forms of Fe in MN, we can determine that Fe will combine with SO_4^{2-} and generate $Fe_2(SO_4)_3$, Fe acts as a cation as well as Cd, and they will compete with each other because the number of anions is uncertain. As a consequence, the number of cadmium ions fixed on the magnetic biochar will reduce. In summary, the in situ remediation mechanism for heavy metal cadmium by biochar MN is same as the original biochar, but the iron oxide covering on the surface of the magnetic biochar will compete with Cd and form a fixed combination.

Protection mechanism of lettuce by biochar

Figure 13 is a protection mechanism diagram which portrays how the cadmium-contaminated soil after in situ remediation by biochar protects the lettuce. When applying biochar to cadmium-contaminated soil, biochar can fuse with the soil tightly and form aggregates. The aggregates are easy to touch with the heavy metal cadmium. At the same time, heavy metal cadmium in the soil can be taken to the loose interstitial surface of the biochar to a great extent under the action of water flow and can be fixed on the surface of the biochar in situ in two ways. One way is that the biochar includes a large number of organic functional groups (−C–OH, −C=O, COO−) that can act in a complexing reaction with heavy metal Cd(II) or ion exchange. The other way is that the inorganic salt ions (Si, S, Cl, etc.) in biochar can combine with cadmium and generate a stable combination. Biochar can reduce plant absorption of heavy metals from the root and prevent plants from transporting cadmium from the root to the ground part at the same time. As a result, biochar has a good effect for remediating cadmium-contaminated soil in situ.

Conclusions

(1) The content of cadmium in the different parts of lettuce is as follows: root > stem > leaf. The appearance mentioned above illustrates that biochar can reduce plant absorption of heavy metals from the root first and prevent plant transport of cadmium from the root to the ground part at the same time. Biochar has a good effect in remediating cadmium-contaminated soil in situ. Compared with the blank sample (CK), the content of cadmium in plants is reduced significantly, and applying biochar BC treated by pyrolysis under a CO_2 atmosphere can obtain the best remediation effect.

(2) Through analysis of the change of the morphological structure after in situ remediation, we can determine that biochar BC can fuse tightly with soil and will be easy to touch with the heavy metal cadmium. At the same time, heavy metal cadmium in the soil may be taken to the loose interstitial surface of the biochar to a large extent under the action of water flow. The heavy metals taken to the biochar will go through a series of physical and chemical adsorptions and be fixed tightly in situ,

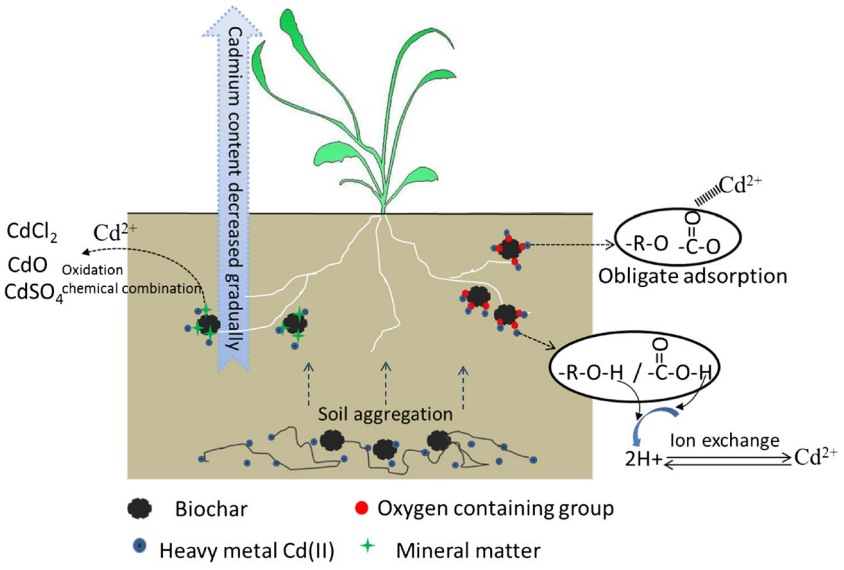

Fig. 13 A mechanistic diagram of plant protection by biochar

blocking cadmium and achieving the purpose of in situ remediation in soil. Because the surface of the magnetic biochar is covered with iron oxide, the magnetic biochar aggregation for the soil is weak, so the heavy metal cadmium in the soil could not be fixed well by the magnetic biochar.

(3) Through EDX semi-quantitative analysis of biochar near the rhizosphere and XPS morphological analysis on cadmium, we can determine that biochar can fix the heavy metal cadmium in soil highly effectively. The remediation mechanisms are as follows: one mechanism is that biochar includes a large number of organic functional groups (−C–OH, −C=O, COO−) that can act in a complexing reaction with heavy metal Cd(II). The other mechanism is that the inorganic salt ions (Si, S, Cl, etc.) in biochar BC can combine with cadmium and generate a stable combination, but the iron oxide covering on the surface of the magnetic biochar will compete with Cd, so the number of cadmium ions fixed on the magnetic biochar will be reduced.

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