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Review

Efficient Remediation of Cadmium Contamination in Soil by Functionalized Biochar: Recent Advances, Challenges, and Future Prospects

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Abstract: Heavy metal pollution in soil seriously harms human health and animal and plant growth. Among them, cadmium pollution is one of the most serious issues. As a promising remediation material for cadmium pollution in soil, functionalized biochar has attracted wide attention in the last decade. This paper summarizes the preparation technology of biochar, the existing forms of heavy metals in soil, the remediation mechanism of biochar for remediating cadmium contamination in soil, and the factors affecting the remediation process, and discusses the latest research advances of functionalized biochar for remediating cadmium contamination in soil. Finally, the challenges encountered by the implementation of biochar for remediating Cd contamination in soil are summarized, and the prospects in this field are highlighted for its expected industrial large-scale implementation.

Keywords: biochar; soil remediation; cadmium contamination; recent advances; challenges and prospects

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1. Introduction

Nowadays, heavy metal contamination is widely recognized as a serious global environmental issue [1,2]. Cadmium (Cd), one of the most dangerous heavy metals, has been listed as an environmental priority pollutant [3]. Cd is a soluble heavy metal, and it can more easily transfer into soil compared with other heavy metals. According to the 2020 Bulletin on China's ecological environment, the main pollutants affecting the environmental quality of farmland soil around the country are heavy metals; among them, cadmium is the primary pollutant [4,5]. The sources of cadmium pollution in farmlands mainly include sewage irrigation, atmospheric deposition, chemical fertilizers, pesticides, mineral mining activities, and used fossil fuels [6,7]. Cadmium, as a toxic metal, is easily absorbed by plants through roots and then transferred to other plant parts for continuous enrichment and accumulation, finally entering the human body through the food chain, which poses a serious threat to human health [8]. Knowing how to scientifically and effectively control cadmium pollution in the soil is a critical and urgent issue, especially in agricultural countries [9,10].

The passivation and remediation methods for cadmium in soil include physical, chemical, biological, combined remediation, and ecological remediation [11–13]. The chemical passivation method is widely used in practice, which involves adding a passivation material to contaminated soil, allowing for heavy metal ions to adsorb, chelate, precipitate, and redox, and then the heavy metals in the soil are transformed from an active state to residual state [14]. In this manner, bioavailability and environmental mobility in the soil are reduced, and the contaminated soil can be repaired. Passivation materials can be divided into inorganic, organic, microbial, and compound types [15,16].

Biochar is a kind of refractory, stable, highly aromatic, and carbon-rich solid material produced from biomass residues under the condition of oxygen limitation [17,18]. As a novel and efficient organic in-situ passivation material, biochar is crucial to the remediation of heavy metals in soil. The raw material sources for biochar production vary greatly. Examples include agricultural waste (fruit shell, straw, and rice husk) [19,20], industrial organic waste (bagasse and papermaking sewage) [21], urban sludge [22], kitchen waste [23], and livestock manure [24]. Biochar can interact with heavy metals through direct electrostatic attraction, complexation, ion exchange and precipitation, and cation-π bonding [25]. It typically has the characterization of a large specific surface area (SSA) and a porous structure, which are more conducive to the accumulation of soil water, formation of soil aggregates, and improvement of the retention capacity of soil water and nutrients [26]. The richness of oxygenated surface functional groups (O-SFGs), such as hydroxyl, carboxyl, and carbonyl, can effectively adsorb heavy metals in the soil and form complexes to reduce the bioavailability and migration ability of soil heavy metals [27,28]. Furthermore, the high quantities of mineral and trace elements of biochar can provide the elements necessary for crop growth, improve soil health, and promote crop growth [29]. Given the low cost and wide sources of biochar, it has been widely considered an effective strategy for repairing the heavy metal contamination of soils [30,31].

The application of biochar in environmental remediation has been widely investigated in the last decade [27,32], but specific reviews on treating cadmium pollution in soil using functionalized biochar are extremely limited. Especially, there is a lack in summarizing and discussing the latest studies of functionalized (modified) biochar. In the last five years, the number of articles in this field has sharply increased (Figure 1). Many good results have been achieved by exploring the change in the characteristics of biochar (e.g., increasing SSA, changing the porosity, or introducing O-SFGs) or co-applying biochar with other remediating materials or technologies.

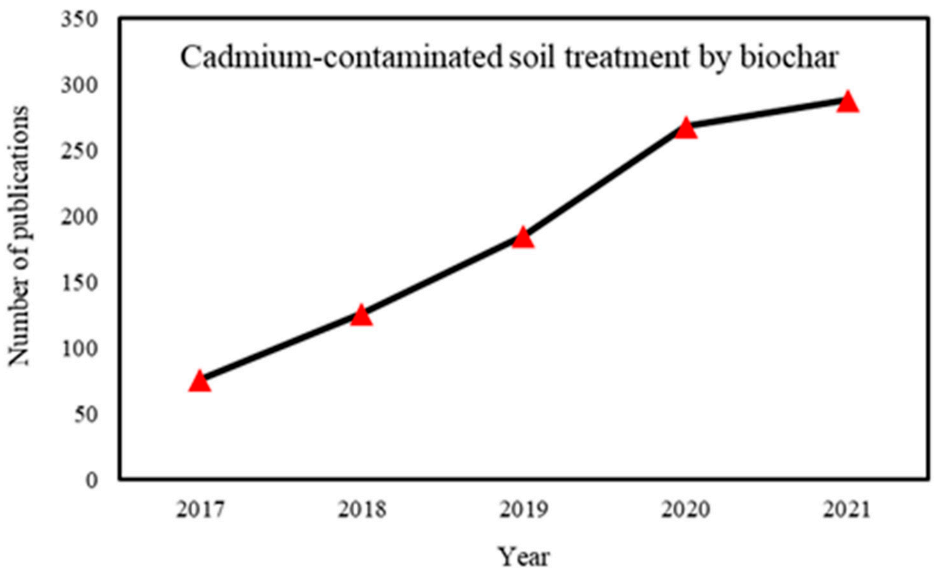

Figure 1. Publications on cadmium-contaminated soil treatment by biochar according to Web of Science (June 2022: "soil," "biochar," and "cadmium").

This paper first classifies and summarizes the preparation process of biochar, the existing forms of heavy metals in soil, and the remediation mechanism of biochar for heavy metal cadmium, and discusses the factors that influence biochar's effect on the remediation of cadmium contamination. The latest advances in functionalized biochars, with respect to the remediation of cadmium contamination in soil, are critically reviewed. Finally, the challenges faced by designing and producing functionalized biochars, as well as applying them in Cd-contaminated soil remediation, are summarized, and prospects are put forward for their large-scale implementation.

2. Remediation Mechanism of Cd Contamination in Soil by Using Biochar

2.1. Comparison of the Preparation Processes for Raw Biochar

In general, the preparation of biochar involves the thermochemical decomposition of biomass under anaerobic conditions to produce carbon materials. The three main preparation methods are pyrolysis, hydrothermal carbonization, and torrefaction [33,34]. A clear intuitive comparison of the differences in biochar preparation processes can be seen in Table 1.

Table 1. Comparison of biochar preparation processes [33–36].

Preparation Method	Temperature	Product	Biochar Characteristic
Pyrolysis	300–900 °C	Solid; Liquid; Gas	Porous; SSA = 200–2000; Carbon content is 60–80 wt%; Rich SFGs; Residence time <2 s or >2 h
Hydrothermal carbonization	<250 °C	Solid; Liquid	Poor porosity; SSA < 10; Carbon content is 45–65 wt%; Rich SFGs; Residence time 2–16 h
Torrefaction	200–300 °C	Hydrophobic solid	Poor porosity; SSA < 10; Carbon content is 30–55 wt%; Very limited SFGs; Residence time >10 h

SFGs: surface functional groups.

Pyrolysis, in which raw materials are heated and decomposed at temperatures ranging from 300 to 900 °C under oxygen-limited conditions, is generally divided into fast pyrolysis and slow pyrolysis [27]. Fast pyrolysis involves a very high heating rate, with a residence time of steam being usually less than 2 s [35]. A high pyrolysis temperature reduces the yield of biochar, while a high heating rate can increase the carbon content of the biochar. By contrast, slow pyrolysis, with a low heating rate and long residence time (> 2 h), is conducive to more sufficiently ensuring heat conduction, which is conducive to the carbon deposition reaction, thus increasing the yield of the biochar. The solid, liquid, and gas produced during pyrolysis are called biochar, bio-oil, and syngas, respectively.

Hydrothermal carbonization is a thermochemical process that typically selects biomass for pretreatment and utilizes a fast carbonization method under moderate temperatures (150 to 250 °C) and pressures (0.5 to 2 MPa) in an aqueous environment to obtain hydrochar [37]. Compared with pyrolysis and torrefaction, the biochar prepared using this method has a higher content of oxygen-containing groups and better surface functionality and tends to show a spherical carbon structure [38]. Hydrothermal carbonization is highly suitable for wet biomass.

Torrefaction is the method of directly or indirectly heating biomass raw materials under oxygen-limited conditions within the temperature range of 200–300 °C, with a low heating rate (less than 50 °C/min) and a relatively long residence time (>10 h) [35]. This technique can remove most of the water from the raw materials and convert them into hydrophobic solid products. The energy density of this biochar can be increased to close to that of coal, which can be used for heating and power generation.

2.2. Existing Forms of Cd in Soil

The biological toxicity of Cd is not only related to its overall content but also determined by its existing form [39]. The bioavailability of different forms of Cd as a heavy metal comes in the order of water-soluble state (WS) > exchangeable state (EX) > carbonate bound state (CB) > Fe–Mn oxide bound state (OX) > organic matter bound state (OM) > residue state (RES) [40]. The WS and EX states are the main bioavailable chemical forms of Cd in soil. More than 20 analytic methods for handling the states of heavy metals in soil have been proposed now, among which the most commonly used ones are shown in Table S1 (Supporting Information).

The Tessier method and the European Community Bureau of Reference (BCR) method are the most widely used methods for the academic analysis of the state of Cd in soil

(Table S1). In the Tessier method, the forms of Cd are usually divided into five states: EX, CB, OX, OM, and RES [41]. The EX state is related to the bioavailable state. This existing form of Cd is susceptible to changes in the soil environment. It can also be easily absorbed by organisms and has a strong migration ability. The CB, OX, and OM states are related to the potential bioavailable state. When some environmental variables, such as acidic conditions and redox potentials, change, these existing forms of Cd can be transformed into the bioavailable state, which can harm organisms and lead to potential hazard risks. The RES state, which is also called the non-available state, refers to the ability of Cd to occur as a stable form in the soil and is generally unchanged despite an altered soil. This existing form of Cd essentially does not enter the plant and thus cannot be absorbed and utilized [10,30].

Thus, not all existing forms of Cd can be absorbed by plants or other organisms. Many relevant studies have shown that the toxic effect of heavy metals in soil on organisms depends on the content of bioavailable states rather than the total amount of heavy metals. This bioavailability of Cd can be taken up from the soil and retained in the organisms through adsorption and ingestion, forming bioaccumulation. Thereby, it can significantly affect ecological characteristics, such as soil microbial biomass and activity, microbial community structure/function and diversity, soil enzyme activity, and soil respiration intensity [42,43]. Therefore, the key points for remediating Cd contamination in the soil are the reduction of the bioavailability of Cd in the soil by promoting the conversion of its bioavailable states (WS or EX) to the potential bioavailable and non-available states (CB, OX, OM, and RES).

2.3. Remediation Mechanisms

The mechanisms of remediating Cd-contaminated soil with biochar include electrostatic attraction, ion exchange, complexation, coprecipitation, and cation-π bond interactions (Figure 2) [25,44]. The illustrations of the mechanisms are as follows: (1) electrostatic attraction occurs when Cd ions in the soil come into contact with the negatively-charged surface of biochar, and the strength of electrostatic adsorption is affected by the soil pH and the zeta potential of the biochar. The magnitude of zeta potential is determined by the surface charge, derived from the negative charging of active groups on the biochar surface. (2) Ion exchange is closely related to the chemical bond composition, charging properties, and diffusion effect of Cd ions on the biochar surface. In essence, it is the physical exchange between abundant O-SFGs on the biochar surface and cadmium ions in the soil. (3) Complexation means the forming of stable complexes to immobilize Cd ions. The complexes are formed through coordination bonds between the isolated electron pairs on the oxygen atoms in the O-SFGs on the biochar surface and the outer orbitals of cadmium ions. (4) Coprecipitation indicates that the mineral elements contained in the biochar co-precipitate with the metallic phase to form relatively stable insoluble precipitates, such as hydroxide, carbonate, and metal phosphate, under alkaline conditions. These processes depend on the specific minerals contained in different biochars. (5) Cation-π bond interactions, which have been recognized and have attracted wide attention in recent years, involve combining the conjugated electrons in the π bond with the empty orbits of metal cations to realize reversible physical adsorption [5]. This is determined by the self-aromatization structures of the biochar and is not affected by the number of negative charges carried on the biochar's surface.

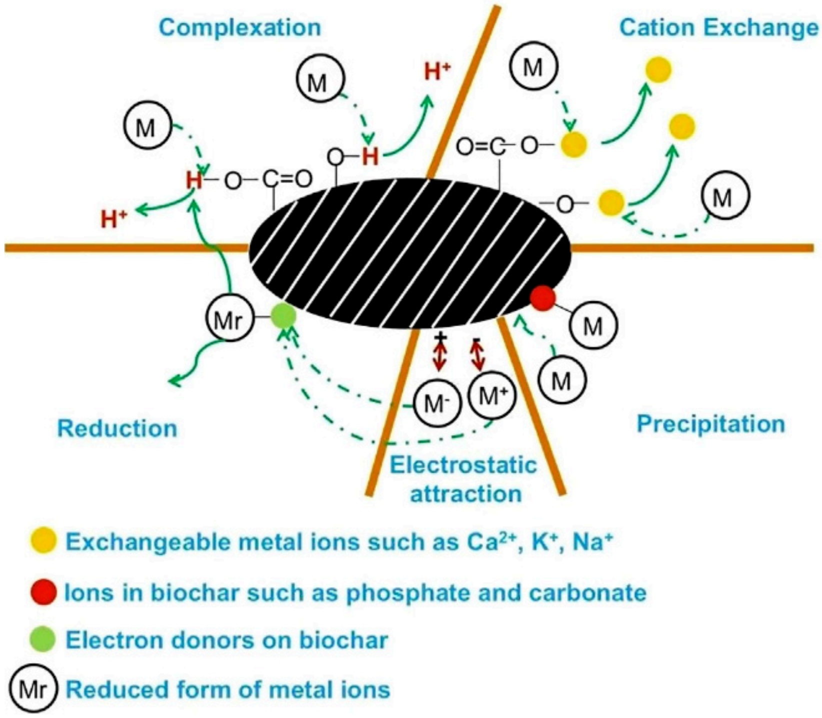

Figure 2. Mechanism of adsorption of heavy metals by biochar [45] (Reproduced with permission from Li et al., Chemosphere, published by Elsevier, 2017).

3. Factors Affecting the Remediation of Cd Pollution in Soil by Using Biochar

3.1. Physicochemical Properties of Biochar

The raw feedstocks for biochar production vary greatly, and the element contents and properties of biochars produced from different biomass also differ. Biochars derived from different sources of biomass materials are diverse in terms of their Cd remediation capacities [46]. Xu et al. [47] compared the immobilization effects of biochar derived from corn straw (CSB), kitchen waste (KWB), and peanut hulls (PHB) on Cd and Pb contaminated soils by batch experiments. Their results showed that the carbon content of PHB was the highest, which could be explained by the high content of lignin and cellulose in peanut hulls. KWB contains numerous inorganic elements, such as Na, K, Ca, and Mg. The SSAs are in the order of PHB > CSB > KWB, and the intensities of the hydroxyl group-related peaks of KWB and PHB were higher than those of CSB. Their final comprehensive analysis revealed that the immobilization of Cd and Pb performance of the three biochars was achieved in the order of KWB > CSB > PHB. Xu et al. [48] used the same treatment method to process biochar from different sources. Their results showed that the reduction of cadmium availability in soil was closely related to the type of biochar.

Pyrolysis temperatures for producing biochar also influence the remediation effects of Cd-contamination in soil [49]. Cai et al. [3] reported the effects of pyrolysis temperatures (350, 450, 550, and 650 °C) from *S. alterniflora*-derived biochar (SDB) on the bioavailable Cd content in soil. The SDB prepared at the low pyrolysis temperatures (350 °C and 450 °C) promoted the polarity and O-SFGs amount of biochar, which is conducive to the passivation of Cd in the soil. The SDB prepared at the high pyrolysis temperatures (550 °C and 650 °C) obtained larger SSAs and porosity, yet the effective Cd content increased in the soil samples. Chen et al. [50] used wheat straw-derived biochar, which is pyrolyzed at 350 °C and 500 °C, to research the effect of cadmium migration through water-saturated soil-packed columns. The biochar pyrolyzed at high temperatures presented the best effect on fixing Cd(II) in soil, with high ionic strength. However, when biochar under high-temperature pyrolysis was used for the in-situ remediation of Cd(II)-contaminated soil with low ionic strength, it lead to the potential risk of "colloid-facilitated contaminant transport". Azadi and Raiesi [21] reported the effect of pyrolysis of sugarcane bagasse biochar (SCB) at 400 °C and 600 °C on

Cd-contaminated soil and Cd-Pb co-contaminated soil. Their results showed a significant decrease in the effectiveness of SBC pyrolyzed at 600 °C on cadmium compared with SBC pyrolyzed at 400 °C. According to the subsequent analysis of soil microbial and enzyme activity, low-temperature SCB was better for soil microbial and biochemical function.

3.2. Soil Properties

3.2.1. pH

Soil pH is one of the critical factors impacting the dissolution and transformation of Cd in soil [51]. In general, Cd migrates more readily at relatively low soil pH values [52]. Therefore, understanding the effect of biochar treatment on the pH value of soil is extremely important. Researchers found biochar generally increased the soil pH value. The ability of functional groups (e.g., –OH, –COOH, –CH, –C=O, and C=C) on the biochar surface to bind H^+ in soil may explain the increase in the soil pH value [29]. In addition, the increase in the soil pH value with biochar application can be explained by the high ash content of biochar and its liming effect [29]. Gong et al. [26] studied a non-magnetic silicate-bonded biochar (SBC) and found that, after the application of the biochar, the pH of the soil increased by 0.67–0.85, owing to the production of $Ca(OH)_2$ after silicate hydration. Some researchers used citric acid to adjust the soil pH value. Islam et al. [53] discovered that biochar can convert reducible and acid-soluble Cd into more stable oxidizable and residual forms when a small amount of citric acid is applied. However, high levels of citric acid can significantly increase the mobility of Cd.

3.2.2. Cation Exchange Capacity

Soil cation exchange capacity (CEC) refers to the capacity of adsorbing and exchanging cations by soil colloids [54]. CEC is not only an important representation of soil fertility retention and buffer capacity, but also reflects the negative charge of a soil colloid. When CEC is enhanced, the net negative charge on the soil surface increases and the heavy metal ions adsorbed by electrostatic interaction also increase. Thus, ions can more easily exchange with heavy metal cations to perform an ion exchange adsorption. Researchers have determined that biochar mineralization can increase soil CEC by releasing humic acid [55]. Other researchers have shown that biochar modified by zero-valent iron significantly improves soil CEC [56].

3.2.3. Organic Matter

Organic matter is vital to the process of Cd adsorption and desorption in soil. It contains a large number of functional groups that can be complexed and chelated with cadmium ions, such as hydroxyl, carbonyl, carboxyl, and amino groups. Increasing the organic matter content in soil is conducive to Cd adsorption, and it can improve soil structure and regulate soil nutrients. Many researchers have proved that applying biochar increases soil organic matter content [13,57]. Soil organic matter can also be adsorbed onto the surface and pores of the biochar to promote the formation of SFGs in biochar [58], further increasing the organic matter content in the soil if treated with biochar [59]. Moreover, the increase of soil organic matter after using biochar can be explained by the flow of dissolved organic matter (DOM) from the biochar to the soil [60].

4. Recent Advances in Remediation of Cd Contamination in Soil with Biochar

4.1. Raw Biochars without Modification

The rich sources of biochar raw feedstocks and the low production cost, remarkable effects, and good economic benefits of biochars have attracted many researchers to investigate its application in polluted soil. The recent works on the removal of Cd from soil by using raw biochar are summarized in Table 2. Given the differences in the environmental conditions and soil types in various regions, knowing how to find highly matching types of biochars according to soil properties and local environmental conditions is the key point of current research.

Table 2. Remediation effects of raw biochar on Cd pollution in soil.

Materials	Pyrolysis Temperature (°C)	Soil Type	Cd Content in Soil (mg/kg)	Material pH	Soil pH		Application (w:w)	Method	Remediation Effect	Ref.
					Before Treatment	After Treatment				
Spartina alterniflora-derived biochar	450	Nutrition soil (kaolin)	3	8.25	7.30–7.90	6.98–7.39	0%, 2.5%, 5%, 10%	Pot trials	The toxic Cd forms reduced by 8.43%, 10.48%, 13.12%.	[1]
Biochar from rice husk (RHB)	400–450	Fluvial	5.125	8.7–8.9	6.6–6.8	7.23–7.98	2.5%, 5%	Pot trials	The Cd content in grains was controlled from 82.47% to 83.94%.	[2]
Vinegar residue biochar (VBC)	700	-	0.5, 1, 2.5	9.33	8.57	8.64–8.92	1%, 2%, 5%, 10%	Soil incubation experiment	The 10% VBC treatment was more effective in highly Cd-contaminated soil.	[61]
Biochar	-	Research farm	10	-	7.31	8.23	0%, 1%, 2%, 4%	Pot trials	Cd was significantly immobilized with 4% of biochar application (reduced by 58%).	[62]
Cocoa pod derived biochar	300	Uncultivated fallow agricultural land	10	10.3 ± 1.12	7.8	-	1%, 3%	Pot trials	The readily extractible Cd decreased by 24.8% and 47.1%.	[8]
Biochar	600	A mining site (Sn, Zn, and Pb mine)	1.29–46.58	9.66	5.36–6.76	5.7–8.01	3%	Soil incubation and pot trials	The available Cd contents were reduced by 10.5% to 64.8%.	[54]
5% acidic wood shaving biochar (WS) Neutral chicken litter biochar (CL)	WS: 650 CL: 550	Vertisol Entisol Inceptisol Andisol	43.3 48.8 46.5 47.7	WS: 3.25 CL: 7.00	6.31 6.14 8.47 7.87	6.4–7.5 8.0–8.75	0%, 5%	Pot trials	CL biochar was better in reducing bioavailable Cd.	[17]
Spartina alterniflora-derived biochar	350, 450, 550, 650	Saline-alkaline soil	2.73 ± 0.46	7.02–9.97	8.34 ± 0.10	8.54–9.40	1%, 5%, 10%	Pot trials	Available Cd content decreased 26.9%.	[3]
Biochar	400	Saline soils Sodic soils Saline-sodic soils Normal soils	50	8.4	7.21–7.8 8.5–8.87 8.05–8.67 7.88–7.90	-	0%, 2%, 4%	Pot trials	Cd availability in saline and sodic soils was decreased.	[63]
Bamboo biochar (BB) Rice straw biochar (RSB)	600 600	An experimental field	50	9.8 10.2	5.46 ± 0.04	5.46–5.87 5.59–5.98	0.5%, 1%, 2.5%, 5%	Pot trials	The Cd content of the crop were reduced by 12.0–48.3% (BB) and 17.0–35.4% (RSB).	[64]
Biochar (reed) Bamboo willow biochar (BWB)	800 800	Bamboo willow Sandy loam Bamboo willow Sandy loam	0.83 1.09 0.83 1.09	9.07 9.62	4.75 6.87 4.75 6.87	5.30–5.96 6.87–7.24 5.43–6.37 7.28–7.52	1%, 3% 1%, 3%	Incubation experiment	BWB showed slightly better reduction effect on bioavailable Cd.	[65]

Table 2. *Cont.*

Materials	Pyrolysis Temperature (°C)	Soil Type	Cd Content in Soil (mg/kg)	Material pH	Soil pH		Application (w:w)	Method	Remediation Effect	Ref.
					Before Treatment	After Treatment				
Cinnamomum biochar (CIBC) Garden waste biochar (GABC) Mulberry biochar (MUBC)	450 450 450	Udept Ustalf Udult	1.97 ± 0.01 14.02 ± 1.35 4.2 ± 0.41	CIBC: 4.25 GABC: 9.45 MUBC: 9.28	7.26 ± 0.06 7.55 ± 1.10 4.9 ± 0.35	7.44–7.52 7.45–7.54 4.23–6.25	3%	Pot trials	GABC and MUBC showed great potential in diminishing the mobility of toxic metals in soil.	[7]
Chestnut fruit shell biochar (SBC) Shell covered with thorns biochar (TBC)	600 600	Silty loam	30	9.52 9.71	6.5	- -	0.1%, 0.5%, 1.5%	Pot trials	1.5% TBC was better for remediating Cd- contamination.	[66]
Rice straw derived biochar Rice hull derived biochar Maize stover derived biochar	500 500 500	Red soil (Ultisol)	41	10.1 9.2 9.6	6.21	7 6.6 6.7	0%, 1.5%, 3%	Pot trials	The bioavailable Cd decreased (via $CaCl_2$ extraction) by 58.6, 39.7 and 46.49%, respectively at 3% application rate.	[14]

Qi et al. [17] investigated Cd solubility and bioavailability in various soils (Vertisol, Entisol, Inceptisol, and Andisol) treated with acidic wood biochar (AWB) and neutral chicken litter biochar (NCLB) through pot experiments. It was indicated that the NCLB reduced the bioavailable Cd (determined via 0.01 M $CaCl_2$ extraction) in the lower sorption capacity soils of Entisol and Vertisol by 52.3% and 53.7%, respectively, on day 0 (not cultured). Furthermore, Cd bioavailability in Entisol, Vertisol, and Inceptisol (higher sorption capacity) soils decreased by 82.0%, 78.7%, and 32.2%, respectively, on day 140. By contrast, AWB did not show any effect on soil bioavailability. Studies also showed that neutral biochar can effectively reduce cadmium solubility and bioavailability under both neutral and acidic conditions, even without lime action. Houssou et al. [7] conducted similar experiments to investigate the effect of three biochars: (*Cinnamomum* biochar (CIBC), garden waste biochar (GABC), and mulberry biochar (MUBC)), applied at the rate of 3% on three different soils (Udept, Ustalf, and Udult). They also explored Cd and Pb's bioavailability in relation to Chinese cabbage (*Brassica chinensis* L.) uptake. Their findings indicated that the reduction of the potential of toxic metals to be assimilated by plants in biochar-treated soil is closely related to the properties of biochar, such as nutrient concentration, active SFGs, and pH value. Soil pH and the available phosphorous (P) concentration in biochar, as the main factors controlling toxic metal phyto-availability and phyto-uptake, play an important role in metal immobilization by forming metal phosphates or phosphide precipitates. Their results further showed that GABC and MUBC decreased the available concentration of toxic metals (Cd and Pb) to the plants in alkaline and acidic soils and reduced the plants' uptake of toxic metals. Soil nutrients, such as N and P, increased. However, CIBC did not have a significant impact on the phyto-availability of Cd and Pb in both alkaline and acidic soils. This difference may be explained by the higher nutrient component, pH, and ash content of GABC and MUBC, compared with those of CIBC. At the same time, some researchers have also explored the ability of biochar to remediate cadmium pollution under extreme conditions, e.g., with respect to high salinity. Zahedifar [63] conducted incubation experiments to evaluate the effect of sugarcane bagasse derived biochar applied at 0 wt%, 2 wt%, and 4 wt%, in saline, sodic, saline sodic, and normal soils, respectively, on the state of Cd in soil. The author discovered that the prepared biochar had no significant influence on the exchangeable Cd in both normal and sodic soils. However, the availability of Cd in saline and saline-sodic soils could be significantly affected, shifting the Cd fraction from EX, CB, and OX to OM, thus mitigating the pollution of these soils.

4.2. Modified Biochars

Different techniques have been used for modifying biochar to make it have higher SSA and porosity, more O-SFGs, and better CEC, thereby enhancing the immobilization capacity of biochar for Cd [57]. The methods of biochar modification can be divided into chemical, physical, and biological modifications [67].

4.2.1. Chemical Modification

Acid-Base Modification

Chemical modification is the most common method for biochar modification, and it generally includes acid-base, oxidant modification, metal salt modification, and organic solvent modification. The latest research advances on the immobilization of Cd in soil using chemical-modified biochar are listed in Table 3.

Table 3. Remediation of Cd-contaminated soils by chemically modified biochar.

Materials	Pyrolysis Temperature (°C)	Soil Type	Cd Content in Soil (mg/kg)	Material pH	Soil pH		Application (w:w)	Method	Remediation Effect	Ref.
					Before Treatment	After Treatment				
Peanut shell biochar (HBC) Mg-modified peanut shell biochar (MHBC)	300, 600	Brown soil	10	- -	6.17	6.17–8.28 7.09–8.67	0%, 1%, 2% 0%, 1%, 2%	Pot trials	MHBC was better than HBC in reducing bioavailable Cd^{2+}.	[68]
KOH-modified rice straw-derived biochar	500	Red soil (Ultisol)	42	-	6.12	7.20	0, 15, 30 (g kg^{-1})	Incubation experiment	The application at the 30 g kg^{-1} was better in Cd immobilization.	[12]
Sulfur-modified biochar (S-BC) Sulfur and iron modified biochar (S-Fe-BC)	550 550	Farmland in the rice cultivation area	5	10.82	6.43	6.610 ± 0.020 6.580 ± 0.286	0%, 1%	Pot trials	S-BC and S-Fe BC significantly reduced bioavailable Cd in pore waters and decreased the accumulated Cd in plant tissues.	[10]
Sulfur-modified biochar (S-BC) Sulfur iron modified biochar (SF-BC)	550 550	A typical metallurgical plant farmland	33.45	10.82	7.43	7.55 7.58	0%, 1%	Pot trials	pH and soil organic matter was increased, and DTPA-extractable Cd was decreased.	[13]
Reed biochar (BC) Iron-modified biochar (Fe-BC)	500 500	Typic Haplocalcids	15, 30	10.18 ± 0.07 10.34 ± 0.06	7.7 ± 0.07	8.0–8.03 7.86–7.93	2%	Incubation experiment	Fe-BC was better than BC in immobilizing Cd and improving soil microbial attribution.	[69]
Biochar derived from *Platanus orientalis* branches (RawBC) Iron (Fe)-modified biochar (FeBC)	650 650	Silty clay loam soil	0.5	9.25 ± 0.14 4.41 ± 0.03	5.8	7.13 5.67	3%	Pot trials	Raw BC might be more suitable for remediation of Cd under a continuously flooded system.	[9]
Iron-zinc oxide composite modified corn straw	500	Acidic paddy Alkaline wheat field	1.28 ± 0.10 2.49 ± 0.09	10.86	5.69 ± 0.07 7.87 ± 0.02	5.75–6.51 7.97–8.19	0.5%, 1%, 3%	Incubation experiment	pH and CEC of the soil was increased, and the bioavailable Cd was also reduced.	[31]
Fe-modified biochar (FBC)	600	Sewage-irrigated area	0.49	7.83	8.52	8.56–8.62	0%, 0.1%, 0.2%, 0.5%	Field experiment	0.5% FBC showed optimal effect.	[42]
Thiol-modified rice straw biochar (RS)	500	Contaminated vegetable field	9.18	2.36	7.42	7.52–7.80	0%, 1%, 3%	Soil incubation experiment	RS showed better performance for Cd immobilization.	[70]

Acid-base modification is the chemical modification of biochar by using acids or bases [71–73]. This method alters the porous structure and increases the number of SFGs in biochar, creating new binding sites for metal immobilization. Bashir et al. [12] reported a rice straw-derived biochar modified with KOH, in which the biochar was first prepared at 500 °C and was then mixed at the ratio of 2 g biochar to 500 mL KOH (2 mol/L), followed wby filtration and oven-drying. According to their Fourier transform infrared spectrometer (FTIR) and scanning electron microscope (SEM) analyses, this modified biochar presented a higher CEC, surface area, and microporous structure, and new SFGs appeared on the surface of the modified biochar, which was identified as –COOH. The KOH-modified rice straw biochar can significantly reduce the acid-soluble and bioaccessible Cd in soil, converting part of the Cd from soluble to the most stable residual form. Meanwhile, the significant increase in soil nutrients may be explained by the dissolution of organic carbon and mineral elements in biochar. Peiris et al. [74] modified tea waste biochar with nitric acid, sulfuric acid, and hydrochloric acids (NMBC, SMBC, and HMBC, respectively), and this significantly increased the surface area from 8.11 m^2/g, before modification, to 216.33, 59.68, and 110.76 m^2/g, respectively (Figure 3a). In the NMBC and SMBC, a strong peak belonging to carbonyl stretching appeared near 1690–1720 cm^{-1} in the FTIR, which is related to the introduction of carboxylic acid. At the wavenumber of approximately 1200–1250 cm^{-1}, a peak representing the C–O stretching bond appeared, which may be attributed to the formation of a single bond of the C–O group in lactone and phenol in HMBC (Figure 3b). An analysis of the surface morphologies and functionalities of the three kinds of acid-modified biochars showed a key reaction mechanism. During nitric acid modification, the new O-SFGs could be introduced through the oxidative ring opening of aromatic rings (electrophilic addition reaction), along with the further oxidation of existing O-SFGs. Among the three acid treatment methods, the observed decrement in carboxylic moieties upon sulfuric acid modification can be attributed to decarboxylation reactions (Figure 3c). The introduction of binding sites, pore broadening, and the opening of unavailable pores were considered to be the main reasons for the increase in CEC in the acid-modified biochar (Figure 3d).

Rehman et al. [75] prepared a modified rice husk biochar treated with three acids (HCl, HNO_3, and H_3PO_4) and found that the treated biochar significantly decreased the extractable Cd in contaminated soil. The soil-available concentrations were reduced by 86.6, 76.6, and 60.5%, compared with the control upon the application of biochar treated with phosphoric, nitric, and hydrochloric acids, respectively.

Oxidant Modification

Oxidant modification is mainly conducted by increasing the content of O-SFGs, especially the carboxyl groups in biochar, thereby increasing their attraction capacity to cadmium. The commonly used oxidants are hydrogen peroxide [76] and potassium permanganate [77,78]. Liu et al. [79] demonstrated the use of the potassium permanganate solution using different concentrations (0.05, 0.1, and 0.2 mol/L) to immerse rice straw biochar for their percolation leaching columns experiments. According to FTIR spectral analysis, as the $KMnO_4$ concentration increased, more cellulose hydroxyl groups were generated, and more C=O was simultaneously activated. With the increase in $KMnO_4$ concentration, the yield, pH, and ash content of the derived biochar also increased, but its SSA decreased. The results indicated that potassium permanganate-modified biochar can effectively decelerate the release of Cd, and the base-treated rice biochar may serve as a promising soil remediation agent for the immobilization of Cd.

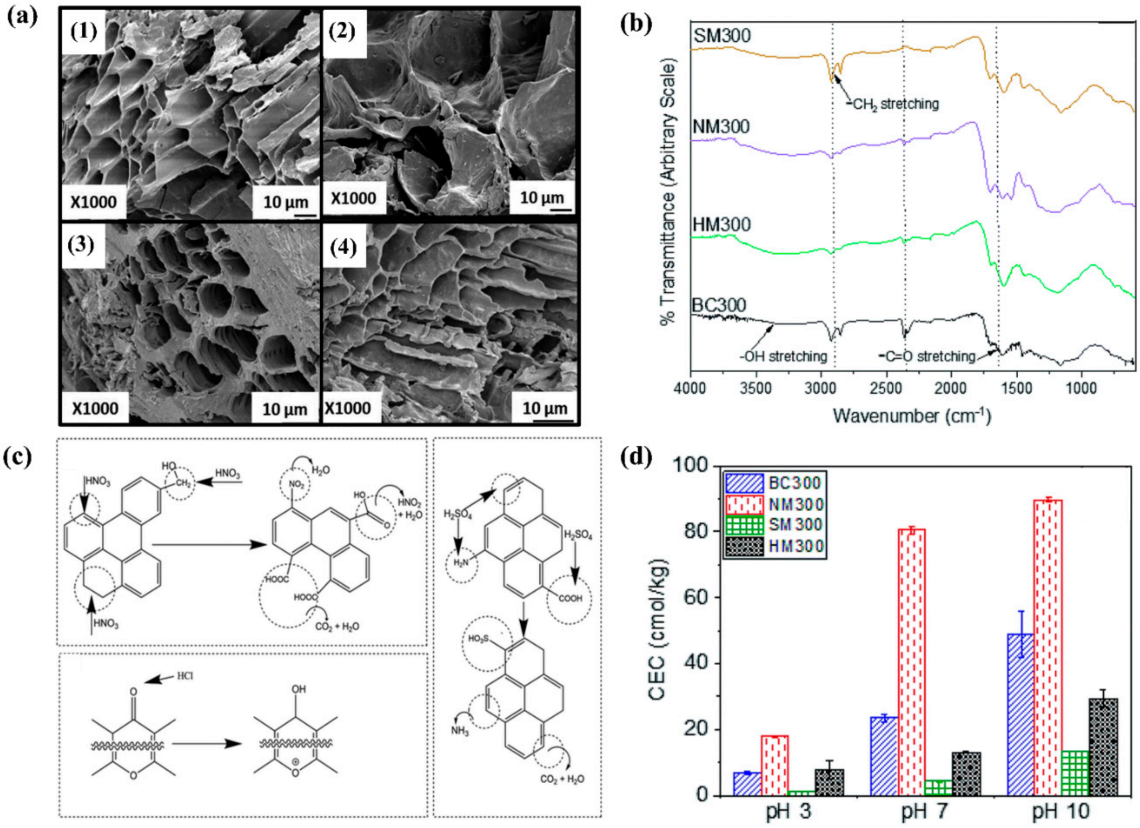

Figure 3. (**a**) SEM images of raw BCs, (**b**) FTIR spectra of modified BCs pyrolyzed under 300 °C, (**c**) proposed key reaction mechanisms involved in nitric, sulfuric, and hydrochloric modification, (**d**) CEC variation under different pH values modified 300BCs [74] (Reproduced with permission from Peiris et al., RSC Advances, published by the Royal Society of Chemistry, 2019).

Metal Salt Modification

Modification using metal salts can also improve the ability of biochar to remediate cadmium by changing the characteristics of adsorption, catalysis, and magnetism in the biochar. The commonly used methods can be described as follows. (1) Biochar is first obtained via pyrolysis, and then it is soaked with a metal salt or metal oxide. (2) The metal salt or metal oxide is mixed with biomass first, and then the biochar is obtained via biomass pyrolysis. Currently, the metals commonly used for biochar modification are Fe [80], Mg [68,81], and Mn [82,83]. Sun et al. [42] demonstrated that Fe-modified biochar could be obtained by adding crushed rice husk to 1 M ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), with a mass ratio of 1:25 for Fe^{3+} to biomass, and then pyrolyzed at 600 °C. Their field experiments showed that the DTPA–Cd concentration in soil, with the Fe-modified biochar treatment, decreased by 37.74–41.65% compared with that in the control group. The BCR sequential extraction showed that the acid-soluble and reducible state of Cd could be transformed into oxidizable and residual states. The analysis of soil alpha bacteria diversity indicated that the Fe-modified biochar could also promote both the richness and diversity of bacterial communities. In recent years the combination of nano-zero-valent iron (nZVI) and biochar has attracted much attention. nZVI has the characteristics of a large SSA and high reactivity, which can effectively remediate various pollutants in water and soil. Moreover, biochar can effectively overcome the aggregation problem of nZVI by distributing nZVI particles on the biochar surface and pores, enlarging the contact area of nZVI and forming a good synergistic effect. Table 4 summarizes the remediation effects of biochar-supported nZVI in Cd-contaminated soil.

Table 4. Remediation of Cd-contaminated soils by biochar-supported nZVI.

Materials	Heavy Metal Pollution Types	Mix Proportion	Material Application	Method	Remediation Effect	Ref.
A porous biochar-supported nanoscale zero-valent iron (BC-nZVI)	Cd, Pb	The biochar (2.0 g) was mixed with $FeSO_4 \cdot 7H_2O$ (0.1 M)	0.5, 1.0, 2.0, 3.0 g/L 6 g of soil and 30 mL of BC-nZVI	Batch remediation experiments	Cd and Pb could be effectively immobilized by BC-nZVI. Heavy metals immobilization, soil pH, and organic matter was induced and the metal bioavailability was reduced.	[84]
Biochar-supported nanoscale zero-valent iron (nZVI-BC)	Cd, As	12.00 g biochar and 9.68 g $FeCl_3 \cdot 6H_2O$	0%, 0.25%, 0.50%, 1.00% (*w*/*w*)	Pot trials	Lower nZVI-BC additions reduced metal bioaccumulation in plant while the high nZVI-BC addition (1.00%) enhanced Cd's transportation into rice grains.	[85]
Biochar-supported nanoscale zero-valent iron (nZVI-BC)	Cd, As	1.50 g of biochar and 2.42 g of $FeCl_3 \cdot 6H_2O$	0.05%, 0.10%, 0.25%, 0.50%, 0.75%, 1.00% (*w*/*w*)	Pot trials	The contents of metal availability decreased after treating with nZVI-BC compared with the control group, and the soil nutrient contents and soil enzyme activity were improved significantly.	[86]

Organic Solvent Modification

Some organic compounds can also be used to modify biochar. The commonly used organic compound modifiers are chitosan [87], thiourea [88–90], and cyclodextrin [91]. These modifier compounds generally can promote the binding ability of SFGs of biochar with heavy metal ions, improving the adsorption of biochar to heavy metals. Fan et al. [70] used an esterification reaction with β-mercaptoethanol to prepare thiol-modified rice straw biochar (RSB) and remediate Cd and Pb contaminated soils. According to the elemental, porous, field emission SEM, FTIR, and X-ray photoelectron spectroscopy (XPS) analysis, the thiol modification increased the adsorption capacity of Cd^{2+} threefold, and RSB decreased the bioavailable cadmium by 34.8% to 39.2% in soil incubation experiment (28 days).

4.2.2. Physical Modification

Ultraviolet Radiation Modification

Physical modification involves changing the pore structure, SSA, and O-SFGs of biochar via steam modification [92,93], ultraviolet radiation [94], ball milling [95,96], and gas purging [97] to improve the performance of biochar. Among them, UV radiation is the most widely used method, and it entails the use of a fixed-wavelength UV light to irradiate biochar, after which its surface functional group content and SSA are significantly increased. The UV radiation method offers the advantages of introducing O-SFGs, low cost, and easy control. Zhang et al. [94] selected two plant residues, namely, *Brassica napus* L. and *Lolium perenne* L., pyrolyzed in N_2 atmosphere at 600 °C to obtain biochar (BNBC and LPBC, respectively). Then, the biochars were modified by ultraviolet irradiation under an ultraviolet lamp with a main wavelength of 365 nm. The BET surface area of the BNBC and LPBC increased from 12.22 to 42.16 $m^2\ g^{-1}$ and from 11.07 to 37.91 $m^2\ g^{-1}$, respectively. Moreover, according to the in-situ diffuse reflectance infrared Fourier transform spectroscopy analysis, the content of carboxyl functional groups increased, and the polarity of the biochar surface was enhanced. At the same time, the modification increased the average pore size of the biochar, which may be related to the dredging of pores by the ultraviolet light. The results of the pot experiment showed that the UV-modified biochars had a better effect on the fixation of Cd in soil and the reduction of Cd absorption by plants compared with the unmodified biochars.

Gas Purging Modification

Gas purging modification can increase the SSA and improve the structure of biochar, thus enhancing the adsorption capacity of biochar. In particular, CO_2 purging modifications are often performed to increase the SSA of carbon, promote the formation of pores, and improve the structure of the pores. Meanwhile, NH_3 modification can introduce N-containing groups into biochar. Igalavithana et al. [97] used red pepper stacks as the raw material and purged them with N_2 or CO_2 gas at a flow rate of 500 mL min^{-1} at 650 °C. Then, they compared the potential of the two types of biochar to fixate As, Pb, Cd, and Zn in soil. The CO_2-modified biochar presented higher surface area and aromaticity and significantly increased the number of exchangeable cations in soils.

4.2.3. Biological Modification

Biological Treatment before Pyrolysis

Biologically modified biochar (BMB) can be obtained through two routes. The first route involves the pretreatment of biomass feedstock with biological techniques (e.g., anaerobic digestion) before pyrolysis. The second route entails the coupling of prepared biochar and microorganisms [98,99]. Recent innovations in the use of BMB for Cd remediation in soil are summarized in Table 5.

Table 5. Remediation of Cd in soil by using biochar microbial composites.

Materials	Strains of Type	Mix Proportion	Application	Remediation Effect	Ref.
Multiple biochemical material	A novel plant growth promoting bacteria (PGPR) strain SNB6	SNB6 suspension and BC (20:1, v:w)	-	Cd accumulation of hyperaccumulators could be effectively enhanced and the soil biochemical qualities was improved.	[100]
Biochemical composites material	Plant growth promotion bacteria (PGPB) strain TZ5	bacteria suspension and BC (20:1, v:w)	100 mL of BCM suspension	It could effectively increase biomass and reduce Cd accumulation.	[101]
Biochar-supported microbial cell composites (BMCs) produced from agricultural waste	*Delftia* sp.	Bacteria suspension 1×10^8 CFU/mL (~0.4 g/L, dry weight): biochar powder = 1:4	0.5%	BMCs could reduce Cd accumulation in rice grains and increase soil residual Cd.	[102]
Biochar-immobilized *Arthrobacter* sp. (CRB) Biochar-immobilized *Micrococcus* sp. (CRB)	*Arthrobacter* sp. TM6 *Micrococcus* sp. MU1	Cell suspensions (OD_{600} of ~0.1): 2% (*w*/*v*) biochar	0.20%	CRB could achieve a high efficiency of cadmium phytoextraction, in particular, in low cadmium-contaminated soil.	[103]
The combination of microorganisms and biochar (maize straw, cow manure, and poultry manure), respectively	*Trichoderma harzianum* L. (M1), *Bacillus subtilis* L. (M2), combined microorganism inoculation (M3)	-	5%	Cd bioavailability was reduced significantly, and soil properties was enhanced.	[104]
Biochar and Ca modified biochar physical adsorption of microbes (BCM) Sodium alginate encapsulated biochar and microbes (BCB)	Mixed bacteria (*Bacillus amyloliquefaciens, Bacillus cereus, Bacillus velezensis, and Bacillus* sp.)	Biochar: Ca modified biochar: mixed bacteria suspension at a dry weight = 20:20:1 Biochar: mixed bacteria suspension at a dry weight = 40:1	1%, 2%, 3%	BCM and BCB showed higher immobilization effects than raw biochar, and BCM showed higher stability compared with BCB.	[40]

As for the first route, anaerobic digestion is often preferred and is a promising method for managing waste biomass [105]. Tao et al. [106] successfully prepared a BMB derived from the digestion residue of corn straw silage through transabdominal transformation (TCB). Compared with the pristine biochar derived from maize straw, TCB significantly increased the biochar's SSA, O-SFGs, and mineral components ($CaCO_3$, KCl, iron oxide, and magnesium oxide), all of which are very important in Cd adsorption. Most recently, Tao et al. [107] further performed an anaerobic fermentation on maize straw using pretreated 30-day-old silage. Rumen microorganisms were selected as the starter, and then different incubation times (12, 16, and 24 h) were set to simulate the residue time of corn stalk silage from the rumen. Finally, pyrolysis of the pretreated straw was performed under an N_2 atmosphere. The maximum cadmium adsorption capacity increased significantly from 25.38 to 47.39 mg g^{-1} as the fermentation time increased, which was much higher than that of the pristine biochar (22.27 mg g^{-1}). This result also showed that anaerobic fermentation could accelerate the adsorption capacity of Cd by increasing the surface area and the number of O-SFGs. Liu et al. [108] presented an innovative approach to preparing efficient biochar using fallen leaves as a biomass feedstock, which underwent natural biological decay for 60 days. Then, natural bioaugmentation biochar (NBC) was obtained after the pretreated leaves were pyrolyzed. After modification, the SSA increased from 3.974–20.745 m^2/g to 5.326–171.095 m^2/g (Figure 4a). In the adsorption experiments (isotherms, kinetics, thermodynamics, and desorption), characterization analysis (SEM-EDX, X-ray diffraction (XRD), FTIR, thermogravimetry and differential thermogravimetry (TG-DTG), and BET porosity) and characterization observation also found that NBC possessed more O-SFGs than the pristine biochar, which enhanced the active adsorption sites on Ca(II), and the internal pores formed microporous adsorption and mesoporous diffusion structures (Figure 4b), which were favorable for Cd immobilization. Ca clearly decreased, whereas Cd increased after adsorption, which was probably due to ion exchange (Figure 4a). Moreover, studies have also shown that NBC has a good application potential in Cd immobilization (Figure 4c,d). The biochar prepared from decaying leaves has great potential in heavy metal remediation, indicating a novel, efficient, and direct strategy for the green modification of biochar.

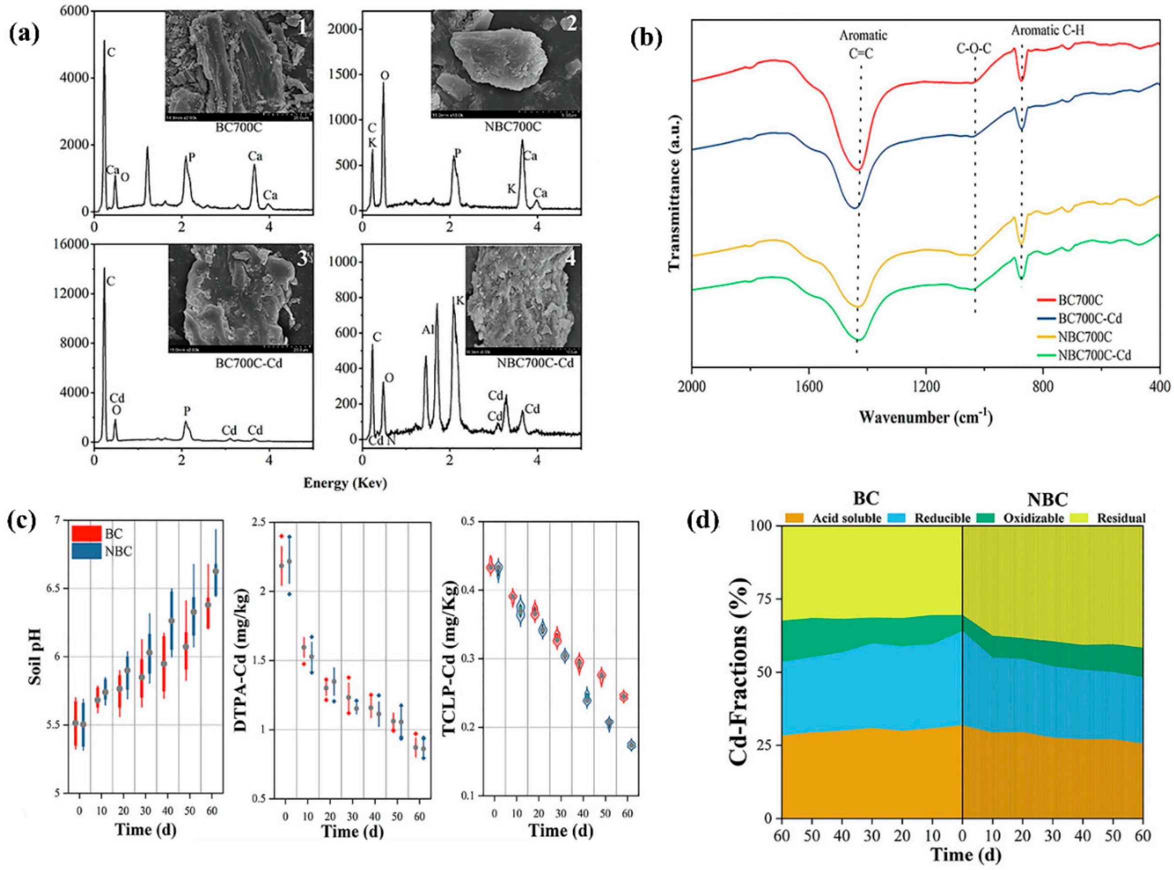

Figure 4. (**a**) Characterization of BC700 and NBC700 before and after Cd(II) adsorption, (**b**) FTIR spectra, (**c**) Cd(II) remediation application potential test. Soil pH, DTPA-Cd concentration, and TCLP-Cd solubility over time, (**d**) soil Cd(II) morphological classification over time [108] (Reproduced with permission from Liu et al., Separation and Purification Technology, published by Elsevier, 2022).

Coupling Prepared Biochar with Microorganisms

The second route involves coupling prepared biochar with microorganisms and is also regarded as an emerging technology for the effective remediation of Cd contamination in soil. This technique involves loading free microbial cells onto biochar and utilizing the synergistic effects of biochar and certain functional microorganisms to co-immobilize Cd. Functional microorganisms themselves can diminish the bioavailability of heavy metals via biosorption and biomineralization. Microorganisms can be supported on biochar because of its large SSA, large pore size, and good adsorption performance. At present, this technology is mainly divided into two categories. The first category entails the use of newly isolated single dominant functional species and combining them with biochar [109]. Wu et al. [100] successfully isolated a novel plant growth-promoting bacteria (PGPR) strain, SNB6. The strain was immobilized on biochar to obtain BMB, which can significantly decrease the Cd accumulation in plants and effectively raise the number of microorganisms and activity of soil enzymes. Liu et al. [102] also demonstrated the use of biochar-supported microbial cells (BMC) prepared using agricultural waste (cornstalks) with Cd-resistant Gram-negative bacterium *Delftia* sp. B9. Their pot experiment showed that the bacteria supported on biochar could more easily grow compared with the free cells, and the metabolites were more abundant, suggesting enhanced remediation efficiency. Chuaphasuk and Prapagdee [103] obtained similar results by combining two strains of cadmium-resistant bacteria with biochar. The second category is the immobilization of the mixed bacteria onto biochar to obtain BMB [110],which is generally divided into physical adsorption and sodium alginate embed method. Qi et al. [111] compared the synthesis of mixed bacteria-loaded biochar materials with different admixture proportions among three strains (*Bacillus subtilis*, *Bacillus cereus*, and *Citrobacter* sp.) and found that BMB with a mixed bacteria ratio of 3:3:2 was most effective using the physical adsorption method, and the extractable DTPA-Cd content could be reduced by 56%. This performance was much better than that of untreated biochar and the BMB prepared by the sodium alginate-embedded method. Ji et al. [40] prepared a BMB by immobilizing a microbial community containing four functional bacteria (two phosphorus-solubilizing bacterium, arsenic oxidizing bacterium, and heavy metal-tolerant bacterium) onto biochar. The microbial community was screened from a lead–zinc smelter site. Their comparative results showed that the BMB had high Cd immobilization efficiency and could significantly improve the metabolic activities of microorganisms and soil enzymes. Most of the Cd in the EX state was converted into the harder-to-utilize RES state. They obtained similar conclusions to Qi et al. [111]. Furthermore, Haider et al. [104] proved that biochar, simultaneously inoculated with multiple microorganisms, is generally more effective than biochar inoculated with sole microorganism.

At present, studies on BMB are limited. Future research may focus on BMB, owing to the advantages of this technique, namely its low manufacturing cost, good environmental protection, and high efficiency. The interaction of soil-indigenous microbes with biochar may be a promising strategy for environmentally friendly and sustainable remediation of contaminated soil in the future.

4.3. Co-Application of Biochar and Other Remediation Materials or Technologies

Some researchers have also used biochar coupling with inorganic amendments, animal remediation, and other materials with similar capabilities, forming synergistic and mutually reinforcing effects to remediate Cd contamination in soil (Table 6). Noronha et al. [43] investigated the effect of simultaneously using coconut shell biochar (CSB) and earthworms (*Eudrilus euginea*) for the bioremediation of Cd contamination in soil and the growth of spinach (*Spinacia oleracea* L.). Fifteen infant epigenic earthworms (average weight is 190 mg) were selected, and 10% (w/w) of cow manure was added as the food source for the earthworms. The simultaneous application of CSB and earthworms improved the physical properties, enzyme activities, and fertility of the soil. The maximum removal rate of total Cd content was 94.38%. The highest germination percentage (92.13%) for *Spinacia oleracea* L. was obtained for the contaminated soil sample containing 1.25% CSB and earthworms, with a mean germination time of 4.59 days, which were both superior to the results of using solely CSB or earthworms. Some researchers also reported similar findings through the co-application of biochar with earthworms or compost to remediate cadmium-contaminated soil [112,113]. It is recognized that the effect of the composite materials or technologies on the remediation of cadmium contamination in soil is significantly higher than that of using solely biochar [114].

Table 6. Remediation of Cd pollution in soil by co-applying biochar and other remediation materials.

Materials	Mixing Proportion of Materials	Method	Remediation Effect	Ref.
Maize straw biochar and thiourea (TU) application in combination	Maize straw-derived BC: 0%, 2.5%, 5% TU dose rates: 0, 600, 1200 mg L^{-1}	Pot trials	BC: 5%, TU: 1200 mg/L was best, the Cd concentrations in shoot and root were reduced by 42 and 49%, respectively.	[115]
Combined application with biochar and P fertilizer	Biochar: 0, 20 g kg^{-1} P fertilizer: 0, 20, 40 mg P kg^{-1}	Pot trials	It Cd availability and plant Cd uptake in soil was inhibited significantly.	[116]
Beef cattle manure biochar + Compost mixture Poultry litter biochar + Compost mixture Lodgepole pine feedstocks biochar + Compost mixture	0%, 2.5% and 5% of each biochar and 0%, 2.5%, and 5% (w/w) compost mixture (wood chips + beef cattle manure)	Greenhouse experiment	5% beef cattle manure biochar + 5% compost showed better reductions in total Cd and Zn concentrations.	[114]

5. Challenges and Prospects in Using Biochar for the Remediation of Cd Contamination in Soil

The utilization of biochar has consistently been a research hotspot, owing to its low production cost and richness of feedstock resources. In recent years, many researchers have been engaged in the remediation of cadmium contamination in soil using biochar, which entails a low investment cost to reduce Cd bioavailability. However, given the complexity of the edatope, the existing biochar materials still have many defects and deficiencies, and their wide application still faces challenges. The following summarizes the current lack of research in the field of biochar development and application in remediating Cd remediation in soil and puts forward prospects for future exploration.

Challenges:

(1) The long-term potential release and secondary pollution of Cd. In essence, Cd in the soil is not fundamentally removed because biochar adopts the in-situ remediation and passivation. As the soil environment changes, Cd may be released again from the used biochar and absorbed by plants;

(2) Large-scale soil application. Some researchers have reported field experiments on the application of biochar in cadmium-contaminated soil, and the results have been very good [15,42]. Sun et al. [42] investigated the effect of Fe-modified biochar on weakly alkaline Cd-contaminated soils through field experiments. It was found that the DTPA-Cd concentration of Fe-modified biochar treatment was reduced by 37.74%~41.65% compared with the control ($p < 0.05$). Given the long period and numerous uncertain factors of experiments in large-scale real soils, the present investigations and applications of biochar materials have almost only been carried out based on incubation or pot experiments;

(3) Lacking in-depth exploration of the basic effect mechanism. A lot of research on modifying or composing biochars via the introduction of functional groups and other remediators has been reported. However, research on the effects of different biochars on plant growth and metabolism is not comprehensive, as is the gene-level study.

Prospects:

(1) At present, most of the biochar studies do not achieve the removal of Cd from soils; instead, Cd is transformed into a more stable form. Measures such as the use of recyclable biochar (e.g., magnetic biochar) and combing this with other removal technologies might improve the real removal of Cd. For instance, magnetic biochar immobilized with Cd can be separated in solution by magnetic force. Alternatively, the biochar-based remediation may be combined with hyperaccumulators;

(2) Systematic exploration of the application of biochars in real, large-scale soil environments. More field experiments should be carried out. Many factors should be considered in the large-scale application of biochar in soil. The actual soil composition is complex (i.e., DOM, inorganic matter, microorganisms, animals, plant roots, etc.), which may affect the

restoration of biochar. The current soil pollutants are also complex. Thus, there should be more exploration of the interaction and transformation between different pollutants;

(3) The impact of biochar at the micro-level in relation to cadmium pollution treatment may be further explored by deeply analyzing the community structure of microorganisms, soil microorganisms, plant growth and metabolism, and metagenomic changes.

6. Conclusions

Much advance has been achieved in the application of biochar in the remediation of Cd contamination in soil. Biochar remediation is considered an effective and promising technology for reducing or stabilizing soil pollution, which basically equates to a carbon sequestration process with promising possibilities based on biochar's highly controllable structure and surface properties, as well as it being readily combinable nature with other materials or technologies. However, there are still many aspects (e.g., the vital parameters such as safety, cost, and industrial conditions) that need to be explored and evaluated in depth to forward the large-scale application of biochar in remediating Cd contamination in soil.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr10081627/s1, Table S1: Common speciation analytic methods of heavy metals in soil.

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