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Review

A Comprehensive Literature Review on Cadmium (Cd) Status in the Soil Environment and Its Immobilization by Biochar-Based Materials

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Abstract: Cadmium, Cd(II) pollution of soils is a serious environmental and agricultural issue, posing a threat to crop production, environmental quality, food safety, and human health. Therefore, immobilization of Cd(II) in soils is crucial. Biochar-based materials are receiving significant attention as Cd(II) immobilizers, due to their multifunctional surface properties. The remediation/immobilization mechanisms involved are, mainly, surface complexation, chemical reduction, precipitation, ion exchange, π–π interactions, hydrogen bonding, and adsorption. These mechanisms are mostly dependent on biochar surface pore size, oxygen-containing functional groups, pyrolysis temperature used in biochar preparation, biochar feedstock, and soil characteristics. So far, various pristine and modified biochar substrates have been used to remediate heavy metal-contaminated soils. Therefore, in this review paper, we briefly summarize the chemical forms, release sources, and maximum permissible limits of Cd(II) in soil. We also summarize recent scientific findings on the performance of biochar substrates in Cd(II)-contaminated soils to minimize Cd(II) mobility, bioavailability, and potential accumulation in crops. Finally, we identify challenges associated with the use of biochar and suggest areas for future research. The review presents an overview of the knowledge of biochar as a promising amendment for the decontamination of Cd(II)-polluted soils.

Keywords: soil pollution; Cd(II); soil remediation; immobilization; adsorption; biochar-based materials

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1. Introduction

In recent decades, different types of pollutants in the soil may exert harmful effects on human health and the overall ecosystem [1–3]. Among these pollutants, potentially toxic elements (PTEs) have raised significant concern due to their toxicity, mobility, and non-biodegradable nature [4,5]. These PTEs include antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), selenium (Se), silver (Ag), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), and zinc (Zn) and are reported to pose threats to agricultural production, food security, food safety, and human health [6–10]. Among the PTEs, Cd (II) is considered a pollutant responsible for ecological and human health hazards [11].

Cd(II) is one of the most highly mobile and potentially harmful heavy metals in the soil. Even though it is not an essential element for plant growth, it is still taken up by crop roots and translocated to other plant parts [12–15]. Rice grains readily accumulate Cd(II) and are hence a considerable source of Cd(II) in the human diet compared to other crops [12,16,17]. Acute and chronic symptoms of Cd toxicity include adverse effects on the pulmonary, cardiovascular, and musculoskeletal systems as well as carcinogenicity and kidney damage [18].

Various conventional remediation technologies are adopted to remove Cd from contaminated soils. These technologies/mechanisms include immobilization, precipitation, ion exchange, use of organic amendments such as compost, electrokinetic, soil washing, use of various nanomaterials, advanced oxidation, adsorption, bioremediation, and combined applications of amendments and technologies [19–22]. However, there are some constraints associated with the use of conventional methods. Similarly, reverse osmosis and membranes, which have their main applications in the removal of excess cations and anions, are not very efficient in the removal of organic compounds and solvents, including phenols, pesticides, and benzene [23]. Other methods also have specific limitations by generating secondary pollution, which may have more deleterious effects on the overall environment than the original contamination. The conventional remediation technologies also require sophisticated instruments and have high operating costs. Hence, there is a need to shift from conventional to eco-safe and green nanoremediation technologies such as carbon-based nanomaterials. Adsorption has been identified as a highly efficient approach for Cd(II) removal from contaminated soils due to its unique characteristics, such as to low cost, in situ use, simple operation, absence of secondary pollutants, and high selectivity [24,25].

Biochar, a carbon-based solid adsorbent prepared by pyrolysis of various types of feedstocks in the absence of oxygen, has gained interest as an innovative, green, and sustainable tool in agriculture, environment preservation, and energy production, due to its specific physicochemical attributes. These include high specific surface area, high surface activity, porous structure, oxygen-containing functional groups, and high ion exchange capacity [26–31]. Research on biochar in agriculture is ongoing since the discovery of terra preta soil in the Amazon basin by James Orton in 1870 [32,33]. However, in recent decades, biochar has attracted particular interest for environmental pollution remediation and soil management, with benefits including improvement of soil quality and fertility, immobilization of metal ions, degradation of organic pollutants, carbon sequestration, and many others [34–37].

A number of studies have been published on feedstock-specific biochar, e.g., wheat straw, rice straw, corn stalk, bamboo hardwood, etc., and on how efficient they are in Cd(II) immobilization; however, a comprehensive review on the performance of pristine and modified biochar against Cd(II) soil pollution has not yet been compiled. Therefore, in the current review, we aimed to briefly summarize the literature findings on the use of pristine and modified biochar in the efficient restoration of soil contaminated with Cd(II), its chemical forms, release sources, and maximum permissible limits of Cd(II) in soil. Our final aim was to identify challenges connected with biochar use and suggest areas for future research.

2. Literature Search

The content of this review article is outlined in Figure 1. The published studies reviewed here were the ones that provided clear experimental results. Most papers delt with the removal of metal ions from water and soil systems using various kinds of adsorbents, such as clay minerals [38], carbon-based adsorbents [39], biochar-based materials [40], nanoscale zero-valent iron (nZVI) [41], and graphene oxides materials [42]. Regarding the remediation of Cd-contaminated soils using biochar and biochar-based materials, the published literature in that area is quite novel. To find the most recent and relevant studies, we searched the Web of Science core collection database, Scopus, and Google Scholar. As expected, this resulted in numerous hits in terms of research and review papers published since 2020. The details of the review papers are briefly summarized in Table 1. It is crucial to state that most of these review papers reported the removal of heavy metal ions and organic pollutants as a whole from soil and water system by pristine and modified biochar. However, in this review paper, we restricted our criteria to Cd remediation in soil by biochar-based materials.

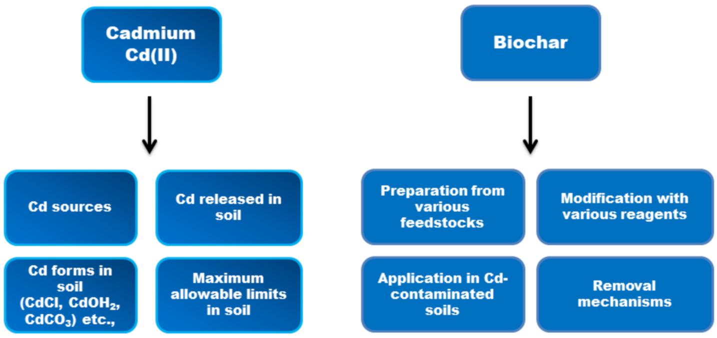

Figure 1. Summary of the main content of this review article.

Table 1. Summary of review papers published since 2020 on the preparation, characterization, and potential application of biochar and biochar-based materials for the restoration of soil polluted with metal ions.

Material	Summary of Review Paper Content	Ref.
Biochar-supported metal nanoparticles	This paper reviewed the synthesis, characterization, environmental applications, and underlying mechanisms in the removal of contaminants from soil and water by biochar-supported metal nanoparticles.	[26]
Preservative-treated wood biochar	In this paper, the authors discussed the synthesis of biochar from preservative-treated wood, with particular focus on feedstock, synthesis method, characterization, application in pollutant removal, and ecotoxicity.	[43]
Biochar	This review paper discussed the molecular interaction mechanisms between biochar and potentially toxic elements such as those in soil systems.	[44]
Biochar-based composites	This paper reviewed the role of biochar-based composites with metal oxides, surface agents, and nanoparticles in the remediation of contaminated soil. Future research directions to verify the underlying mechanisms involved in biochar composite–soil microbial interactions and remediation of heavy metals.	[45]
Biochar and Biochar-based materials	This paper discussed the potential applications of biochar and its composite materials for the removal of organic and inorganic contaminants from soil and water.	[34]

3. Cadmium (Cd) in the Soil Environment

3.1. Chemical Forms of Cd in Soil

The ecological influence of Cd is associated with its forms in the soil [46], which cause toxicity to plants and living organisms. Different forms of Cd are present in various environmental compartments, such as soils, water, atmosphere, aquatic ecosystems, and sediments. This review paper deals with the different cadmium forms in soil. To understand the ecological toxicity of Cd pollution in soils, it is crucial to understand its forms in relation to their bioavailability, mobility, uptake, and accumulation by plants and living organisms. Cd in the soil system can be present in different physico-chemical forms, varying in charge. Dissolved Cd in soil solution can be present as free, hydrated cations or as species complexes with organic or inorganic ligands. Experimental results showed that Cd is present as inorganic cationic species (chemical forms in which Cd is present in soil solution), such as free Cd(II), but a significant amount of Cd is also present as organic and inorganic neutral species, e.g., $Cd(OH)_2$ [47], particularly in farm soils with elevated pH [48–50]. The most common types present are Cd(II), hydroxide $Cd(OH)_2$, and carbonate ($CdCO_3$) solids, which dominate at elevated pH, while Cd(II) and aqueous Cd sulfates are dominant at low pH. Stable solid Cd(s) is produced when sulfide is present in reducing conditions. Cd also forms precipitates with P, As, Cr, and other anions, although the solubility of these compounds varies depending on the pH and other chemical factors. Plants tend to prefer free Cd(II), while $CdCl^+$ is taken up more slowly, and Cd humate is not adsorbed by plants [51].

3.2. Sources of Cd in Soil

Substantial environmental concentrations of Cd typically originate from anthropogenic activities. Cd can be released into the soil environment with the leaching and runoff of non-ferrous metals from various industries. Irrigation of farmland with water contaminated by industrial effluents can also cause Cd pollution. In addition, atmospheric deposition of Cd-containing dust released from metallurgical activities, as well as fossil fuel combustion, can affect distant farmland, but the impact of these sources is difficult to quantify [52]. Phosphorus-based fertilizers are also a significant cause of Cd accumulation in agricultural soils [53]. Phosphate fertilizers are primarily manufactured by chemically treating phosphate rocks that contain a substantial amount of Cd(II) [14].

3.3. Permissible Limits of Cd

The critical levels of metal ions in soil associated with health hazards can be measured using a model that integrates all related exposure pathways into one metric, such as the acceptable daily intake (ADI) in µg/kg/day [54]. It has been found that the average daily intake of Cd is 25–75 µg/day [55], which is higher than the tolerance level of 10–53 µg/day indicated by the FAO/WHO [56]. This intake is directly related to the accumulation of Cd in crops. Some crops, such as rice, can accumulate significant levels of Cd (more than 1000 µg/kg), while wheat accumulates 0.032 mg/kg [57] when grown in Cd-polluted soil. The average daily Cd intake from food in European and North American countries is 15–25 µg, but this can vary greatly depending on age and dietary habits. The average daily intake in Japan is 40–50 µg, but it can be much higher in cadmium-polluted areas. Cd is absorbed through the gastrointestinal tract at a rate of 5% in humans, but nutritional factors may increase this up to 15% in cases of iron deficiency. As a result, the average amount of Cd ingested through food is estimated to be about 1 µg/day [58,59].

4. Biochar and Cd (II) Immobilization in Soil: Recent Progress

Pristine biochar prepared from various feedstocks and surface-modified biochar treated with different metals, metal oxides, and other additives have received tremendous attention in studies on the immobilization of soil Cd(II) to reduce its uptake and accumulation in plants, as illustrated in Figure 2 [60–64]. The application of biochar to soil could also influence the soil physicochemical characteristics, such as organic matter content, microbial communities, redox potential, and pH [65]. Recent innovations in the use of biochar for Cd removal from the soil are briefly discussed. The main influencing parameters are summarized in Table 2.

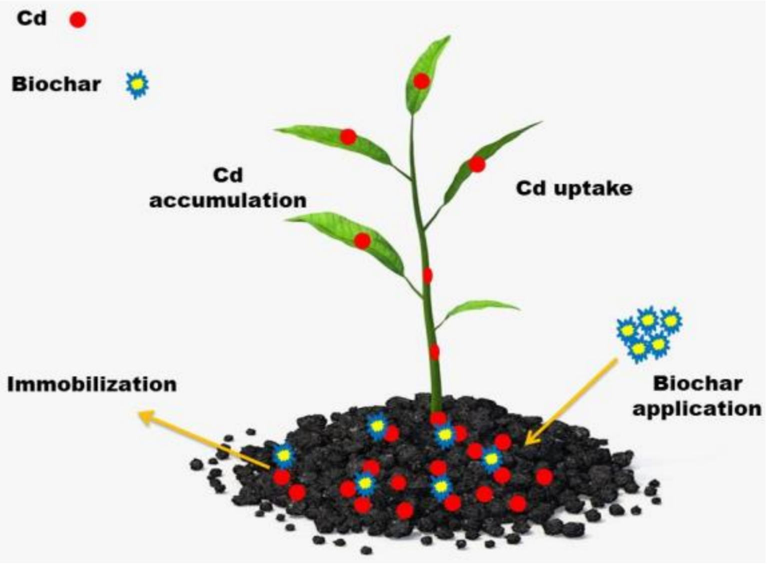

Figure 2. Uptake, accumulation and immobilization of Cd in soil by biochar-based materials.

4.1. Description and Main Findings of Experiments with Pristine Biochar in Cd-Contaminated Soil

To date, various feedstock-based pristine biochar under various temperatures (300–800 °C) are prepared and used to immobilize Cd(II) in the soil. In a recent study examining the effect of pristine biochar on Cd immobilization in soil, wheat straw biochar was prepared by anoxic pyrolysis at 450 °C and applied at a rate of 0 and 5% (w/w) to remediate Cd-contaminated soil. Two different vegetables, green peppers (*Capsicum annuum*) and eggplant (*Solanum melongena*) were selected as the test crops. It was shown that biochar application (5% w/w) reduced the Cd concentration in green pepper by 6.8–11.5% and in eggplant by 15.1–15.4% [66]. In another study, rice straw-derived biochar was prepared at various temperatures (300, 400, 500, 600, and 700 °C) in a CO_2 atmosphere and applied to critically evaluate the biochar negative surface charge effect on Cd(II) removal from Cd-contaminated soil cultivated with wheat (*Triticum aestivum*). The results showed that when the biochar preparation temperature increased from 300 to 700 °C, the negative charge on the surface of the biochar decreased, and Cd(II) fixation increased. Ash content, pH, oxygen-based functional groups, polar groups, and hydrogen bonds were all found to influence the negative surface charge of biochar in that study [67]. Similarly, Xiao and co-workers critically evaluated the effect of biochar application rate (0, 1, 2.5, and 5%) on Cd content in a legume–grass mixture and concluded that increasing the proportion of legumes in the legume–grass mixture did not reduce Cd(II) adsorption by the biochar. The amount of biochar added had complementary effects on nutrient uptake in the plant species mixtures [68]. In a study assessing the influence of biochar particle size and dosage on Cd(II) sorption through batch tests in sandy soil, wood-derived biochar with two different sizes was used, i.e., macro-size (particle size 0.5–1.0 mm) and nano-size as-prepared biochar, separated by sieving and ball milling. The maximum Cd sorption in sandy soil was 328.9 and 1062.4 mg/kg with 2% (w/w) of macro- and nano-size biochar, respectively, which was 58.6% and 412.2% higher than in control soil. Ball milling created nano-biochar that was more successful in Cd(II) amelioration in the contaminated environment [69]. A field experiment was conducted to test the biochar application rates of 0, 10, 20, 30, and 40 t/ha on cadmium availability and its accumulation in rice (*Oryza sativa*). The results revealed that biochar at 40 t/ha effectively decreased the Cd content in the soil, increased the available Cd(II) in micro aggregates, and reduced Cd(II) transport in rice [70]. In conclusion, pristine biochar has a limited impact on the remediation of Cd-contaminated soils due to diverse mechanisms on the surface of biochar, and the use of modified-biochar, with high surface area and diverse functional groups, is preferred for remediation purposes. The details of various modified biochars for Cd immobilization are discussed below.

4.2. Description and Main Findings of Experiments with Metal-Modified Biochar in Cd-Contaminated Soil

The application of metal-modified biochar to immobilize soil Cd is an environmentally sustainable and cost-effective technique. Recently, Moradi and coworkers investigated the effects of raw biochar and iron (Fe)-modified biochar made from common reed on Cd fractionation, mobility, and microbial communities in calcareous soil. The treatments were based on two factors: type of biochar (control, pristine biochar, Fe-modified biochar) and amount of Cd in the soil (0, 15, and 30 mg/kg). The treatments were incorporated into the soil and left for 90 days. The results showed that Fe-modified biochar could immobilize Cd(II) and boost soil microbial attributes [71]. A 2-year field test in a wheat–rice rotation system was conducted to evaluate the influence of Fe-modified biochar on the extractability and availability of Cd along with As in soil and its effects on crop performance. The application rate of Fe-modified biochar was 1.5 and 3.0 t/ha, and as well as using manure compost and a control for comparison. It was found that Fe-modified biochar at 1.5 t/ha achieved successful immobilization, justifying its use as a pollutant remediation amendment [72]. In another study, magnetic biochar-based adsorbents with Fe_3O_4 particles were prepared through thermal pyrolysis and applied to remediate multi-contaminated soil. The findings indicated that the application of the as-prepared adsorbent to a multi-contaminated soil slurry concurrently removed 20–30% of As, Cd, and Pb within 24 h [73].

Sulfur-engineered biochar can intensify the benefits of biochar and elemental sulfur in Cd(II) removal from soil. In this context, the effect of pristine wheat straw biochar and sulfur-modified biochar on Cd(II) amelioration mechanisms was investigated. Scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS) characterization proved that sulfur was fully incorporated onto the surface of biochar, while X-ray photoelectron spectroscopy (XPS) characterization revealed substantial differences in the Cd(II) amelioration mechanisms of pristine biochar and sulfur-modified biochar. Cd(II) sorption onto the surface of pristine biochar was primarily due to the formation of $Cd(OH)_2$ and $CdCO_3$ precipitates and the interactions with carbonyl and carboxyl groups, while sorption onto the surface of sulfur-modified biochar was primarily due to the formation of CdS and $CdHS^+$ precipitates and the interactions with organic sulfide groups [74]. To fill a research gap about the effect of sulfur-modified biochar on Cd(II) phytoavailability in paddy soils, Rajendran et al. conducted a pot experiment on Cd(II) mobility and transition in a soil–rice system treated using sulfur-modified biochar and sulfur–iron (S–Fe)-modified biochar. According to the sequential extraction results, both biochars facilitated the conversion of exchangeable Cd(II) to Fe–Mn oxide, organic, and residual bound forms, consequently reducing Cd(II) availability in the paddy soil [75].

4.3. Description and Main Findings of Experiments with Metal Oxide-Modified Biochar in Cd-Contaminated Soil

Studies using metal oxide-modified biochar have made significant progress in reducing Cd(II) pollution in farm soils and wastewater in recent years. In one study, magnesium oxide (MgO)-loaded biochar was successfully synthesized as a potential adsorbent by co-pyrolysis of corn straw and $MgCl_26H_2O$ at 600 °C and used to immobilize heavy-metal ions of Cd/Pb in contaminated environmental components. According to the experimental findings, MgO-loaded biochar had remarkably high Cd(II) sorption potential compared with the original biochar. The adsorption kinetics and isotherm of Cd(II) were well defined by pseudo-second-order and Langmuir/Langmuir–Freundlich models. The underlying reaction mechanisms were hydrolysis of MgO, ionization of $Mg(OH)_2$, and precipitation of Cd(II) and OH on MgO-laden biochar composites, while oxygen-containing groups also triggered Cd(II) immobilization [76]. In another study, the use of a MgO–biochar–chitosan composite, modified with $MgCl_2$ and chitosan, as an adsorptive material in the stabilization of Cd(II) in aqueous and soil systems was investigated. The results of soil incubation tests showed that the application of this biochar product at 2% was highly efficient in Cd(II) stabilization in comparison with the control, reducing the amount of bioavailable Cd by 22.3%. It also decreased the acid-extractable Cd(II) content by 24.8% and increased the residual Cd(II) content by 22.2%; synergy between surface complexation and precipitation mechanisms was shown to make a vital contribution to the sorption of Cd(II) [77].

The efficacy of potassium hydroxide (KOH)-modified rice straw-derived biochar and pristine rice straw-derived biochar in reducing Cd(II) solubility and bioavailability in Cd(II)-polluted soil was investigated. Cd(II)-polluted soil was treated with 15 and 30 g/kg of biochars for 60 days. Both biochars markedly decreased Cd(II) leaching in the toxicity characteristic leaching procedure (TCLP) and NH_4NO_3-extractable Cd(II) in the amended soil in comparison with untreated soil. The reduction in Cd(II) solubility and bioaccessibility was attributed to a notable increase in the soil pH and subsequent surface complex formation. The viability of KOH-modified biochar in the stabilization of soil Cd(II) and Pb(II) and the influence of pyrolysis temperature and alkaline concentrations used in biochar modification were examined in another study. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS), Tessier sequential extraction, and X-ray diffraction (XRD) techniques were used to investigate the stabilization mechanisms of the alkaline-enhanced biochar. The results showed that rice husk biochar pyrolyzed at low temperature (300 °C) and activated with moderate alkaline concentrations (1 M or 3 M KOH) provided the best stabilization [78].

4.4. Description and Main Findings of Experiments of Biochar Combined with Other Amendments in Cd-Contaminated Soil

Other than metal-modified and metal oxide-modified biochars, a variety of facile combinations were used for the immobilization of Cd(II) in soil. In this regard, *Sporobolus alterniflora* (saltmarsh cordgrass)-derived biochar was applied at rates of 0, 2.5, 5, and 10%, for the immobilization of Cd(II). The test crop was pak choi (*Brassica chinensis*). It was found that soil minerals facilitated Cd(II) immobilization by biochar, decreased Cd bioavailability and enhanced its recalcitrance [79]. The use of biochar in combination with plant growth-promoting (PGP) bacteria in the bioremediation of Cd-polluted soil has been widely reported. A novel Cd-immobilizing PGP bacterial strain TZ5 was isolated. SEM–EDS and Fourier transform infrared (FTIR) analyses revealed changes in surface morphology and functional groups of TZ5 cells after exposure to Cd(II). The strain TZ5 was then successfully loaded onto biochar for use as a biochemical composite material (BCM). In a pot experiment, the percentage of acetic acid-extractable Cd(II) in BCM treatments was found to be 11.34% lower than in the control. Compared with the control, BCM increased the dry weight of ryegrass by 77.78% and decreased the Cd(II) concentration of ryegrass by 48.49% [80]. In a similar study, a 75-day pot experiment was conducted to examine the complex effects and possible mechanisms of maize biochar and of the heavy-metal-tolerant strain Pseudomonas sp. NT-2 on the stabilization of mixed Cd- and Cu-polluted soil. It was found that the incorporation of NT-2-biochar greatly increased the remaining proportions of Cd and Cu in the soil, reducing the proportion of exchangeable and carbonate-bound species and thus decreasing the plant and human bioavailability of the metal in the soil, as measured by diethylenetriamine pentaacetic acid (DTPA) chelation and simulated human gastric solution (UBM) extraction [81].

For remediation of heavy metal-contaminated soil, biochar in combination with compost has been commonly used. A study on the effects of sole biochar, compost, and a combination of biochar and compost on heavy metals availability, soil physicochemical properties, and enzyme activities was conducted. The results found that both amendments reduced the availability of Cd and Zn in the soil, but only marginally activated As and Cu. The biochar and compost products used as a single amendment and in combination also had important effects on the physicochemical properties, metal availability, and enzyme activities in heavy-metal-polluted soil [82]. Xu et al. performed batch experiments to determine the efficacy of biochar pyrolyzed from kitchen waste, corn straw, and peanut hulls on the immobilization of Cd and Pb in polluted soil planted with *Swamp cabbage* (*Ipomoea aquatica* Forsk.). Analyses using a combination of toxicological and physiological tests showed that kitchen waste, corn straw, and peanut hull biochars all improved soil pH and reduced extractable Pb and Cd by 22.61–71.01%, 18.54–64.35%, and 3.28–60.25%, respectively. At an application rate of 60.00 mg/kg soil, all biochars reduced Cd and Pb accumulation in roots, stems, and leaves by 45.43–97.68%, 59.13–96.64%, and 63.90–99.28%, respectively [83].

4.5. Cd(II) Removal Mechanisms

Cereal crops, especially rice, wheat, and maize, are the most common sources of Cd in human diets. As a result, reducing Cd transfer from soil to cereal grain is a critical task to protect food safety [84]. During the past decade, great progress has been made in identifying the mechanisms by which biochar can reduce soil Cd transport to cereal crops. Multiple equipment and techniques, such as XPS, XRD, FTIR, and SEM–EDS, were used in one study to explore the interaction mechanisms between Cd and biochar [85]. Further analysis showed that mineral precipitation, surface complexation, and cation–π interactions were the main mechanisms of Cd sorption on biochar in soil [86]. The mechanisms of biochar fixation of Cd are depicted in Figure 3. Among these, immobilization by electrostatic attraction between molecules and ions is the main mechanism explaining the physical adsorption. There are also complex mechanisms, such as agglomeration and sedimentation of biochar colloidal particles after the immobilization of heavy metals in soil [87,88]. The underlying mechanisms in heavy-metal (Cd) fixation by biochar mostly depend on biochar surface pore size, oxygen-containing functional groups, the pyrolysis temperature used in biochar preparation, feedstock, and soil characteristics [67,86,89].

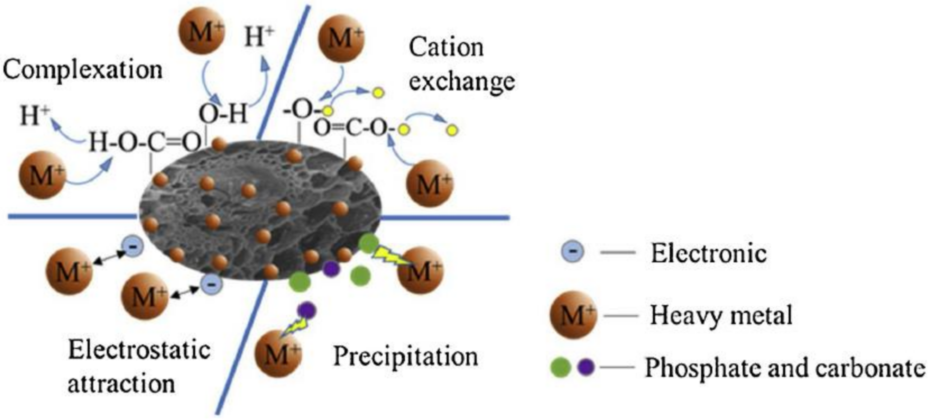

Figure 3. Underlying mechanisms in soil cadmium (Cd) fixation by biochar [68].

Table 2. Efficiency of the remediation of cadmium (Cd(II))-contaminated soils by pristine biochar and modified biochar in different studies. NR = not relevant.

Feedstock Used for Biochar	Surface Modifier for Raw Biochar	Test Crop	Dose	Removal Efficiency	Ref.
Wheat straw biochar	Pristine	Green pepper and eggplant	0 and 5% (*w*/*w*)	0–5% (*w*/*w*) = 6.8–11.5% (green pepper) 0–5% (*w*/*w*) = 15.1–15.4% (eggplant)	[66]
Corn stalk	Manganese (Mn)	Wheat	1, 2 and 3% (*w*/*w*)	Among all the Mn-modified biochar treatments, 1%, 2%, and 3% treatments of MBC_2-500-5:1, showed the potential to convert the mild acid-soluble fraction Cd to the reducible, oxidizable, residual fraction Cd, thereby controlling the migration, transformation, and enrichment of Cd in the soil.	[90]
Rice straw	Pristine	Legume–grass mixture	0, 1, 2.5, and 5%	Biochar addition did not reduce Cd uptake when increased the amount of legumes in the legume–grass mixture	[68]
Sporobolus alterniflora-derived biochar	Pristine	Pak choi	0, 2.5, 5, and 10% in pots	Biochar facilitated Cd immobilization in soil, which decreased Cd bioavailability and enhanced Cd recalcitrance.	[79]

Table 2. *Cont.*

Feedstock Used for Biochar	Surface Modifier for Raw Biochar	Test Crop	Dose	Removal Efficiency	Ref.
Coconut shell	*Bacillus* sp. TZ5	Perennial ryegrass	5 g in 100 mL suspension + 100 mL bacteria suspension	The application of biochemical composite material (BCM) significantly decreased the Cd concentration of ryegrass by 48.49% in soil, thus providing a practical approach for bioremediation of Cd-contaminated soil.	[80]
Wheat straw	Bare wheat straw-derived biochar	Rice	0, 10, 20, 30, and 40 t/ha	Biochar at 40 t/ha decreased the available Cd (49.4 and 51.7) significantly, compared with 0 t/ha	[70]
Wheat straw	Phosphoric acid (H_3PO_4)	Quinoa	1 and 2% (*w*/*w*)	H_3PO_4-treated biochar effectively alleviated Cd toxicity in quinoa by reducing Cd(II) accumulation and regulating Cd-induced oxidative stress by the antioxidant enzymatic system.	[91]
Wheat straw	Pristine	Paddy rice field	0, 10, 20 and 40 t/ha	Biochar at 40 t/ha altered the chemical properties of soil and reduced the mobility of Cd along with Pb in paddy soil.	[92]
Cattle carcass biochar	Carbonate-bearing hydroxyapatite (CHAP)	NR (Sorption test)	0.1 g sample	Cattle-derived biochar from cattle carcasses containing a substantial amount of naturally occurring mineral form of carbonate-bearing hydroxyapatite (CHAP) allowed a 97.% reduction in Cd in soil.	[93]
Bamboo hardwood	Sulfur-modified and S–Fe-modified biochar	Rice	1%	Addition of S–Fe-modified biochar to Cd-contaminated paddy soil reduced Cd(II) accumulation in rice grain by 0.018 mg kg^{-1}.	[75]
Rice straw biochar	Zinc oxide (ZnO)	Rice seedlings	0, 50, 75, and 100 mg/L of ZnO, alone or with 1.0% (*w*/*w*) biochar	Cd content in shoots was reduced by 30% and in roots by 31% at a dose of 100 mg/L ZnO; Cd content in shoots was reduced by 39% and in roots by 38% at a dose of 100 mg/L ZnO + biochar.	[94]
Ferromanganese binary oxide–corn straw–biochar composite (FMBC)	$KMNO_4$ and $Fe(NO_3)^3$	NR (Adsorption experiment)	0.5, 1, 2, and 4% wt/wt FMBC and biochar	The adsorption capacity of FMBC was the highest (6.72 mg g^{-1}) when compared to those of pristine biochar (4.85 mg g^{-1}) and control (2.28 mg g^{-1}).	[95]

Table 2. *Cont.*

Feedstock Used for Biochar	Surface Modifier for Raw Biochar	Test Crop	Dose	Removal Efficiency	Ref.
Sugar cane bagasse	Pristine	NR (Adsorption experiment)	0, 2, and 4% (wt/wt).	A 2% biochar application reduced Cd(II) contamination in saline–sodic soils, but increasing the biochar rate from 2 to 4% decreased Cd adsorption.	[96]
Bamboo hardwood	Sulfur-modified and S–Fe-modified biochar	NR (Incubation experiment)	1% (wt/wt).	Treatments with BC, S–BC, and SF–BC significantly reduced the exchangeable Cd by 12.54%, 29.71%, and 18.53%, respectively.	[97]
Rice straw	Pristine	Pak choi	0, 2.5 and 5% (wt/wt).	Rice straw-derived biochar at a dose of 5% showed potential to reduce the bioavailability of Cd(II) in soil by 16.64%, and increased pak choi yield.	[98]
Fe–Mn oxide-modified BC composite(FMBC)	Fe and Mn	Indica rice	0.5–2.0% (wt/wt).	A 2% FMBC application reduced Cd(II) accumulation in rice grain by 66.7–74.1% and improved grain quality.	[99]

5. Concluding Remarks and Future Work

In this review, available knowledge on Cd(II) forms in the soil environment, their release sources, and maximum permissible limits in soils were summarized. The recent scientific literature on the use of biochar and biochar-based materials for the efficient removal of Cd (II) to reduce its mobility and bioavailability in the soil system was also reviewed. The literature findings indicated that the diverse functional groups and actives sites on the surface of modified biochar, a large specific surface area, and a porous structure could improve the potential of modified biochar for the immobilization of Cd(II) in soil as compared to pristine biochar. The Cd(II) immobilization mechanisms appear to be hybrid, including adsorption, precipitation, reduction, ion exchange, surface complexes formation, hydrogen bonding, π–π interactions, and pore filling. However, the challenges reported below associated with biochar application in soil were identified as areas for future research.

Many studies described the use of pristine, metal-modified, and metal oxide-modified biochar for the removal of Cd(II) pollution from aqueous solutions, but few studies addressed the removal of Cd(II) pollution from agricultural soils. Thus, this area requires more research.

Based on the literature, the most promising mechanism for Cd(II) removal from soil by biochar appears to be immobilization, but biochar addition is less effective in field conditions than in laboratory studies. Further research in natural environments, such as farm fields, is needed to gain in-depth insights into Cd(II) immobilization mechanisms in soil.

Many studies described the positive effects of biochar in soil remediation, but little is known about the adverse effects of biochar addition. Therefore, the adverse effects of biochar in the soil system should be addressed in future research.

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