


REVIEW

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A critical review of the interactions between rhizosphere and biochar during the remediation of metal(loid) contaminated soils

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Abstract

Biochar has a large specific surface area, well-developed pore structure, abundant surface functional groups, and superior nutrient supply capacity, which is widely available and environmentally friendly with its advantages in waste resource utilization, heavy metal(loid) remediation, and carbon storage. This review focuses on the interactions between biochar (including raw biochar, functional biochar (modified/ engineered/ designer biochar), and composite biochar) and rhizosphere during the remediation of soil contaminated with heavy metal(loid)s (Pb, As, Cd, Hg, Co, Cu, Ni, Zn, Cr, etc.) and the effects of these interactions on the microbial communities and root exudates (enzymes and low-molecular-weight organic acids (LMWOAs)). In terms of microorganisms, biochar affects the composition, diversity, and structure of microbial communities through the supply of nutrients, provision of microbial colonization sites, immobilization of heavy metal(loid)s, and introduction of exogenous microorganisms. With regard to root exudates, biochar provides electron transfer support between the microorganisms and exudates, regulates the secretion of enzymes to resist the oxidative stress stimulated by heavy metal(loid)s, ameliorates rhizosphere acidification caused by LMWOAs, and promotes the activity of soil enzymes. The roles and mechanisms of biochar on rhizosphere soils are discussed, as well as the challenges of biochar in the remediation of heavy metal(loid)-contaminated soils, and the issues that need to be addressed in future research are foreseen.

Highlights

- The interactions between biochar and rhizosphere in the remediation of soil with heavy metal(loid)s have been focused
- Biochar affects rhizosphere microorganisms by changing population diversity and community structure

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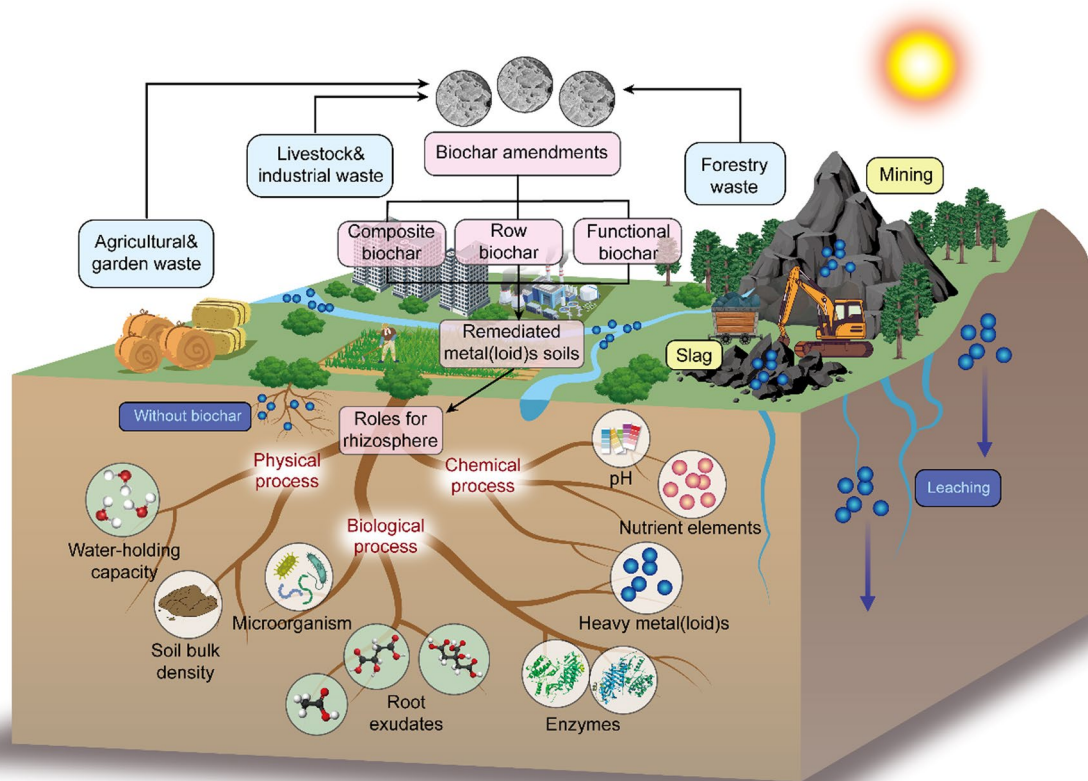


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- Biochar regulates root exudates secretion and promotes soil enzyme activity in contaminated soil

Keywords Green and sustainable remediation, Sustainability, Biochar, Soil, Root, Heavy metal(loid)s

Graphical Abstract



1 Introduction

Heavy metals (e.g., lead (Pb), cadmium (Cd), chromium (Cr), zinc (Zn), mercury (Hg), copper (Cu), cobalt (Co), and nickel (Ni)) and metalloids (e.g., arsenic (As)), henceforth collectively referred to as heavy metal(loid)s, are caused by both natural activities and human-induced activities (such as mining and smelting, agricultural activity, as well as urban and industrial emissions) (Yuan et al. 2023a; Hou et al. 2020; Narayanan and Ma 2022). The leaching of large amounts of heavy metal(loid)s into soil and water can accumulate in living organisms through the food chain, and cause irreversible damage to the human body due to the non-biodegradable properties of heavy metal(loid)s (Gao et al. 2022; O'Connor et al. 2020). In addition, once the content of heavy metal(loid)s in the soil exceeds the self-purification capacity of the

soil, the ecological balance of the soil will be disrupted, such as the death of beneficial organisms and microorganisms will lead to the reduction of soil biota, and severe heavy metal(loid) contamination will lead to the loss of soil production capacity and agricultural use value (Lin et al. 2022). Therefore, appropriate remediation of heavy metal(loid)-contaminated soils is imperative. For this purpose, a number of remediation strategies, such as bioremediation, physical remediation, and chemical remediation, have indeed been developed based on the mechanism of mobilization or immobilization of heavy metal(loid)s (Xiang et al. 2022). However, these strategies are usually expensive and require large amounts of energy and chemicals, as well as potential secondary contamination (Ghosh and Maiti 2021; Wang et al. 2020d). Therefore, nature-based remediation substances are emerging,

which ought to be cost-effective and environmentally beneficial in remediation (Yuan et al. 2023b; Narayanan and Ma 2022).

Remediation of heavy metal(loid)s in soils with biochar is one such viable approach that is cost-effective and environmentally beneficial because biochar can be obtained from abundant and widely available waste biomass resources, which mainly include agricultural and garden waste, forest waste, industrial waste, and livestock waste (Feng et al. 2021; Khan et al. 2020; Li et al. 2019c; Novak et al. 2019). Furthermore, the 196 parties to the United Nations Framework Convention on Climate Change have agreed to achieve a balance in the anthropogenic greenhouse-gas (GHG) budget between 2050 and 2100, and this objective necessitates that both agriculture and industry strive towards achieving zero emissions or actively removing GHGs from the atmosphere (Williamson 2016). Yang et al. (2021a) showed that Converting 1 ton of agricultural waste into biochar can sequester over 920 kg CO₂-equivalent. Each hectare of soil amended with biochar saves 91 metric tons of CO₂-equivalent through the soil conservation effect, with 13 metric tons of CO₂-equivalent being sequestered in the soil (Lan et al. 2021; Latawiec et al. 2019). Biochar application as a soil amendment is a critical technology that combines zero carbon emissions with co-benefits for both the soil environment and agricultural yields (Buss et al. 2022).

The carbon (C), nitrogen (N), potassium (K), calcium (Ca), phosphorus (P), magnesium (Mg), and other organic matter contained in biochar can increase soil fertility, which provides nutrients for the growth of plants, soil animals, and microorganisms (Chen et al. 2016; El-Naggar et al. 2019; Wang et al. 2020b). The excellent pore structure of biochar has the capacity to adsorb soil heavy metal(loid)s, improve soil physicochemical properties, retain soil moisture, and provide sites for microbial colonization (El-Naggar et al. 2019; Wang et al. 2021a). Moreover, the surface functional groups of biochar are abundant and capable of transforming free heavy metal(loid) ions into less bioavailable forms through precipitation, coordination, and complexation (Alam et al. 2018; Chen et al. 2016; Yuan et al. 2021b). In addition to raw biochar, functional (modified/engineered/designer) biochar, which is commonly used to indicate application-oriented, result -based synthesis or modification of biochar with specific functions, can have more specific properties attached to it through various modifications (e.g., nano-, iron (Fe)-, aluminum (Al)-, manganese (Mn)-, nitrogen (N)-, sulfur (S)-, and acid/base-modification) that can enhance the immobilization of heavy metal(loid)s in soil (Hazrati et al. 2021; Liu et al. 2020b, 2022b; Zhu et al. 2020). Furthermore, co-composite biochar, which works synergistically through biochar and

some remediation materials, such as biochar-compost, biochar-microorganisms, biochar-biomass waste, biochar-cement, and biochar-zeolite, has also been used to remediate the soil contaminated with heavy metal(loid) (Chuaphasuk and Prapagdee 2019; Risueno et al. 2021; Simiele et al. 2021; Zhu et al. 2022b). These biochar amendments (raw, functional, and co-composite biochar) enable the pre-remediation of heavily heavy metal(loid) contaminated soils that are difficult to remediate by bioremediation and provide favorable conditions for the survival and colonization of soil organisms, thus contributing to the establishment and recovery of soil ecosystems (Gao et al. 2022). Thus, using waste biomass to create biochar can remediate soil contaminated with heavy metal(loid)s while achieving multiple goals such as immobilizing heavy metal(loid)s, utilizing waste resources, and achieving net zero.

The rhizosphere system is the basis for plant-environment interactions, plant growth, and crop production (Sun et al. 2020). Microorganisms, including bacteria and fungi, as well as root exudates (such as enzymes, amino acids, organic acids, and sugars), are crucial for plant-soil interactions and rhizosphere function, performing important functions such as mobilizing and uptaking soil nutrients, exchanging information, and transferring energy (Gargallo-Garriga et al. 2018). The chemical and biological processes in the rhizosphere of heavy metal(loid) contaminated soil differ significantly from those in the bulk soil (non-rhizosphere soil) because of the influence of rhizosphere microorganisms and exudates on the consumption, accumulation, or immobilization of heavy metal(loid)s (Sterckeman et al. 2005; Wang et al. 2002; Zhang et al. 2022). The rhizosphere, as the first interface between the soil and the root, is the major battlefield where biochar plays its role in soils contaminated with heavy metal(loid)s (Zhang et al. 2022). The interactions between biochar and the rhizosphere include (1) direct interactions, such as the direct contact between biochar and plant roots, the enrichment of rhizosphere microorganisms on biochar, and the adsorption of root exudates on biochar; and (2) indirect interactions, where biochar causes changes in soil physicochemical properties that result in the immobilization of heavy metal(loid)s, changes in microbial communities and activities, enzyme species and activities, and types and concentrations of root exudates (Jones et al. 2009; Lehmann et al. 2015; Prendergast-Miller et al. 2014). In addition, rhizosphere-biochar interactions are also influenced by soil properties such as water-holding capacity, pH, bulk density, minerals, and heavy metal(loid)s (Jones et al. 2012).

Biochar has been shown to regulate the rhizosphere environment of plants. To obtain a comprehensive overview of the present application of biochar in soil

biochar significantly improves the remediation effect on Pb and Cd) (Gasco et al. 2019; Lebrun et al. 2018; Martins et al. 2018; Su et al. 2021). In this study, the modifications of functional biochar are classified as non-metallic modification (e.g., N, P, S, and thiol modification), single/multi-metallic modification (e.g., Fe-, Mn-, Co-, Ni-, Fe-/Zn-, Fe-/Mn/Ce-modification), non-metallic/metallic modification (e.g., S/Fe-modification), acid and base modification, and other modifications (e.g., nanomodification, zeolite modification). Moreover, co-composite biochar includes biochar combined with compost, biochar combined with sewage sludge, biochar combined with lime and fertilizer, and biochar combined with microorganisms, etc.

Non-metallic modification of biochar, such as grafting of N-, P-, and S-containing functional groups, is an effective strategy for enhancing heavy metal(loid) adsorption capacity. Some studies have found that thiol groups have high affinity for heavy metal(loid)s (e.g., Hg^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , and Zn^{2+}) (Chai et al. 2010; Zhang et al. 2012). Xia et al. (2019) modified biochar with sulfhydryl groups using 3-mercaptopropyltrimethoxysilane and found that thiol-modified biochar showed a significant increase in adsorption capacity of Hg^{2+} . Fan et al. (2020) modified rice husk biochar with thiol groups by β -mercaptoethanol esterification reaction, and found that thiol-modified biochar effectively removed Pb^{2+} and Cd^{2+} from soil by surface complexation.

Single-metallic modification of biochar with Fe, Mn, Co, or Ni results in biochar that obtains magnetic properties and can be easily recovered by external magnetic fields (Wang et al. 2020c). Some studies have found that the introduction of iron oxides into biochar promotes the formation of inner-sphere complexes, which leads to a decrease in the mobility and bioavailability of heavy metal(loid)s and promotes plant growth (Wan et al. 2020; Wu et al. 2020). In addition, multi-metallic modification of biochar can form layered double hydroxides on the surface of biochar, which is a type of ionic layered compound with positively charged metal hydroxide layers and exchangeable negative ions with strong anion exchange capacity, and such materials have strong remediation effects on anionic heavy metal(loid)s (such as AsO_4^{3-} , $\text{H}_2\text{AsO}_3^{3-}$) in soils (Meili et al. 2019). Furthermore, the effect of metal-modified biochar on the soil rhizosphere may be due to the fact that these metals provide essential elements for the growth of rhizosphere plants and microorganisms (Lu et al. 2018).

Biochar modified by acidification usually has higher specific surface area and pore volume as well as more acid-binding sites for adsorption of contaminants and hydrophobic groups (e.g., lactone, phenolic, and carbonyl functional groups) (Ghorbani et al. 2022; Li et al.

2014). In addition, acid modified biochar can increase the concentration of water-soluble K, Ca, Mg, and Fe, which contribute to soil nutrients and promotes plant growth (Wang et al. 2020c). However, when the biochar itself contains heavy metal(loid)s, acid modification may not be a suitable modification method because the heavy metals will be washed out during the acid modification process, increasing the bioavailability of the heavy metals (Wang et al. 2020c). Base modification of biochar can increase the specific surface area and the content of oxygenated functional groups (e.g., hydroxyl, carboxyl, carbonyl, and ether) of raw biochar (Wang and Wang 2019). Wang et al. (2020a) found that low concentrations of KOH-modified biochar were beneficial for the stabilization of Pb and Cd in soil. However, acid- and alkali-modified biochar ought to be neutralized by a large amount of water after application to the soil in order to avoid excessive acid and base that may cause negative impacts on the environment.

In addition, co-composite biochar contributes to play a better role of biochar itself and synergizes with microorganisms, lime, compost, and other materials to significantly improve the biological, chemical, and physical characteristics of soil (Haider et al. 2021). For example, in order to improve the properties and minimize the defects of the remediation amendments, Forján et al. (2018) combined compost with biochar to increase the pH and total carbon of soil, and thus reduce the concentration of available Cu, Ni, Pb, and Zn. Furthermore, contaminated soil cannot support the rapid growth of microorganisms with remediation capacity for soil due to the biotoxicity of heavy metals, and nutrient deprivation and competition from native microorganisms have a negative impact on the growth and proliferation of exogenous microorganisms (Ma et al. 2020). Therefore, the combined application of microorganisms with biochar enables microorganisms with remediation capacity for heavy metals to have higher bioactivity, greater population density, better regeneration capacity, and higher resistance to environmental disturbances (Wei et al. 2022).

3 Effect of biochar amendment on the physicochemical properties of heavy metal(loid)-contaminated soil

3.1 The effect of biochar amendments on heavy metal(loid)s

Since heavy metals and metalloids exist as both anionic and cationic forms, the behavior of heavy metal(loid)s is closely related to the anionic and cationic charges present on the surface of biochar (Fijałkowska et al. 2021). When added to soil, biochar with a positive charge holds anionic heavy metal(loid)s (e.g., arsenate and arsenite) while biochar with a negative charge binds to the cationic fraction

(e.g., Pb^{2+} , Zn^{2+} , and Cd^{2+}) (Gupta et al. 2021). For cations, the mechanisms of biochar remediation of heavy metal(loid)s are mainly surface precipitation, adsorption, and surface complexation with reactive functional groups, while anionic heavy metal(loid)s (including Cr, Se, and As) are more mobile in alkaline soils than cationic heavy metal(loid)s, and they are less likely to be adsorbed by negatively charged soils (Gupta et al. 2021; Narayanan and Ma 2022). Therefore, improvements in soil properties by biochar, such as reduced or increased soil pH caused by the use of acid- or base-modified biochar, can further reduce the bioavailability of heavy metal(loid)s. In addition, the mobility of heavy metal(loid)s in soil is also affected by their redox potential, which is influenced by the oxidation-reduction state of the soil (Narayanan and Ma 2022). The study of Dong et al. (2017) showed that the presence of oxygen-containing active functional groups on the surface of the biochar allowed the conversion of Cr^{6+} to the less mobile Cr^{3+} . The physicochemical properties of biochar depend on the feedstock, prepare and modify biochar, so it is necessary to screen the appropriate feedstock, preparation and modification of biochar according to the properties of heavy metal(loid)s in the soil, thus enabling biochar amendments to remediate specific types of soils. Table 1 summarizes the significant effects of biochar amendments on the remediation of heavy metal(loid)s in soil, and in general, the remediation mechanisms (Fig. 2b) of biochar amendments for heavy metal(loid)s mainly involve (1) electrostatic adsorption by π - π electron donor-acceptor interactions or electrostatic attraction between biochar amendments and cations/anions of heavy metals(loid)s (Yang et al. 2019); (2) ion exchange between cations on the surface of biochar (Ca^{2+} , Mg^{2+} , etc.) and heavy metal(loid) cations (Qiu et al. 2021), or anions on the surface of biochar (e.g., OH^- , CO_3^{2-} in layered double hydroxide-modified biochar) and heavy metal(loid) anions (AsO_4^{3-} , H_2AsO_3^- , etc.) (Dai et al. 2022); (3) complexation between abundant oxygen-containing functional groups ($-\text{COOH}$, $\text{C}-\text{OH}$, and $-\text{OH}$, etc.) on the surface of biochar amendments and heavy metal(loid) ions to form stable complexes (Vithanage et al. 2017); and (4) precipitation of heavy metal(loid)s with minerals on the surface of biochar to form insoluble precipitates ($\text{Pb}(\text{OH})_2$, $\text{Cd}(\text{OH})_2$, and As-bearing Fe mineral, etc.) (Ghosh and Maiti 2021; Palansooriya et al. 2022; Zhang et al. 2020b).

3.2 Effect of biochar amendments on soil physicochemical properties

Biochar amendments significantly affect the biophysical and chemical properties of the rhizosphere in soil contaminated with heavy metal(loid)s (Fig. 2a). Several studies have demonstrated that biochar amendments could improve

soil health, which is beneficial for arid and degraded soils, especially for mining soils with low organic matter, nutrient content, and water-holding capacity (Malyan et al. 2021; Rodriguez-Franco and Page-Dumroese 2021). The various physical and chemical properties of biochar have different effects on heavy metal(loid) remediation and the soil fertility improvement (Sizmur et al. 2017; Zhang et al. 2018b). For example, Chen et al. (2022) investigated the effects of agricultural waste (peanut shell, corn straw, and wheat straw) and forest waste (pine chips) biochars on Pb-contaminated soil, which revealed that agricultural waste biochar had higher specific surface area and abundant surface oxygen functional group contents compared to forest waste biochar, and the soil acid-soluble Pb contents reduced by 49.51%, 50.71%, and 52.71% after 150 days of remediation with peanut shell, corn straw, and wheat straw biochars, respectively, which showed a better remediation capacity than that of pine chip biochar (37.30%). Research indicates that as pyrolysis temperature increases, the absorption peaks of O-H, C-O-C, C-O, and $-\text{CH}_2-$ on biochar surface decrease, with only peaks of C-O and C-C remaining on the aromatic ring of high-temperature biochar (Chen and Chen 2009). And these functional groups have a large number of hydrophilic and hydrophobic groups, and therefore, they are closely related to the water-holding capacity which is closely relevant to the growth and health of soil rhizosphere plants and microorganisms in the soil (Gao et al. 2022). Additionally, the well-developed pore structure and large specific surface area of biochar amendments promote water-holding capacity and provide a favorable habitat for rhizosphere microorganisms (Malyan et al. 2021; Palansooriya et al. 2019; Tomczyk et al. 2020). Additionally, mineral element concentrations in biochar, such as Mg, Fe, Na, Ca, P, and K, increase with pyrolysis temperature and are influenced by the type of feedstock used (Tomczyk et al. 2020). Saletnik et al. (2016) concluded that the maximum C and N contents (73.6% and 1.9%, respectively) were found at a pyrolysis temperature of 400 °C, while the highest P, K, and Mg contents (4.3 g/kg, 9.9 g/kg, and 2.8 g/kg, respectively) were found at 500 °C. Thus, the contribution of biochar obtained in different conditions to the nutrients required by soil plants and microorganisms is different. Nair et al. (2017) reported that the biochar stimulated carbon sequestration and humification processes through the increased carbon content, reduced bulk density, and improved water-holding capacity. Furthermore, biochar amendments are usually alkaline, which can regulate the pH of the rhizosphere soil, especially in acidic soils or acidified soils due to organic acid production by roots, and biochar amendments can also improve the fertility of the rhizosphere soil due to the abundant elements of C, N, P, and K, all of which provide favorable conditions for the growth of soil plants and microorganisms

Table 1 Studies on the application of biochar amendments in the remediation of soil contaminated with heavy metal(loid)s (HMs) in recent years

Type	Name	Feedstock	T* (°C)	HMs	Soil sources	Remediation mechanisms	Effects of biochar amendments on soil	References
Raw biochar	Biochar	Distilled waste of lemongrass	450	Cr, Cu, and Pb	Acidic mining site	Acid-base neutralization; complexation and electrostatic adsorption	Decreasing soil acidity and bioavailability of HMs; improving soil health and plant productivity	(Jain et al. 2020)
	Biochar	Rabbit manure waste	450 600	Co, Cr, Cu, Pb, Zn, and As	Mining site	Sorption	Reducing total HMs concentration; increasing biomass production; benefiting the microbial community; improving soil quality	(Gasco et al. 2019)
	Biochar	Birch and pinewood	500	Pb and As	Ag-Pb extraction mining site	Sorption	Increasing soil water-holding capacity, organic matter, pH, and electrical conductivity; decreasing Pb concentration in soil pore water; improving plant growth	(Lebrun et al. 2018)
	Biochar	Sugarcane bagasse	600	Sn, Zn, and Pb	Mining site	Adsorption; ion exchange; complexation; π interactions	Reducing available Cd; altering the characteristics of soil and pore water; mitigating the harm to corn caused by Cd	(Su et al. 2021)
Functional biochar	Mg-modified biochar	Peanut shell	300 600	Cd	Brown soil	Precipitation; adsorption	Increasing soil pH; decreasing the bioavailable Cd ²⁺	(Shan et al. 2020)
	KOH-modified biochar	Rice straw	500	Cd	Red soil	Precipitation; complexation	Increasing soil cation exchange capacity, pH, organic carbon, and nutrients; decreasing soluble, bio-accessible, TCLP, and NH ₄ NO ₃ - extractable Cd	(Bashir et al. 2020)

Table 1 (continued)

Type	Name	Feedstock	T* (°C)	HMs	Soil sources	Remediation mechanisms	Effects of biochar amendments on soil	References
	Sulfur-/sulfur-iron-modified biochar	Bamboo hardwood	550	Cd	Metallurgical plant farmland	Complexation; chelation; precipitation; adsorption	Increasing soil organic matter and pH; decreasing DTPA-extractable Cd; increasing the alpha diversity indices; changing soil bacterial community structure	(Wu et al. 2019b)
	Iron-modified biochar	Common reed	500	Cd	Cd-spiked soil	Adsorption; electrostatic attraction; precipitation	Increasing soil pH, organic carbon content, basal respiration, microbial biomass carbon, substrate-induced respiration, and dehydrogenase activity; reducing DTPA-extractable Cd	(Moradi and Karimi 2021)
	Iron-zinc oxide composite modified biochar	Corn straw	500	Cd	Cd-contaminated acidic and alkaline farmland soils	Complexation; precipitation	Increasing cation exchange capacity, pH, and dissolving organic carbon in acidic soil, and DOC and in pH alkaline soil; increasing the diversity and abundance of bacterial communities in soils	(Yang et al. 2021b)
	Fe-Mn-Ce modified biochar	Corn stalk	600	As	As-contaminated soil	Specific and non-specific adsorption	Improving pH and redox capacity of the soil; reducing bioavailable As	(Zhang et al. 2020a)
	Thiol-modified biochar	Rice straw	500	Cd and Pb	Contaminated vegetable field	Ion and surface complexation; adsorption	Increasing organic matter content and cation exchange capacity; decreasing the availability of Cd and Pb	(Fan et al. 2020)
	Hydroxyapatite-tailored hierarchical porous biochar	Rice husk	750	Cd and Pb	Adjacent smelting site	Ion exchange; complexation; cation-π interaction; precipitation	Reducing DTPA extractable and bioavailable Cd and Pb; supplying nutrients to plants	(Wu et al. 2022)

Table 1 (continued)

Type	Name	Feedstock	T* (°C)	HMs	Soil sources	Remediation mechanisms	Effects of biochar amendments on soil	References
Co-composite biochar	Nanoscale zero-valent iron composite biochar	Municipal sewage sludge	600	Cr(VI)	Cr(VI)-contaminated soil	Adsorption; reduction	Reducing TCLP-leachable Cr(VI) concentrations; improving the properties of soil	(Chen et al. 2023b)
	Nano zero-valent iron composite biochar	Wood sawdust	750	As, Zn, and Pb	Pb/Ag ore smelting site	Precipitation; complexation; electrostatic adsorption	Reducing available HMs	(Dos Santos et al. 2022)
	Biochar + compost	Wood	400	Cu, Ni, Pb, and Zn	Cu mining site	Adsorption; precipitation	Reducing the photo-available metal concentrations	(Forján et al. 2018)
	Biochar + sewage sludge	Wood	350	Cd, Pb, and Zn	Zn mining site	Complexation	Increasing leaching solution and soil pH; reducing the bioavailable Pb, Cd, and Zn concentration	(Penido et al. 2019)
	Biochar + lime + fertilizer	Miscanthus	700	Al, Cu, and Zn	Mining site	Electrostatic attraction; complexation	Increasing soil pH; reducing HMs and DOC contents in the filtrate	(Novak et al. 2018)
	Biochar + coal gangue	Bamboo	500	Cd, Cr, Ni, Cu, Pb, and Zn	Bulk Cu mining tailing	Surface adsorption; precipitation; complexation	Increasing soil pH, soil organic carbon, water-holding capacity; reducing leaching and bioavailability of HMs	(Munir et al. 2020)
	Biochar + Ca-bentonite	Tobacco	500	Cu and Pb	Au mine tailing	Formation of Cu carbonates	Reducing the uptake of Pb by maize and pakchoi; reducing Cu bioavailability	(Lahori et al. 2019)
	Biochar-supported nano-hydroxyapatite + phosphate solubilizing bacteria	Rice husk	–	Cd	Cd-contaminated sediment	Adsorption; ion exchange; precipitation	Increasing soil pH and available phosphorus content; decreasing the acid-soluble Cd content; increasing reducible, oxidizable, and residual Cd content	(Zhao et al. 2022)

Table 1 (continued)

Type	Name	Feedstock	T* (°C)	HMs	Soil sources	Remediation mechanisms	Effects of biochar amendments on soil	References
	Bacteria + biochar	Maize straw	–	Pb and Cd	Pb, Cd-spiked soil	Adsorption; ion exchange; electrostatic reaction; bacteria absorbed Pb and Cd	Reducing the bio-availability of Cd and Pb; increasing biomass; decreasing Cd, and Pb contents of pakchoi plants; improving soil enzyme activity and soil microbial community	(Wei et al. 2022)

TCLP: toxicity characteristic leaching procedure, DTPA: diethylene-triamine pentaacetic acid

*Temperature of pyrolysis

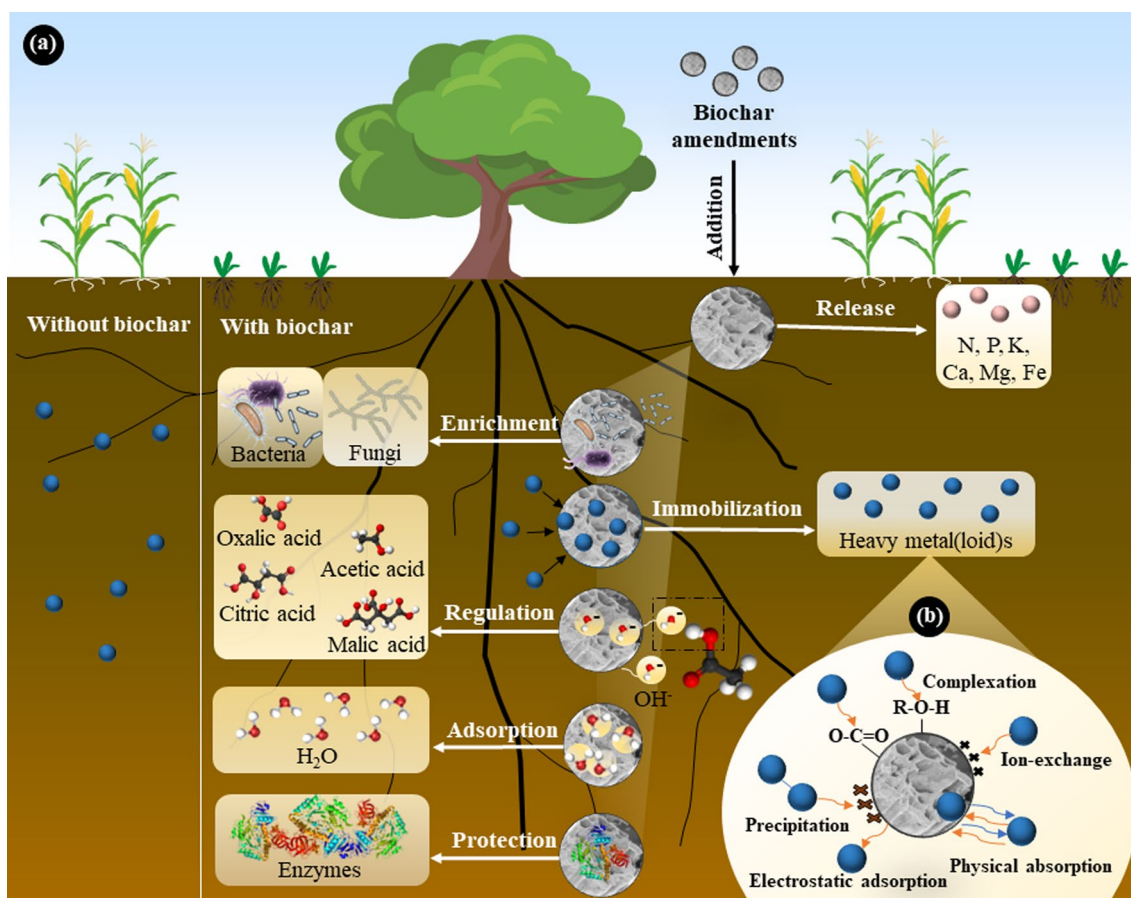


Fig. 2 Effects of biochar amendments on the rhizosphere of soil contaminated with heavy metals(loid)s. **a** Roles of biochar amendments on soil physical and chemical properties; **b** Remediation mechanisms of heavy metals(loid)s by biochar amendments (Narayanan and Ma 2022; Tan et al. 2022; Xiang et al. 2022)

(Bashir et al. 2020; Jain et al. 2020; Lebrun et al. 2018). There are a number of review articles summarizing the application methods, effects, mechanisms, and microbial impacts of various types of biochar in diverse types of soil. In general, soils are categorized into two main types, namely, those contaminated with anionic heavy metal(loid)s (As and Cr) and those contaminated with cationic heavy metal(loid)s (Pb and Cd, etc.), and the selection of biochar depends on the type of soil as well as the properties of the biochar (Batool et al. 2022; Gong et al. 2022). Similarly, the effect of biochar on the soil rhizosphere depends on the plant species and the microbial species of the rhizosphere. However, although there are a number of research articles on the effects of biochar on soil rhizosphere, there is no definitive summary of which type of biochar is best suited for rhizosphere in different soils, plants, and cultivation strategies, which is a target that should be pursued in subsequent studies.

4 Effect of biochar amendments on rhizosphere microorganisms in heavy metal(loid)-contaminated soil

Soil microorganisms include bacteria, fungi, actinomycetes, archaea, algae, and protozoa, which are crucial for the genetic diversity of earth and the functioning of soil ecosystems (Bandara et al. 2019; Zhang et al. 2018d). Some microorganisms are highly resistant to heavy metal(loid)s, such as *Pseudomonas*, *Delftia*, *Enterobacter*, *Arthrobacter*, and *Bacillus*, which can reduce the mobility and bioavailability of heavy metal(loid)s by precipitation or uptake of them (Ma et al. 2020). In addition, the existence of larger microbial biomass itself can enhance the remediation efficiency of heavy metal(loid)s in contaminated soils through direct adsorption of heavy metal(loid)s and participation in redox processes (Chen et al. 2018a; Wang et al. 2019). The heavy metal(loid)s, together with nutrients, water, electron acceptors, and

colonization sites are important factors which affect the growth and activity of rhizosphere microorganisms (Abdu et al. 2016; Giller et al. 2009; Lehmann et al. 2011). The addition of biochar amendments has both positive and negative effects on soil rhizosphere microorganisms, depending on the type of biochar amendments, the soil environment, and the heavy metal(loid)s. Negatively, biochar amendments may release some toxic compounds (such as potentially toxic elements, volatile organic compounds, or environmentally persistent free radicals) or mobilize anionic heavy metal(loid)s (such as Cr, As, and Sb) from soils (Bandara et al. 2019). On the positive side, biochar amendments can immobilize heavy metal(loid)s from soils, thereby reducing the bioavailability of heavy metal(loid)s, and providing electron shuttles, nutrients, and habitats for soil microorganisms.

4.1 Physical structure support

The population diversity and community structure of rhizosphere microorganisms in soil are closely associated with soil ecosystems (Li et al. 2016). The well-developed pore structure and large specific surface area of biochar provide colonization sites for rhizosphere microorganisms in soil contaminated with heavy metal(loid)s, which increases the enrichment of microorganisms, and increases the microbial abundance (Chaudhary et al. 2023; Kolb et al. 2009). Liu et al. (2018a) found that hydrochloric acid pickling and ultrasonication effectively removed or dissolved impurities in coconut shell biochar, which significantly increased the specific surface area and pore size and volume of biochar, and the counts of bacteria and fungi (especially *Actinomyces*) significantly increased in multi-metal (Cd, Ni, and Zn) contaminated soils after the addition of modified coconut shell biochar than the control group. In addition, biochar has been found to promote the colonization and enrichment of specific microbial strains (Chen et al. 2019; Wu et al. 2019a). Tu et al. (2020) investigated the remediation of Cd and Cu contaminated soil using maize biochar loaded with heavy metal(loid)s-tolerant strain (*Pseudomonas* sp.) and observed in scanning electron microscope images that *Pseudomonas* sp. attached well to the biochar, and most cells scattered or aggregated on the pore and surface of the biochar. However, the potential of biochar to serve as a colonization carrier for microorganisms is contingent on the specific microbial groups, physicochemical properties of biochar, and the soil conditions (Zhu et al. 2017). Different microbial groups respond differently to biochar, and the two most common mycorrhizal fungi (ectomycorrhizal and arbuscular) are usually protected by biochar whose internal pore structure may protect the mycelium from predators (Warnock et al. 2007). Mycorrhizal response is usually assessed by the

measurement of root colonization (i.e., the abundance of fungal tissue) (Lehmann et al. 2011). The tip number and the formation rate of ectomycorrhizal infection increased by 19–157% in larch seedling roots, and the colonization of arbuscular increased from 5% to 20% (control) to 20%–40% of wheat roots after the addition of biochar (Lehmann et al. 2011; Makoto et al. 2009). The study by Quilliam et al. (2013) observed that after being buried for three years, biochar had only sparse concentrations of attached microorganisms. This was likely due to high levels of mineral salts and contaminants such as polycyclic aromatic hydrocarbons in the soil, which may hinder microbial colonization.

4.2 Nutrient and micronutrient supply

The organic matter and mineral elements contained in biochar amendments provide nutrients such as C and N sources, and essential elements for the metabolism of cells, the composition of cellular proteins and nucleic acids, as well as the composition of cellular structures of rhizosphere microorganisms in soil contaminated with heavy metal(loid)s (Bruins et al. 2000). It has been reported that long-term exposure of soils to heavy metal(loid) contamination (As, Pb, Cd, Cr, Ni, Cu, V, and Zn) resulted in a decrease in soil basal respiration and microbial biomass carbon (Parelho et al. 2016). The application of biochar amendments reduced the microbial stress caused by high concentrations of heavy metal(loid)s and contributed to an increase in the number of soil bacteria and fungi in soil contaminated with heavy metal(loid)s (Parelho et al. 2016; Zornoza et al. 2016). Haddad and Lemanowicz (2021) studied the effect of biochar application on soybean rhizosphere microorganisms in Cd, Pb, and Ni contaminated soils and found that biochar overcame the inhibitory effect of heavy metal(loid)s on enzyme activities (arginase and urease), and provided more stable and degradable C sources, thereby promoting the growth of soil fungi (Vries et al. 2006; Orwin and Wardle 2004). The nutrient structure of biochar is significantly impacted by the pyrolysis temperature. Increasing the pyrolysis temperature of biochar generally results in an increase in its aromatic carbon structure and in the content of Mg, Fe, Na, Ca, P, and K, while the number of C-, O-, and N-functional groups decreases (Tomczyk et al. 2020). Therefore, the lower pyrolysis temperature of biochar may provide more organic matter and functional groups to rhizosphere microorganisms, while the higher pyrolysis temperature of biochar may provide more mineral elements, allowing for an increase in the abundance and activity of microbial communities in soil contaminated with heavy metal(loid)s (Halim et al. 2020; Kaplan et al. 2016; Tomczyk et al. 2020). *Actinomyces*

are hypersensitive to high concentrations of heavy metal(loid)s in soils (Hiroki 1992). Thus, their reduction is related to the concentration of heavy metal(loid)s in the soil (Frostegård et al. 1993). Igalavithana et al. (2017) observed that *Actinomycetes* were absent in soils contaminated with higher concentrations of Pb and As, whereas *Actinomycetes* were present in soils contaminated with lower concentrations of Pb and As, but the proliferation of *Actinomycetes* increased in both soils with higher and lower concentrations of Pb and As after the addition of vegetable waste and pine cone biochar. The abundance of *Actinomycetes* was higher with 200 °C biochar than with 500 °C biochar because biochar obtained at 200 °C provides more C sources for microorganisms in contaminated soils (Bandara et al. 2019; Igalavithana et al. 2017). In addition, Ahmad et al. (2016) and Igalavithana et al. (2017) observed that adding biochar amendments to heavy metal(loid) contaminated soil increased the population of Gram-negative bacteria. This is because Gram-negative bacteria are more tolerant to heavy metal(loid) stress in soil and can rapidly utilize a variety of C sources for growth, compared to Gram-positive bacteria (Moche et al. 2015).

In the rhizosphere, the interactions of C and N transformations between plants and microorganisms are reciprocal, as plants produce and release inorganic and organic matter while microorganisms take up CO₂ and dissolve inorganic carbon, organic acids, sugars, and amino acids, but the mobility of C and N depends on the plant and environmental conditions (Kaplan et al. 2016; Rilling et al. 2019). The addition of biochar amendments to the soil increases the availability of micronutrients to plants and also promotes microbial growth and metabolism, which further enhances the chemical reactivity of the rhizosphere and affects the mobility of heavy metal(loid)s (Halim et al. 2020; Yin et al. 2020). Zhang and Guan (2022) found that the modified biochar (biochar loaded with polyacrylic acid grafted chitosan composite) reduced the bioavailability of heavy metal(loid)s such as Mn, Cu, Fe, Zn, Ni, Pb, Cr, and As in soil while inhibiting nitrification, enhancing nitrogen fixation, ammonification, and denitrification, which had a significant effect on improving soil N fertilizer utilization. The relative abundance of Firmicutes and Bacteroidetes increased, while that of Actinobacteria, Acidobacteria, and Planctomycetes decreased at the phylum level after the application of the modified biochar, but the proportions of Actinobacteria, Acidobacteria, and Planctomycetes for the total nodes within the networks increased significantly (Zhang and Guan 2022). Firmicutes and Bacteroidetes are widely recognized as groups with resistance characteristics to external stressors such as heavy metal(loid)s (Chen et al. 2018c; Li et al. 2017; Liu

et al. 2018b; Zhao et al. 2020). Therefore, they can grow and multiply rapidly, taking over ecological niches normally occupied by other communities after the addition of biochar amendments (Liu et al. 2018b). Some studies have reported that Actinobacteria communities play important roles in soil N cycling, while Acidobacteria communities play roles in soil organic matter decomposition and denitrification (Kalam et al. 2020; Samaddar et al. 2019). This indicates that biochar amendments optimize the structure of rhizosphere microbial communities, resulting in a more complex and functionally specific symbiotic network of microbial communities (Yuan et al. 2021a; Zhang et al. 2018a; Zhang and Guan 2022).

4.3 Direct and intermediate electron transfer assistance

In biogeochemical redox reactions, some biochar amendments (e.g., modified with Fe²⁺, Fe³⁺, and Mn²⁺), which contain redox-active functional groups and electrical conductivity, electrically support the growth of rhizosphere microorganisms through at least four ways (Fig. 3): (1) as a terminal electron acceptor for microbial respiration; (2) as a source of electrons and/or energy for microbial growth; (3) as an electrical conductor to enhance electron transfer between cells of microorganisms of the identical and distinct species; and (4) as an electron storage material or battery for microbial metabolism (Klöpffel et al. 2014; Wu et al. 2017; Xu et al. 2016; Zhang et al. 2018c). Thus, biochar amendments serve to accelerate electron transfer between microorganisms in the rhizosphere, thereby increasing microbial activity and producing more surface attachment sites that are capable of responding to heavy metal(loid)s. Li et al. (2018) reported that the biochar not only enhanced the interspecies electron transfer, which promoted the detoxification of Cd, but also improved the interaction and stabilization of the microbial community in Cd-contaminated soil. The improvement in nutrient availability and electron transfer favored the supply of substrates and energy after the biochar application, increasing the relative abundance of some species of *Clostridiales*, which were involved in the substrate decomposition, and some species of *Sphingobacteriales*, which play a key role in sulfur metabolism (Cernava et al. 2017; Li et al. 2018; Siripornadulsil and Siripornadulsil 2013).

The interactions between electrons of microorganisms and biochar amendments facilitate the connection of metal ion redox with the oxidation of organic matter, the fixation of CO₂ into organic compounds, and the reduction of nitrate (NO₃⁻) and photosynthesis (Shelobolina et al. 2012). Biochar can serve as an “electron shuttle”, which is an alternative terminal electron acceptor to replace NO₃⁻ in microbial communities, thereby facilitating denitrification activities in soil (Cayuela et al.

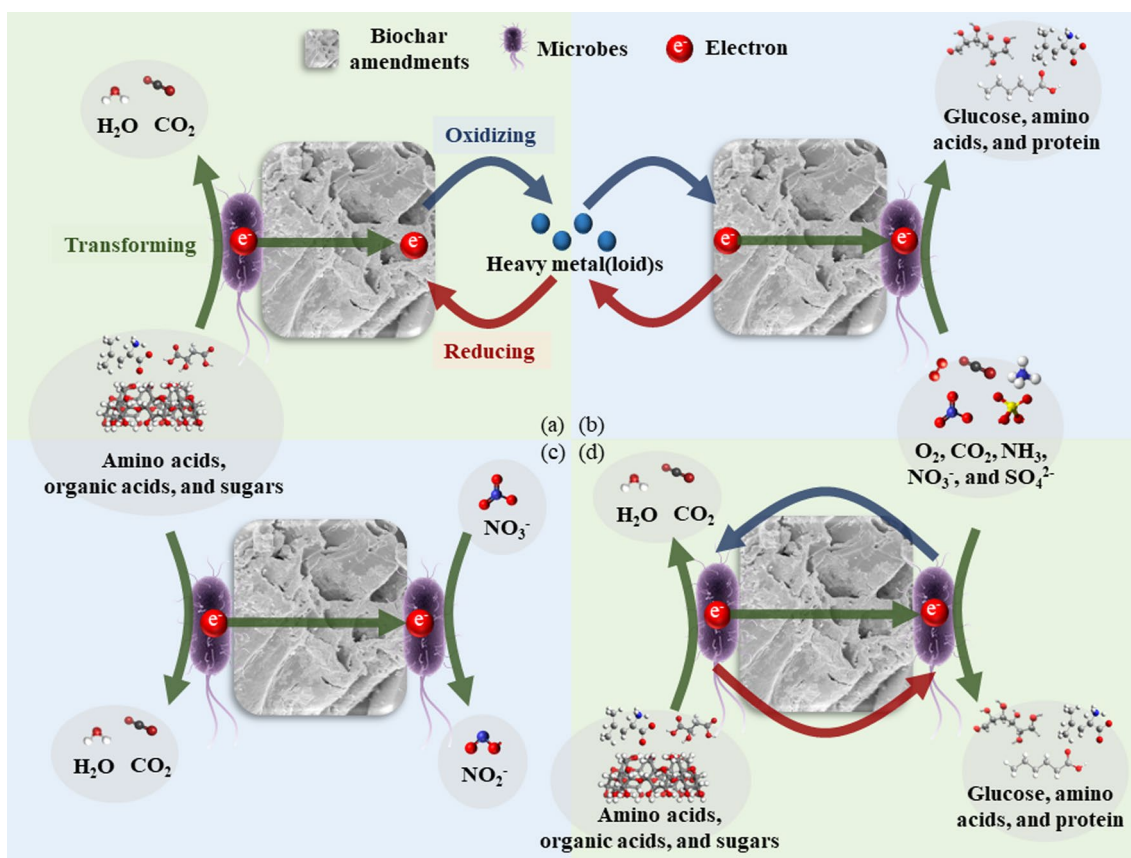


Fig. 3 Electrical conductivity of biochar amendments for the growth of rhizosphere microorganisms in soil contaminated with heavy metal(loid)s. **a** As a terminal electron acceptor for microbial respiration; **b** As a source of electrons and/or energy for microbial growth; **c** As an electrical conductor to enhance electron transfer between cells of microorganisms of the identical and distinct species; **d** As an electron storage material or battery for microbial metabolism (Shi et al. 2016; Zhang et al. 2018c)

2013). Liu et al. (2020a) demonstrated that compost provided a C source for denitrifying microorganisms and promoted microbial metabolism, thereby increasing O₂ consumption, and biochar acted as an alternative terminal electron acceptor for the microbial community to replace NO₃⁻, while metals on the biochar surface could act as catalysts, which created favorable conditions for denitrification and improved the activity and growth of denitrifying microorganisms. It was found that microorganisms had difficulty surviving and performing remediation functions in soils with high concentrations of Pb and Cd, and that the excellent electrical conductivity and nutrient adsorption capacity of biochar increased the microbial extracellular electron transfer rate, which further facilitated the mineralization and immobilization of Pb and Cd (Chen et al. 2023a). The active oxygen-containing functional groups on the biochar allowed the conversion of the more mobile Cr⁶⁺ to the less mobile Cr³⁺ by continuous electron transfer, resulting in the stabilization of heavy metal(loid)s (Dong et al. 2017). Biochar amendments not only act as electron mediators to

accelerate oxidation-reduction reactions between soil organic matter and biochar, but also promote the immobilization of heavy metal(loid)s in soil, reducing their toxicity and ultimately promoting the growth and reproduction of soil organisms (Saquing et al. 2016; Xu et al. 2019).

4.4 Heavy metal(loid)s immobilization

Heavy metal(loid)s have a negative impact on the growth, morphology, and activity of microbial populations, ultimately resulting in a reduction of both biomass and diversity (Roane and Pepper 1999). Heavy metal(loid)s such as Hg, Pb, Cd, and As serve no necessary function in the life cycle of organisms and can damage cell membranes, alter the specificity of enzymes, disrupt cellular functions, and even damage DNA structures (Bruins et al. 2000; Göhre and Paszkowski 2006). The toxicity of heavy metal(loid)s occurs through the displacement of essential metals from their natural binding sites or ligand interactions, as well as alterations to oxidative phosphorylation and conformational structure in osmotic equilibrium

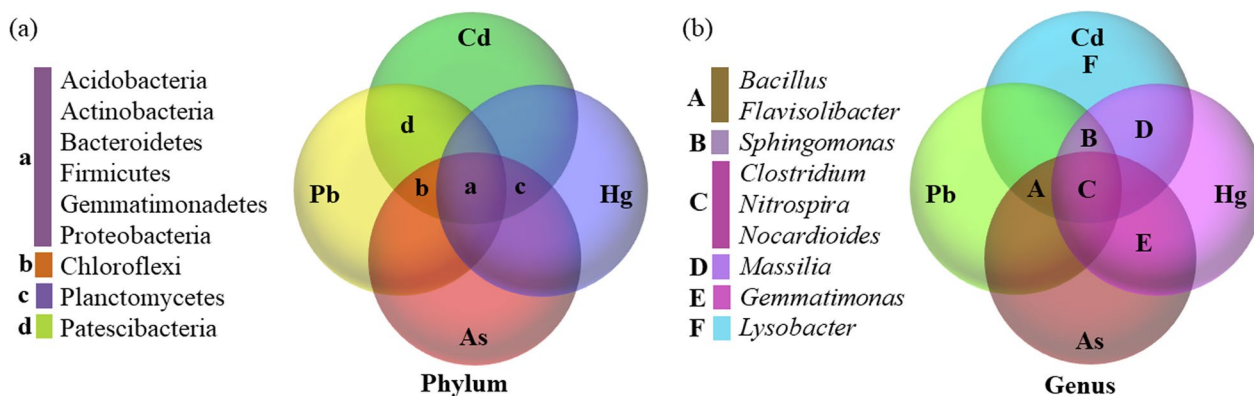


Fig. 4 The dominant bacterial communities in different heavy metal(loid)-contaminated soils at the **a** phylum level (a: As, Pb, Cd, and Hg; b: As, Pb, and Cd; c: As, Cd, and Hg; d: Pb and Cd) and **b** genus level (A: As, Pb, and Cd; B: Pb, Cd, and Hg; C (except Pb and Hg): As and Cd; D: Cd and Hg; E: As and Hg; F: Cd) after remediation with biochar amendments (Chang et al. 2019; Igalavithana et al. 2017; Irshad et al. 2022; Liu et al. 2020b, 2017b, 2022a; Ma et al. 2020; Qi et al. 2022; Tu et al. 2020; Wan et al. 2022; Wei et al. 2022; Wu et al. 2019a; Zhang et al. 2020a, 2021; Zhou et al. 2022)

(Bruins et al. 2000). Moreover, heavy metal(loid)s are harmful to microorganisms due to their long biological half-life, toxicity, and non-biodegradability (Abdu et al. 2016). The microbial abundance and community diversity of metal(loid) contaminated soils are significantly lower than those of clean soils due to heavy metal(loid) stress (Chang et al. 2019; Wan et al. 2022). The addition of biochar amendments to soil facilitates the stabilization of heavy metal(loid)s, reducing their bioavailability and mitigating stress to microorganisms, ultimately contributing to the growth and metabolism of microorganisms, and improving both their abundance and activity. Zhang et al. (2020a) discovered that the addition of Fe-Mn-Ce oxide biochar to As-contaminated soil not only reduced the bioavailable forms of As but also converted specifically and non-specifically bound forms of As to amorphous and crystalline hydrous oxide bound forms, created a microbial growth-friendly environment, and significantly impacted the relative abundance of Ascomycota, Gemmatimonadetes, and Acidobacteria at the phylum level. Figure 4 analyzes the changes in microbial population diversity and community structure after the addition of biochar amendments to soils contaminated with heavy metal(loid)s (mainly Pb, Cd, As, and Hg) in recent years.

In general, the relative abundance changes in dominant groups Acidobacteria, Actinobacteria, Bacteroidetes, Firmicutes, Gemmatimonadetes, and Proteobacteria at the phylum level are found in Pb, As, Cd, and Hg contaminated soils after the biochar amendments addition. Besides these dominant groups, the relative abundance changes in Chloroflexi and Patescibacteria are easily detected in Pb contaminated soils (Liu et al. 2022a; Wan et al. 2022), the relative abundance changes in Chloroflexi and Planctomycetes are easily monitored in As contaminated soils

(Irshad et al. 2022; Liu et al. 2017b; Zhang et al. 2020a), the relative abundance changes in Chloroflexi, Planctomycetes, and Patescibacteria are easily observed in Cd contaminated soils (Liu et al. 2020b, 2022a; Zhou et al. 2022), and the relative abundance changes in Planctomycetes are easily measured in Hg contaminated soils after the biochar amendments addition (Chang et al. 2019). At the genus level, the relative abundance changes in *Bacillus*, *Flavisolibacter*, *Sphingomonas*, *Clostridium*, *Nitrospira*, and *Nocardioides* are generally observed in Pb-contaminated soils after biochar addition (Liu et al. 2022a; Wei et al. 2022; Zhang et al. 2020a), while the relative abundance changes in *Bacillus*, *Flavisolibacter*, *Clostridium*, *Nitrospira*, *Nocardioides*, and *Gemmatimonas* are generally observed in As contaminated soils (Irshad et al. 2022; Liu et al. 2017b; Zhang et al. 2020a), and the relative abundance changes in *Bacillus*, *Flavisolibacter*, *Sphingomonas*, *Clostridium*, *Nitrospira*, *Nocardioides*, *Massilia*, and *Lysobacter* are generally detected in Cd contaminated soils (Liu et al. 2022a; Qi et al. 2022; Wu et al. 2019a; Zhou et al. 2022), while the relative abundance changes in *Sphingomonas*, *Clostridium*, *Nitrospira*, *Nocardioides*, *Massilia*, and *Gemmatimonas* are generally detected in Hg contaminated soils (Chang et al. 2019).

The addition of biochar amendments immobilizes heavy metal(loid)s, thereby reducing toxicity and stress on metal-sensitive microorganisms, resulting in an increase in the abundance and activity of microbial communities (Zhou et al. 2022). Liu et al. (2020b) found that nanoscale zero-valent iron-loaded biochar reduced leachability of Cd toxicity characteristic leaching procedure by 42% compared to the control and converted the labile Cd into the stable fraction, which increased the relative abundance of Firmicutes and Bacteroidetes by 33–90% and 9–88% at the phylum level, respectively,

Table 2 The literature statistics of the changes in the abundance of microbial populations in heavy metal(loid)-contaminated soils after the addition of biochar

Classification unit	Microorganisms	Number of papers countable	Changes of abundance of microbial populations		
			Increase	Decrease	No change
Phylum	Proteobacteria	9	1	7	1
	Bacteroidetes	8	4	3	1
	Firmicutes	7	4	3	0
	Actinobacteria	6	3	2	1
	Chloroflexi	5	2	2	1
	Acidobacteria	5	3	2	0
	Gemmatimonadetes	5	3	2	0
	Planctomycetes	4	2	1	0
	Verrucomicrobia	2	1	1	0
	Cyanobacteria	2	0	2	0
	Patescibacteria	2	0	2	0
	Bacillus	2	1	0	1
Genus	<i>Bacillus. sp</i>	8	6	2	0
	<i>Sphingomonas. sp</i>	5	1	3	1
	<i>Flavisolibacter. sp</i>	3	1	2	0
	<i>Lysobacter. sp</i>	3	2	1	0
	<i>Nitrospira. sp</i>	2	1	1	0
	<i>Massilia. sp</i>	2	0	1	0
	<i>Nocardioides. sp</i>	2	2	0	0

through reduced heavy metal(loid)s toxicity. In addition, many studies have found that applying biochar amendments to reduce heavy metal(loid) toxicity increases the relative abundance of genus-level *Bacillus*, which can survive in adverse soil conditions and are tolerant to heavy metal(loid)s (Irshad et al. 2022; Ma et al. 2020; Qi et al. 2022; Zhou et al. 2022). Although biochar amendments can help reduce heavy metal(loid)s in contaminated soil, they can also negatively impact the abundance and activity of certain microorganisms. Several studies have found that even though Proteobacteria can tolerate toxic heavy metal(loid)s, the relative abundance of Proteobacteria decreases after biochar amendments addition due to the competition between Proteobacteria and other microorganisms which are sensitive to heavy metal(loid)s and can grow rapidly after heavy metal(loid) stress reduction (Liu et al. 2020b, 2017b, 2022a; Zhang et al. 2020a). Fifty papers on biochar remediation of heavy metal(loid)s since 2017 were summarized, fifteen of which describe changes in microbial population abundance, and Table 2 counts the changes in microorganisms that co-occur in two or more papers. It is known from the statistics that the response of microbial population abundance to biochar is not static, and the change can be influenced by the type of soil, biochar and plant. For example, as a result of the addition of biochar, at the phylum level, the number of papers showing an increase in the relative

abundance of Bacteroidetes, Firmicutes, Actinobacteria, Acidobacteria, Gemmatimonadetes, Planctomycetes, and Bacillus is higher than the number of papers showing a decrease; the number of papers showing a decrease in the relative abundance of Proteobacteria, Cyanobacteria, and Patescibacteria is higher than the number of papers showing an increase. At the genus level, the number of papers showing an increase in the relative abundance of *Bacillus. Sp*, *Lysobacter. Sp*, and *Nocardioides. Sp* is higher than the number of papers showing a decrease; the number of papers showing a decrease in the relative abundance of *Sphingomonas. sp*, *Flavisolibacter. Sp*, and *Massilia. sp* is higher than the number of papers showing an increase. However, due to the limited number of data samples, the trends in microbial population abundance shown by this result may not be universally applicable and therefore this result is only informative.

4.5 Exogenous microorganisms import

The changes in microbial communities, abundance, and activity in soil contaminated with heavy metal(loid)s by biochar can be attributed to the incorporation of exogenous microorganisms carried by the biochar in addition to the physical, nutrient, and electronic support, and reduction in heavy metal(loid) toxicity that biochar provided to the microorganisms. Soil rhizosphere microorganisms usually do not grow well in soils contaminated

with heavy metal(loid)s due to nutrient deficiency and metal stress (Reddy and Cutright 2003). Some specific strains can adapt to the local environment and immobilize heavy metal(loid)s, and perform well in various contaminated sites (Ma et al. 2020). Biochar is considered an ideal carrier to facilitate the effective colonization of microorganisms and can be combined with specific microbial strains with bioremediation capabilities (Chen et al. 2019; Wu et al. 2019a). Therefore, combining biochar with microorganisms is an effective strategy for the remediation of soils contaminated with heavy metal(loid)s, which can immobilize heavy metal(loid)s via the adsorption of biochar, precipitation through microbial cell walls or exudates, and uptake by microorganisms (Li et al. 2018; Liu et al. 2018d; Pramanik et al. 2018). Hazrati et al. (2021) investigated that sewage sludge-derived biochar supported diverse microbial communities, which enhanced microbial activity and immobilized heavy metal(loid)s in Zn, Pb, and Cd contaminated soils. Ma et al. (2020) found that loading a novel Cd-immobilized strain *Bacillus sp.* onto biochar significantly increased the number of rhizosphere microorganisms and the proportion of relative abundance of the *Bacillus* genus, resulting in an 11.34% reduction in acetic acid-extractable Cd compared to the control. Although some studies found that biochar combined with specific strains could increase the relative abundance of specific strains in soils contaminated with heavy metals, the Shannon index microbial α -diversity decreased slightly, which could be due to competition between the inoculated strains and native microorganisms for ecological niches in the soil. Interestingly, Acidobacteria is being utilized as an indicator microorganism in the combination of biochar and microorganisms to remediate the soils contaminated with heavy metal(loid)s. In studies by Zhang et al. (2020a), Irshad et al. (2022), and Liu et al. (2017b), the relative abundance of Acidobacteria increased in the rhizosphere following the application of biochar without microorganisms. However, in studies by Liu et al. (2022a) and Chang et al. (2019), the relative abundance of Acidobacteria decreased after the addition of biochar loaded with microorganisms. These findings suggest that changes in community structure are due to competition between exogenously introduced and indigenous microorganisms in heavy metal(loid) contaminated soil (Wu et al. 2019a).

In addition, introducing microorganisms via microorganisms-loaded biochar can enhance the abundance of beneficial microorganisms and decrease the abundance of harmful microorganisms, ultimately improving the ecological stability of rhizosphere systems in heavy metal(loid) contaminated soils. Qi et al. (2022) remediated U and Cd contaminated soils by loading

microbial agents, which included *Citrobacter sp.*, *Bacillus cereus*, and *Bacillus subtilis* on biochar. The study revealed a decrease in the relative abundance of pathogenic bacteria, such as *Fusarium sp.* and *Alternaria sp.*, and an increase in ecologically beneficial bacteria, including *Lysobacter sp.*, *Bacillus sp.*, *Nitrosomonas sp.*, and *Nitrospira sp.* in the rhizosphere soils of vegetables. Many *Fusarium sp.* can be parasitic on multiple plants, causing plant root and stem rot in plants, and *Alternaria sp.* can lead to brown spot and early blight diseases in crops, which is the dominant pathogen (Budde-Rodriguez et al. 2022; Yao et al. 2017). Reducing the abundance of *Fusarium sp.* and *Alternaria sp.* can effectively decrease the risk of crop diseases. *Lysobacter sp.* is an important biocontrol microorganism that is antagonistic to nematodes of phytopathogenic fungi (Christensen and Cook 1978). *Bacillus sp.* can produce antibacterial and antifungal substances, such as lipopeptide antibiotics, which can control plant phytopathogens (Lanna-Filho et al. 2017). Therefore, biochar combined with microorganisms plays important roles in the immobilization of heavy metal(loid)s, improvement of microbial community structure, and stabilization of rhizosphere ecosystems.

5 Interactions between biochar amendments and root exudates in heavy metal(loid)-contaminated soils

Root exudates, which are produced by plant roots, rhizosphere microorganisms, and animals, play a critical role in promoting root-microorganism-soil interactions in the rhizosphere system (Rovira 1969). They can be categorized as follows: low-molecular-weight compounds, which include organic acids, carbohydrates, and some secondary metabolites (such as terpenoids and alkaloids); and high-molecular-weight exudates, which include enzymes and mucilage, as well as other compounds (Grayston et al. 1997; Jones et al. 2009; Pausch and Kuzyakov 2018; Rovira 1969). Studies have shown that root exudates can impact the physicochemical properties of rhizosphere fluids, such as pH and organic matter content, thereby affecting the mobility and bioavailability of heavy metal(loid)s in the rhizosphere soil (Layet et al. 2017; Medyńska-Juraszek et al. 2020). The interaction between biochar amendments and root exudates occurs in two ways: biochar amendments stimulate the production of root exudates, and in turn, root exudates influence the behavior of biochar amendments. The interactions involve three processes: physical adsorption, where root exudates are attracted to biochar amendments via electrostatic attraction and surface functional groups; chemisorption, which occurs through esterification reactions between -OH and -COOH in root exudates and biochar

amendments; and oxidation-reduction reactions between biochar amendments and root exudates. Studies have found that oxygen-containing functional groups in biochar amendments in the rhizosphere are more abundant than those in fresh biochar amendments due to the adsorption of root exudates (Qian and Chen 2014; Ren et al. 2016; Trigo et al. 2014). This section focuses on the interactions between biochar amendments and primary root exudates (enzymes and low-molecular-weight organic acids (LMWOAs)) in heavy metal(loid)-contaminated soil.

5.1 Rhizosphere enzymes

The rhizosphere is an important enzymatic hotspot (Kuzyakov and Blagodatskaya 2015). Soil enzymes act as natural catalysts for various soil processes related to the decomposition of organic matter, leading to the release and accessibility of minerals to the rhizosphere (Ali et al. 2019; Haddad and Lemanowicz 2021). Enzyme activity reflects the intensity of biological processes and serves as an indicator of soil health and the mineralization of organic nutrients, which are typically correlated with the physical and chemical properties of the soil. There are generally three types of enzymes based on their location and role in the rhizosphere: (1) intracellular enzymes, which are located in soil organisms (microorganisms, animals, or roots) and are mainly involved in intracellular reactions of soil organisms; (2) extracellular enzymes, which are produced and released by living soil organisms and mainly catalyze the decomposition of macromolecules or biopolymers in the environment, and (3) enzymes located outside of cells due to the death or damage of soil organisms, which are always immobilized in organic mineral complexes (Burns 1982; Igalavithana et al. 2017). Phosphatase and urease are hydrolytic enzyme systems that are closely associated with the N and P cycles in soil, respectively, with phosphatase activity being related to total phosphorus and urease acting as the catalyst for the hydrolysis of urea to carbon dioxide and water (Jain et al. 2016; Wang et al. 2018). Sucrase, functioning as a hydrolase, plays a vital role in the carbon cycle of the soil system by hydrolyzing sucrose to provide energy for soil organisms and has a significant relationship with the utilization of soil nutrients (Alam et al. 2018; Liu et al. 2015). Hydrogen peroxide causes the oxidation of sulfhydryl groups in protein molecules, disrupting the normal function of cells (Liu et al. 2020b). Catalase is an oxidoreductase enzyme that decomposes hydrogen peroxide in the soil, maintaining normal microbial activities, and increasing the ability of microorganisms to withstand harsh environments (Feng et al. 2022; Sun et al. 2016b). Dehydrogenase acts as a proton acceptor in oxidation reactions, and it mainly controls the

bio-oxidation of organic matter in soil, thereby reflecting the overall microbial activity (Burns et al. 2013; Igalavithana et al. 2017).

Biochar amendments remediate heavy metal(loid) contaminated soil, enhance soil physicochemical and biological properties, and consequently improve soil enzyme activity (Moore et al. 2018). Higher enzyme activity indicates a higher soil quality, while lower enzyme activity indicates an unhealthy change in soil biological processes. The addition of biochar amendments to contaminated soil is an effective option for improving enzyme activity and has a positive impact on soil health, e.g., since biochar amendments have powerful adsorption properties, the adsorption of reaction substrates by biochar amendments contributes to enzymatic reactions; moreover, biochar amendments can also sorb a portion of enzymes, protecting them from other harmful environmental factors and increasing the retention time of enzymes (Jain et al. 2016; Ji et al. 2022). However, biochar amendments can also harm enzyme activity, e.g., the adsorption of organic and inorganic substances by biochar blocks enzyme reaction sites (Ali et al. 2020; Haddad and Lemanowicz 2021). Therefore, the adsorption properties of biochar amendments also increase the complexity of soil enzymes. The impact of biochar amendments on enzyme activity is diverse and depends on soil properties, contaminant characteristics and concentrations, biochar amendment dosage, and mineral composition. Jain et al. (2016) used principal component analysis to investigate the impact of biochar, pH, and mineral solubility on enzyme activity during mine tailings remediation by biochar-Fe complex, revealing that enzyme and biochar interaction primarily influenced the activities of β -glucosidase, alkaline phosphatase, phenol oxidase, and dehydrogenase, whereas pH controlled the activities of alkaline phosphatase, β -glucosidase, and cellulase urease, and mineral solubility affected the activities of acid phosphatase and aryl sulfatase. Therefore, the effects of biochar amendments on enzyme activities were discussed from different viewpoints, including counteracting heavy metal(loid)s toxicity to soil organisms, enhancing soil bio-nutrition, improving soil bio-activity, and providing shelter.

5.1.1 Reduction of heavy metal(loid) toxicity

Biochar amendments regulate the enzymes in contaminated soil by reducing the toxicity of heavy metal(loid)s. Stimulation of heavy metal(loid)s causes damage to electron transfer processes in soil organisms occurring at the substrate end of the respiratory chain in the inner mitochondrial membrane, which disrupts the balance between pro-oxidant and antioxidant homeostasis, resulting in oxidative stress with the release of large

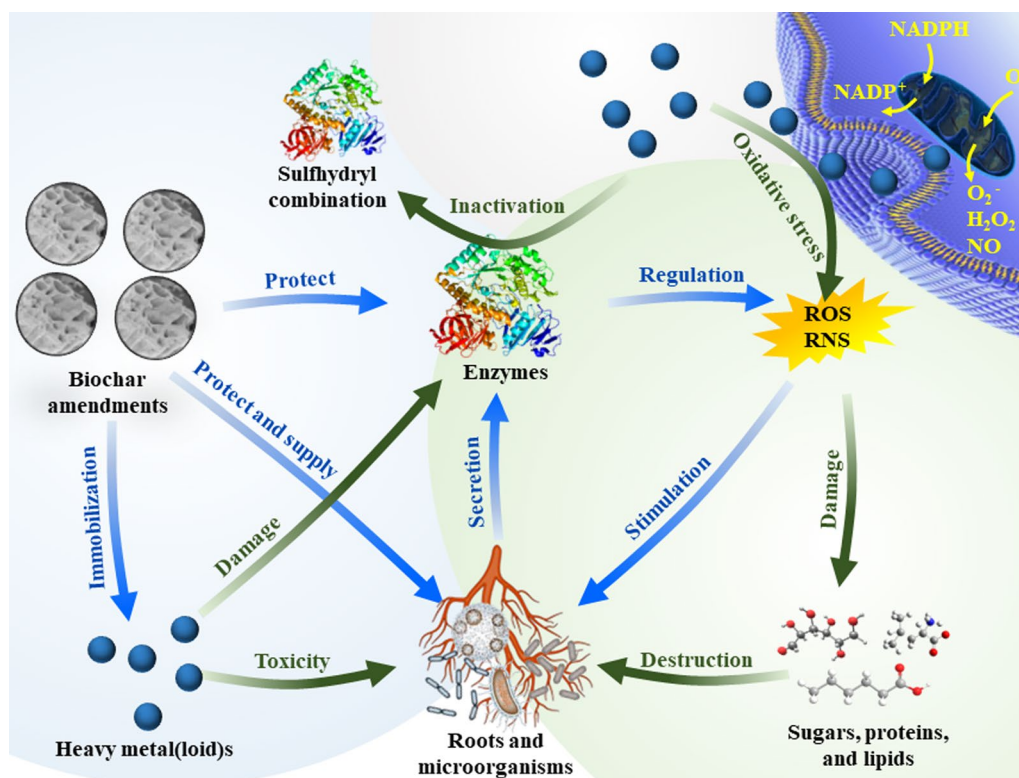


Fig. 5 Regulation of rhizosphere enzymes by biochar amendments in heavy metal(loid)-contaminated soils (ROS: reactive oxygen species, RNS: reactive nitrogen species) (Bhaduri and Fulekar 2012; Ojuederie and Babalola 2017)

amounts of free radicals (reactive oxygen species such as hydroxyl radical ($\cdot OH$), superoxide anion ($\cdot O_2^-$) and hydrogen peroxide (H_2O_2); and reactive nitrogen species such as nitrogen dioxide ($\cdot NO_2$), nitric oxide ($\cdot NO$) and peroxy nitrite ($\cdot ONOO^-$)) (Fryzova et al. 2017; Khan et al. 2022; Paithankar et al. 2021; Stohs and Bagchi 1995). Excess free radicals damage transcription factors, growth factors, sugars, nucleic acids, proteins, and lipids while stimulating soil organisms to produce corresponding antioxidant enzymes that resist free radical damage, such as catalase, superoxide dismutase, and glutathione peroxidase (Abdelgawad et al. 2020; Rahman 2020). Therefore, the oxidative stress of soil organisms is an important factor in the effect of heavy metal(loid)s on the alteration of soil enzymes. Applying biochar amendments to heavy metal(loid) contaminated soil enhances antioxidant enzyme activity, which mitigates excessive oxidation induced by heavy metal(loid)s. Zhou et al. (2022) showed that biochar stimulated the production of indole acetic acid by specific bacterial taxa (*Flavisolibacter* and *Bacillus* spp.) and increased the activity of superoxide dismutase and catalase in Cd-contaminated soil, thereby reducing malondialdehyde and hydrogen peroxide contents and ameliorating the Cd-induced oxidative damage.

In addition, heavy metal(loid)s (especially Pb, Cd, As, and Hg) display a high affinity for sulfhydryl-containing proteins and enzymes responsible for functional cellular defense mechanisms (e.g., regulation of excess free radicals) (Aponte et al. 2020). The combination of heavy metal(loid)s with sulfhydryl groups of enzymes to affect the catalytic action or structural integrity is another mechanism of inhibition of heavy metal(loid)s on enzyme activity (Poole and Gadd 1989). Moreover, some essential metals, such as Co, Cu, and Ni, serve as micronutrients and are components of various enzymes, which can be replaced and compete with the other heavy metal(loid)s for binding to the thiol-containing groups of enzymes, causing changes in the conformational structure of proteins and nucleic acids, thus inactivating the enzymes (Bruins et al. 2000) (Fig. 5). Biochar amendments can mitigate heavy metal(loid) toxicity by preventing their binding to enzyme active sites, such as sulfhydryl groups in urease, and consequently inhibiting the formation of metal sulfides, thus preserving the activity of urease (Liu et al. 2018c). Furthermore, biochar amendments alleviate heavy metal(loid) stress in contaminated soil by immobilizing heavy metal(loid)s through adsorption or the interaction between heavy metal(loid)s and organic matter

functional groups in biochar (e.g., carboxylic acids, phenolic and aliphatic hydroxyl groups, and amino groups) to form organic-heavy metal(loid)s complexes, thereby reducing their biological effects and ultimately enhancing soil enzyme activity via detoxification (Naeem et al. 2021; Shahbaz et al. 2019; Turan 2019).

The impact of biochar amendments on soil enzyme activity varies based on factors such as biochar amendments dose, pH, organic matter, temperature, and remediation time, as demonstrated by various studies (Elzobair et al. 2016). Ali et al. (2020) showed that low doses of biochar (1% and 2.5%) increased dehydrogenase activity in Zn, and Cd contaminated soils, while higher doses of biochar (5% and 10%) inhibited the enzyme activity. Enzyme activity can be promoted by low-dose biochar by immobilizing heavy metal(loid)s and providing a suitable environment for microbial growth while higher doses of biochar result in high soil pH, which results in the inhibition of enzyme activity (Ali et al. 2020; Gong et al. 2019). Tu et al. (2020) found that the urease and catalase activities gradually decreased on the 45th day and then increased at the end of incubation on the 75th day of remediation of Cd and Cu contaminated soils, which was due to the inhibitory effect of high Cd and Cu concentrations at the early stage and the immobilization of heavy metal(loid)s at the later stage. In addition, the positive effects of biochar remediation vary under different conditions, which are related to the type of enzyme, soil properties, etc. It was found that the activities of arginase and urease were increased by 25.5% and 105%, respectively, in clay soils contaminated with Pb, Cd, and Ni by using biochar, while their activities increased by 37.1% and 83.3% in sandy soils, respectively (Haddad and Lemanic 2021). However, the adsorption of inorganic and organic matter in biochar and the blocking of reaction sites by biochar result in the inhibition of some enzyme activities (Bailey et al. 2011; Lehmann et al. 2011). It was found that leucine aminopeptidase, alanine aminopeptidase, phosphomonoesterase, phosphodiesterase, β -N-acetyl-D-glucosaminidase, cellobiosidase, β -xylosidase, β -glucosidase, α -glucosidase, and arylsulfatase were poorly affected by biochar (Niemi et al. 2015).

5.1.2 Regulation of microorganism and plant root

Biochar amendments significantly alter the biomass and activity of soil microorganisms and root growth, which play important roles in regulating soil enzyme activity. Rhizosphere microorganisms and roots employ enzyme production and release as a nutrient acquisition strategy, with higher enzyme expression observed in nutrient-deficient conditions (Harder and Dijkhuizen 1983). However, when nutrients are abundant, rhizosphere microorganisms and roots regulate the exudate levels of

different enzymes. For example, all living microbial cells secrete dehydrogenase enzymes which can be indicative of overall microbial activity (Moeskops et al. 2010). In the study by Igalavithana et al. (2017), the addition of biochar provided microbes with a readily available C source and a significant increase in the abundance of each microbial population was subsequently observed, as well as a significant improvement in the composition and structure of the microbial community, which ultimately led to a significant increase in dehydrogenase activity. Irshad et al. (2022) found that goethite-modified biochar resulted in a significant increase in soil enzyme activity by altering soil nutrients, particularly improving phosphorus and organic matter content, which led to alterations in the soil bacterial community. Pandey et al. (2022) investigated that the higher microbial activity, resulting from increased soil fertility due to the addition of higher C, P, and K contents of Lantana biochar, led to higher activities of glucosidase, urease, dehydrogenase, and alkaline phosphatase compared to lower C, P, and K contents of Parthenium biochar and the control group in heavy metal(loid) contaminated soil. As shown by another study, the application of woody biochar to Au and Zn/Pb contaminated soils improved soil urease and β -glucosidase activities by providing a source of energy and nutrients (C, N, P, and K) for microorganisms (Ali et al. 2019). These researches indicate that biochar amendments not only reduce heavy metal(loid) toxicity through immobilization but also enhance soil microorganism activity by providing colonization sites and increasing soil nutrient levels (e.g., C, N, P, K, and Mg), resulting in increased overall soil enzyme activity (Lehmann et al. 2011).

In addition, the extent of the rhizosphere is determined by root hairs and root radius, which strongly influence enzyme activity within the rhizosphere. Root hairs significantly enhance root surface area, facilitating critical functions such as water and nutrient uptake, microorganism interactions, and regulation of rhizosphere properties and composition through exudate secretion (Ma et al. 2018). The growth, death, and release of exudates from root hairs stimulate microbial activity and further influence the enzyme dynamics such as accelerated substrate turnover (Asmar et al. 1994). Ma et al. (2018) showed that β -glucosidase in the hairy regions of wheat roots has a 1.5 times broader activity area and a 2 times higher substrate turnover rate than in hairless regions, and the extent of the rhizosphere in roots of plants with thin and long root hairs (wheat) was 1.5–2 times wider and had 2–8 times higher enzyme activity than plants without thin and long root hairs (maize, lentil, and lupine). The application of biochar in heavy metal(loid) contaminated soils had a significant effect on plant roots. It was found

that in the application of biochar in soil contaminated with Cd, Pb and Ni, the higher the addition of biochar within the appropriate range, the more developed and widespread the plant root system, and the less inhibitory effect of heavy metal(loid)s on enzyme activities (urease and arginase) (Haddad and Lemanowicz 2021). Xiang et al. (2017) conducted a meta-analysis of 136 articles in 2018 and showed that the root volume, root biomass, root length, surface area, root diameter, and root tip number increased by 29%, 32%, 52%, 39%, 9.9%, and 17% after biochar amendment. Ibrahim et al. (2022) found that Mango, Casuarina, and Salix biochar all increased root biomass in soil contaminated with Co, Cd, Cu, Cr, Pb, Ni, and Zn. In the study by Zhu et al. (2022a), the combination of biofertilizer and biochar improved cotton rhizosphere resistance to Cd stress by regulating phenylalanine metabolism and ABC transporter pathways, which increased taproot and lateral root activity, as well as superoxide dismutase and peroxidase activities in Cd contaminated soils.

5.1.3 Adjustment of rhizosphere pH

The addition of biochar amendments, which forms anoxic microdomains and depletes H⁺ content through the presence of silicates, carbonates, and bicarbonates, has been suggested by some studies as a method for increasing enzyme activity by increasing soil pH (Harter et al. 2014; Liu et al. 2020a). In addition, the increase in precipitation of inorganic salts due to the increase in pH after the soil is remediated by biochar amendments, which reduces the toxicity of soluble salts (e.g., possibly creating reverse osmotic pressure that displaces water from microorganisms) produced by microbial decomposition of organic matter, and this is another reason why the increased pH of the soil can improve enzyme activity (Liu et al. 2020a). Chen et al. (2017a) found that the dairy manure and rice straw-derived biochars increased soil pH, denitrification reductase activity, and functional gene abundance while decreasing Cd bioavailability in Cd contaminated soil. Liu et al. (2020c) found that in Cd contaminated soil, the manure-derived biochar increased soil pH, decreased the acid-soluble Cr, and resulted in higher N-acetylglucosaminidase and β -glucosidase activities compared to the control. However, the decrease in enzyme activity at higher addition rates of biochar amendments may be attributed to either the toxicity of biochar or the excessive adsorption of substrates or enzymes on the porous structures. Bandara et al. (2019) reported that alkaline phosphatase and convertase activities decreased with increasing application rates of biochar and compost (up to 5% w/w). Additionally, the addition

of 5% (w/w) biochar obtained from 700 °C carbonization to serpentine soil significantly reduced the activities of dehydrogenase, polyphenol oxidase, and catalase (Bandara et al. 2017). Furthermore, the difference in the effect of soil pH on enzymes may be attributed to the presence of dominant microorganisms under acidic and alkaline conditions (Turner and Haygarth 2005). Normally, an increase in soil pH generally enhances alkaline phosphatase activity and decreases acid phosphatase activity (George et al. 2002). Application of biochar amendments causing a change in soil pH from acidic to alkaline can result in a shift in the dominant microbial population, leading to a corresponding change in phosphatase activity.

5.2 Low-molecular-weight organic acids

Root exudates play a crucial role in sustaining the activity of the soil rhizosphere system and modifying the bioavailability and mobility of heavy metal(loid)s in soil, contributing to the matter cycle (Martin et al. 2014). Low-molecular-weight organic acids such as malic acid, acetic acid, citric acid, oxalic acid, tartaric acid, fumaric acid, uronic acid, etc., are typical root exudates that significantly contribute to the rhizosphere effects (Jones 1998; Liu et al. 2017a). Biochar amendments can adsorb LMWOAs, thereby increasing nutrient competition between plants and microorganisms and promoting the release of LMWOAs by regulating gene expression (Joseph et al. 2010). In addition, biochar amendments can influence the production of root exudates by immobilizing heavy metal(loid)s and reducing their bioavailability. Therefore, this section mainly discusses the interactions between biochar amendments, LMWOAs, and heavy metal(loid)s in rhizosphere soils.

5.2.1 Regulation of genes over-expression

Root exudates can bind and/or attach heavy metal(loid)s to the cell wall, restricting their entry into the cell and reducing their mobility in the soil (Ghori et al. 2019; Hossein et al. 2012). The LMWOAs can form complexes with heavy metal(loid)s and affect the bioavailability of heavy metal(loid)s in the soil (Chen et al. 2017b). Ligands present in root exudates such as oxalic acid, acetic acid, citric acid, tartaric acid, uronic acid, fumaric acid, and polysaccharides can form complexes with Pb, thereby affecting its mobility and bioavailability in soil (Ghori et al. 2019; Li et al. 2019d). Under specific stress conditions in the rhizosphere system, such as nutrient deficiency, heavy metal(loid) toxicity, and environmental changes, gene expression of the MATE (e.g., maize ZmMATE1 gene) and ALMAT (e.g., soybean GmALMT1 gene) protein families are upregulated in the root, promoting the

exudation of citric acid, malic acid, and other organic acid compounds (Zhang et al. 2022). Moreover, biochar amendments act as a stress that can promote the production and efflux of LMWOAs from plant roots (Akhter et al. 2015; Bais et al. 2006). The composition of root exudates and consequently the microorganisms and their ability to biodegrade heavy metal(loid)s varied with the source, type, and concentration of biochar amendments (Akhter et al. 2015). Pei et al. (2020) found that the exudate levels of indole acetic acid, abscisic acid, and amino acid significantly increased with the biochar addition in rice roots. Cheng et al. (2018) reported that biochar resulted in the overexpression of the ZmMATE1 gene in maize, which increased the production of LMWOAs. The MATE protein mediates the transport of citrate and flavonoids, which is also involved in the detoxification of exogenous agents (e.g., heavy metal(loid)s) and endogenous secondary metabolites (Zhu et al. 2016). Sun et al. (2020) also found that the response to LMWOAs was associated with the transcript levels of the ZmMATE1 and ZmMATE2 genes, and the expression of the ZmMATE1 was upregulated by the addition of straw biochar, which positively correlated with increases in aconitic acid, fumarate, and malonate compared to the control. However, there are fewer studies targeting the direct rhizosphere relationship between biochar amendments, LMWOAs, and heavy metal(loid)s in contaminated soils, and how biochar amendments affect gene expression in the presence of heavy metal(loid)s is an area that needs further research.

5.2.2 Adjustment of soil pH

The changes in pH caused by root exudates, especially LMWOAs, are a critical mechanism affecting the solubility of heavy metal(loid)s in the rhizosphere (Houben et al. 2014). Physiologically, most plants regulate the toxicity of heavy metal(loid)s by root exudates (Chopala et al. 2014). In the phytoremediation process, tolerant plants dissolve heavy metal(loid) oxides and convert them to bioavailable forms for plants under high levels of heavy metal(loid) stress by secreting LMWOAs (Huang et al. 2017; Qiao et al. 2020). Lu et al. (2007) reported that under Cd stress, mangroves with high heavy metal(loid) retention capacity secreted more than double the number of LMWOAs by roots compared to the control, resulting in a reduction of 0.2–0.5 units in the pH of the rhizosphere soil compared to the bulk soil, and a positive correlation between the total amount of LMWOAs and the proportions of Cd bound to carbonate and exchangeable Cd. In addition, the application of biochar amendments alters the rhizosphere response to soil pH, soil nutrients, and microbial communities, which in turn affects the transformation, mobility, and bioavailability of heavy

metal(loid)s (Houben and Sonnet 2015; Park et al. 2011). Achor et al. (2020) investigated the chemical behavior of heavy metal(loid)s in rhizosphere soils in the presence of biochar and LMWOAs, it was found that biochar partially inhibited the mobility of Cd, Cu, and Pb driven by LMWOAs (oxalic, citric, and malic acids), except for the absence of inhibition of Cd release by biochar under citric acid treatment. The liming effect of biochar amendments is the main mechanism for inhibiting heavy metal migration by LMWOAs, despite their ability to protonate the surface of biochar amendments, which can deactivate or reduce their adsorption capacity for heavy metal(loid)s (Achor et al. 2020). However, the mobility and bioavailability of heavy metal(loid)s in the soil can increase again if the alkalinity of the biochar amendments is not sufficient to neutralize the acidity of the LMWOAs (Wang et al. 2022a). The study by Houben and Sonnet (2015) found that 5% biochar significantly reduced exchangeable heavy metal(loid)s and facilitated the transition from the exchangeable to the carbonate bound state in Cd, Pb, and Zn contaminated soils, but the heavy metal(loid)s were remobilized due to the subsequent acidification of root-generated LMWOAs that neutralized the liming effect of biochar. This is consistent with the trend observed in several studies where liming of neutralizing LMWOAs produced by biochar increases with increased application of biochar, resulting in immobilization of metal(loid)s and reduced uptake of heavy metal(loid)s by plants (Al-Wabel et al. 2015; Kim et al. 2015; Rees et al. 2015).

5.2.3 As electron acceptor or donor

The electron transfer behavior of biochar amendments has been extensively studied in the geochemistry and redox reactions of heavy metal(loid) contaminants (Chen et al. 2018b; Kappler et al. 2014; Yuan et al. 2017). The electron transfer between biochar amendments and LMWOAs is generated by the repeated reduction and oxidation processes on the oxygen-containing functional groups (e.g., -OH and -C=O) of their surfaces, which can change the composition of surface groups of biochar amendments (Deng and Stone 1996; Klüpfel et al. 2014; Saquing et al. 2016). Xu et al. (2019) investigated the impact of seven LMWOAs on the interaction of peanut shell biochar and its electron shuttle effect on Cr(VI) reduction and found that the adsorption and interaction of biochar with LMWOAs resulted in redox reactions that modified the Cr(VI) reduction-related functional groups (-C=O and C-O) on the biochar surface. LMWOAs with more reducing functional groups (-OH) or lower redox potential may reduce biochar amendments (LMWOA-CH₂OH + BC-COOH → LMWOA-C=O + BC-CH₂OH + H₂O),

while LMWOAs with more oxidizing functional groups (-COOH) and higher redox potential may lead to oxidation processes ($\text{LMWOA-C=O} + \text{BC-CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{LMWOA-CH}_2\text{OH} + \text{BC-COOH}$) (Xu et al. 2019). Sugars, LMWOAs, and amino acids are the main sources of soil carbon, which not only provide abundantly available C sources for microorganisms but also serve as electron donors in soil electron transfer activities (Kamilova et al. 2006; Zhalnina et al. 2018). Therefore, biochar amendments have the ability to accept electrons from LMWOAs in soil and transfer them to the receptor (heavy metal(loid)s) (Fig. 3) (Deng and Stone 1996; Mu et al. 2018).

5.2.4 Interaction between LMWOAs and biochar

The adsorption mechanisms between LMWOAs and biochar amendments include the formation of internal and external spherical surface complexes, cation bridge bonding, and ligand exchange, which depend on the pH of the solution, and the molecular structure of the LMWOAs (Sokolova 2020). In acidic environments, large amounts of LMWOAs were adsorbed on the biochar, resulting in an increase in bridge (hydrogen) bonding interactions on the biochar surface and a decrease in interparticle repulsion. This is particularly evident in nano-biochar, where aggregation of nano-biochar occurs due to LMWOAs, reducing the mobility of nano-biochar in the rhizosphere soil (Li et al. 2019a; Wang et al. 2022b; Zhang et al. 2010). In addition, LMWOAs and the carboxyl groups (COO⁻) and ionized protons (H⁺) contained in LMWOAs can dissolve minerals (such as CaCO₃, Ca₂Mg(PO₄)₂, CaMg(CO₃)₂, AlPO₄, Pb₂P₂O₇, and K₂Mg(PO₃)₄) contained in soil and biochar amendments, which promotes the release of plant nutrients (e.g., PO₄³⁻, SO₄²⁻, K⁺, Ca²⁺, Mg²⁺, and Fe³⁺) and significantly improves soil fertility (Cao et al. 2009; Liu et al. 2017a; Wang et al. 2015; Yuan et al. 2011). However, it can also dissolve and release toxic metals from rhizosphere soils (Jones 1998). Liu et al. (2017a) found that the erosion of biochar by acetic, malic, and citric acids in the rhizosphere increased the risk of heavy metal(loid)s being released to the environment by mobilizing them from biochar to the aqueous phase. In addition, the adsorption of LMWOAs on biochar amendments promotes the development of the specific surface area and pore structure of biochar amendments, but its effects are closely related to the original pore characteristics (Sun et al. 2016a). Deashing by LMWOAs improves the pore size of biochar amendments by releasing minerals that are dissolved in the biochar amendments (Lou et al. 2011). In particular, low-temperature biochar can release more organic and dissolved inorganic fractions, and the mechanical strength determines that low-temperature biochar undergoes

easier physical erosion during washing, leading to more macropore formation (Braadbaart et al. 2009; Sun et al. 2016a). Liu et al. (2017a) found that LMWOAs also induced pore widening by deashing in high-temperature biochar, and caused fractures of the carbon skeleton in 300 °C and 600 °C biochar, which may be due to the physical stress (e.g., swelling) caused by water adsorption into the pores or interstices within the sheets on the biochar structure (Spokas et al. 2014).

6 Challenges and future perspectives

There are some challenges in the application of biochar in the remediation of heavy metal(loid) contaminated soils and its impact on the soil rhizosphere, such as, how to ensure the stability of the properties of biochar, the effect of overuse of biochar on the rhizosphere microorganisms and plants in the soil, and the effect of the toxic substances (such as heavy metal(loid)s) in biochar on the soil by the use of biochar. The properties of biochar are affected by the type of feedstock, preparation temperature, heating rate, residence time, and modification method (Wang et al. 2020d). The organic matter of different types of feedstocks varies widely, for example, agricultural and forest wastes consist mainly of cellulose, lignin, and hemicellulose, while manure contains not only cellulose and hemicellulose, but also fats, proteins, organic acids, and humic acids (Oliveira et al. 2017; Wang et al. 2017). Due to the different sources of raw materials, the properties of the resulting biochar vary considerably. In addition, even the biochar produced from the same raw material may have different correspondences depending on the nature of the soil; even if the same production equipment is used, it is difficult to maintain the same characteristics of biochar produced from different batches of the same raw material. In addition, preparation temperature, heating rate, and residence time also affect the specific surface area, pore size structure, pH, cation exchange capacity, surface functional groups, and mineral content of biochar. Therefore, the properties of biochar are largely influenced by anthropogenic and non-anthropogenic factors, which can lead to difficulties in standardizing the stability of biochar on soil heavy metal(loid)s as well as its effect on the rhizosphere, so specific methods should be discussed when investigating the remediation of heavy metal(loid) contaminated soils by biochar as well as its effect on the rhizosphere.

A large number of studies have appeared in recent years on the application of biochar to remediate heavy metal(loid) contaminated soils, and in some of these studies, the amount of biochar used was much higher than the potential realistic need. Wang et al. (2020d) summarized 73 recently published research papers on the remediation of heavy metal(loid)s in soils

with biochar and found that although most of the articles had a biochar use rate between 1% and 5%, there were still 15.7% of the articles that had a biochar use rate greater than 10%. Appropriate amounts of biochar can improve soil physicochemical properties, such as increasing soil nutrient content and promoting plant growth, but overuse of biochar increases the risk of soil alkalization, and an imbalance in the nutrient content of biochar can reduce seed germination (Beesley et al. 2013; Liu et al. 2023). Therefore, overuse of biochar may have negative long-term effects on soil or rhizosphere plants and microorganisms. Thus, when remediating heavy metal(loid) contaminated soils with biochar, it is important to consider the effects of biochar dosage on the rhizosphere in the soil to avoid negative effects of over-application that are detrimental to plants and microorganisms.

Some straw harvested from metal(loid) contaminated farmland also contains heavy metal(loid)s, and animal manure from the overuse of additives in animal feed also contains high levels of heavy metal(loid)s, in addition, sewage sludge also contains large amounts of heavy metal(loid)s (Li et al. 2019b; Mierzwa-Hersztek et al.

2018; Shen et al. 2016). Therefore, the application of these biochar, which are enriched with a large number of heavy metal(loid)s in the raw materials, to soil remediation will not only exacerbate the release of heavy metal(loid)s, but also have an inhibitory effect on rhizosphere plants and microorganisms (Shen et al. 2016). Therefore, when considering soil remediation and its effects on the rhizosphere, the feedstock and the biochar modification process should be considered simultaneously to determine whether new contaminants will be introduced.

7 Conclusion

Achieving the UN’s SDGs and sustaining life on Earth requires the search for green and sustainable remediation. The application of biochar amendments to soil contaminated with heavy metal(loid)s is a highly appropriate solution that utilizes waste resources, improves soil health, reduces CO₂ emissions, and generates positive social, economic, and environmental impacts (Fig. 6). Based on the utilization of waste resources, biomass wastes (including forest waste, livestock waste, agricultural and garden waste, and industrial waste) are recovered and carbonized to produce biochar, energy, and bio-products (including bio-gas, bio-oil, and energy). Biochar is used for soil remediation, which reduces heavy metal(loid)s and improves soil properties (N, P, K) and soil organisms. This process leads to plant growth, which produces products and contributes to human health. The entire cycle is sustainable, with zero carbon emissions and efficient waste resource utilization.

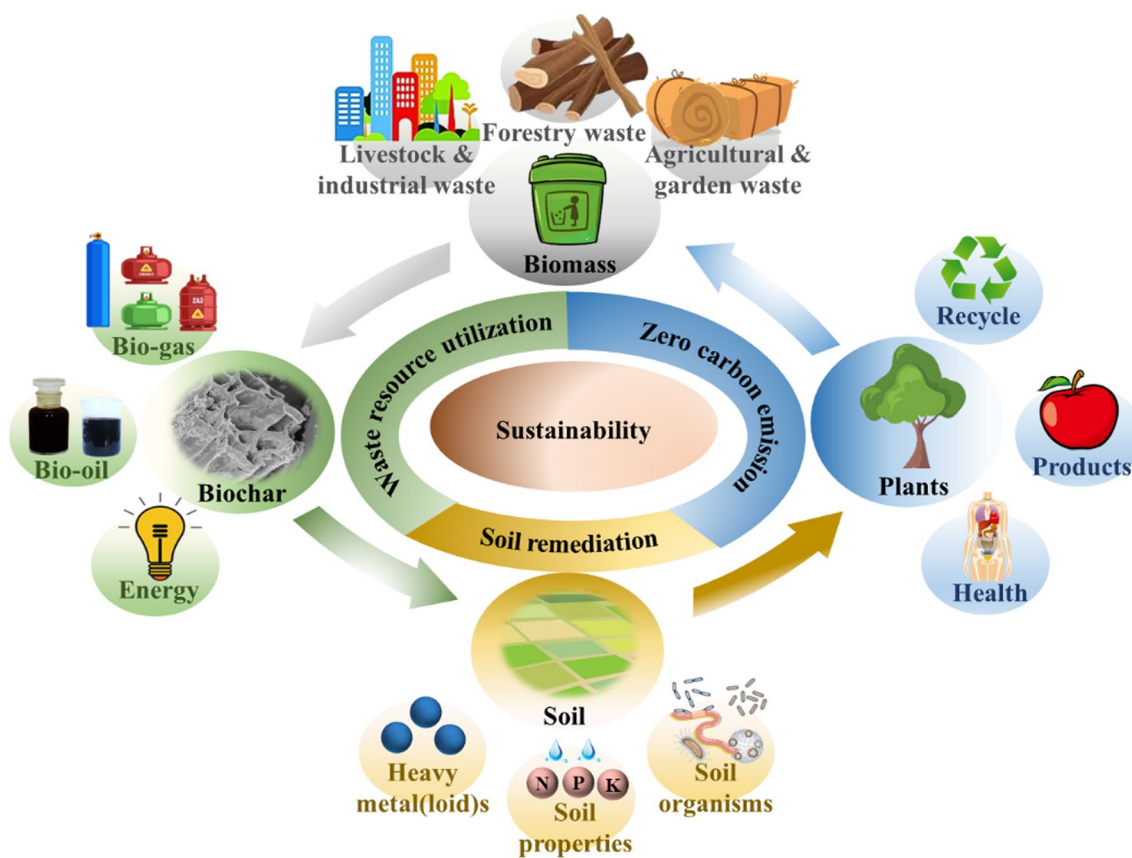


Fig. 6 Sustainable cycling of biomass, biochar amendments, soil, and plants in the environment

and co-products (e.g., bio-oil, bio-gas). This review presents recent research on the application of biochar amendments in the remediation of soil contaminated with heavy metal(loid)s. Three types of biochar amendments, raw, functional, and co-composite, have been studied. Biochar amendments have been found to immobilize heavy metal(loid)s and regulate the physical-chemical properties of the rhizosphere, such as regulating soil pH, increasing soil fertility, water-holding capacity and soil biomass, and promoting the activity of soil organisms. Furthermore, unique physicochemical properties of biochar amendments have been shown to improve the rhizosphere microbial community structure and activity by providing colonization sites, nutrients, and electronic support. Interactions between biochar and root exudates, including enzymes and LMWOAs, have also been observed. These interactions have the potential metal(loid)s toxicity, promote rhizosphere biomass activity, regulate pH, provide physical protection, regulate gene expression, and support electron transfer from biochar to root exudates in soil. The application of biochar amendments has been found to restore the health of contaminated soils, reduce the bioavailability of heavy metal(loid)s, and increase the utilization value for plants. This sustainable cycle can also generate organic waste that can be returned to the cycle, providing social and economic benefits.

Based on the current understanding of the interactions between biochar amendments, heavy metal(loid)s, and the rhizosphere in soil remediation, we propose further research as follows: (1) investigating the long-term stability and rhizosphere microbial dynamics of biochar in heavy metal(loid) contaminated soil remediation; (2) studying the variations in interactions between biochar and rhizosphere microorganisms under different heavy metal(loid)s; (3) examining the direct interaction between biochar and LMWOAs in heavy metal(loid) contaminated soil; and (4) exploring the mechanism by which microorganisms combined with biochar affect the relative abundance of specific species (such as Acidobacteria) in heavy metal(loid) contaminated soil.

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Author contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by CF, YC, QZ, NY, XC, XY, SS, YC, and YSO. The first draft of the manuscript was written by CF and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests

The authors declare that they have no known competing financial interests or personal relationships.

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