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Biochar for the Mitigation of Metal/Metalloid Stress in Plants

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Abstract

Metal(loid) pollution has become one of the most pressing environmental issues, threatening all living organisms. Metal(loid) stress adversely impacts plant growth, physiology, and overall productivity. Numerous physicochemical approaches have been developed and employed to counteract and reduce the detrimental effects of metal(loid)s. However, these methods have raised environmental concerns, leading to questions about their appropriateness and efficacy. Consequently, alternative and eco-friendly solutions, such as the application of biochar, have gained prominence. Biochar is a carbon-rich material derived from the pyrolysis and hydrothermal processes of various organic materials. Due to its exceptional physicochemical properties, biochar is believed to enhance soil quality and fertility. Several global studies have underscored the positive role of biochar in reducing the uptake of metal(loid)s by plants in polluted soils. In this article, we explore various facets of plant reactions to metal(loid)s toxicity and attempt to draw links between biochar use and improvements in plant physiology and performance. We also review the effectiveness of biochar in phytoremediation, its influence on nutrient adsorption mechanisms, and its role in assisting plant growth and defense systems.

Keywords Biochar · Cadmium toxicity · Silicon · Stress physiology · Mitigate stress · Reactive oxygen species

Introduction

Metal(iod) pollution has emerged as a global environmental threat, affecting every facet of life on Earth. This environmental challenge has captured significant public attention, largely driven by increasing concerns over food and health security (Alsafran et al. 2023a, b). Metal(iod) toxicity is characterized by a high density, exceeding 4 g cm^{-3}, and is notorious for its harmful effects even in trace quantities (Rahman and Singh 2019). Various methods exist for the stabilization or removal of metals. While conventional physicochemical approaches have proven effective, they have also faced criticism due to associated environmental issues like air pollution, high energy demands, long-term metal

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leaching, and greenhouse gas emissions (Duan et al. 2021; Alsafran et al. 2023a). In response to these challenges, a green and sustainable initiative has taken root, seeking to develop eco-friendly solutions to these environmental problems. Environmentally friendly soil amendments, such as biochar (BC), stand out due to their minimal environmental impact, affordability, and wide social acceptance (Wang et al. 2021; Boorboori and Lackóová 2023).

Biochar is produced from agriculture, animal waste, and sewage (Mansoor et al. 2021). This carbon-rich organic material is created using thermal processes in anaerobic conditions or under reduced oxygen concentrations (Shaaban et al. 2018). Biochar's agricultural applications are extensive, mainly serving as a soil amendment to assist crop growth by improving soil conditions (Dai et al. 2020). This popularity is due to its exceptional physicochemical properties and beneficial traits. Biochar enhances various soil functions, such as adsorption capacity, cation exchange capacity (CEC), mechanical strength, water retention, organic carbon (C) content, and nutrient-holding capacity, ultimately increasing soil fertility (Palansooriya et al. 2019). Additionally, BC can be a source of essential plant growth elements like macronutrients (e.g., N, P, K, Mg, Ca) and micronutrients (e.g., Zn, Cu, Mn, Fe). It contains ashes, which constitute 5–60% of its weight (Hui 2021). Recently, BC has received notable attention for its roles in bioenergy conversion, carbon sequestration, and metal remediation (Haider et al. 2022). Studies suggest that BC can influence metal abundance and mobility in polluted soils through direct and indirect mechanisms, as outlined by Khan et al. (2022). This review offers a focused overview of the positive impacts of BC on plant responses to metal(loid) stress, highlighting the primary mechanisms. The potential role of BC in future agricultural practices in polluted areas is also discussed in this review.

Plant Responses to Metal/Metalloid Toxicity

Plants respond differently toward different metal stresses, and they are negatively affected due to exposure to high concentrations of metal(loid) (Hidangmayum et al. 2019). The major impact of metal(loid) stress is the accumulation of ROS in plants and the cellular damage caused by free radicals (Nabi et al. 2019). Metal(loid) toxicity impairs plant metabolisms like photosynthesis, respiration, transpiration, minerals/N acquisition, and finally the normal growth and development of plants (Nabi et al. 2019). Moreover, metal(loid) toxicity inhibits root growth as well as root hair formation. Crop yield and quality were also reduced due to the phytotoxicity induced by metal ions. Figure 1 represents the impact of metal(loid) on the plant system.

Effect of Metal(loid) Stress on Seed Germination and Early Seedling Growth

Seed germination, seedling growth, and the development of reproductive stages are inhibited in plants due to metal(iod) stress (Seneviratne et al. 2019). The plants such as *Sorghum bicolor*, *Oryza sativa*, and *Vigna radiata* exhibited low seed germination rate under metal stress due to the loss of turgor pressure (at a higher relative water content). Inhibition of physiological and metabolic activities of seed is also results in the prevention of germination (Seneviratne et al. 2019). Root has direct contact with all these toxic metals in soil and an inhibition of root and coleoptile growth has been observed in seedlings (Muhammad et al. 2015). Metal(iod)s stress is directly reduced the fresh weight, root growth, shoot growth, and biomass production of the plant (Gavrilescu 2022). Metal(iod) exposure induced morphological modification in roots by changing the root length, thickening, root hair formation, and pattern of branching (Rizvi and Khan 2018). Under exposure to Cu and lead (Pb), the roots of maize (*Zea mays*) plants had a substantial distortive impact with prominent cell death (Rizvi and Khan 2018).

Effect of Metal(loid) Stress on Plant Photosynthesis

Chlorophyll biosynthesis, chloroplast structural modification, membrane damage, inefficient electron transport, and reduced ribulose bisphosphate carboxylase oxygenase (Rubisco) activity are the major negative imprints of metal(iod) stress on photosynthesis (Sharma et al. 2020). Cadmium (Cd) toxicity leads to reduced size and number of chloroplasts, degradation of chlorophyll, and reduced accumulation of starch but enhanced accumulation of plastoglobuli in plants (Muhammad et al. 2021). Photosynthetic processes of *Picris divaricata*, *Hordeum vulgare*, *Limnanthemum cristatum*, *Spirodela polyrhiza*, *Oryza sativa*, and *Zea mays* were severely affected under metal(iod) toxicity (Sharma et al. 2020). Metal ions potentially hinder the respiration processes of plants (Nowicka 2022). The impact of Cd on dark respiration and transpiration was evaluated in the leaves of *Acer saccharinum* (Lamoreaux and Chaney 1978). An increase in the rate of respiration is a major effect of metal(iod) stress, especially root respiration (Qi et al. 2021). Inactivation of enzymes such as succinate dehydrogenase complex, malate dehydrogenase, and isocitrate dehydrogenase severely affects the electron transport in Calvin cycles (Garmash and Golovko 2009). Moreover, the alternative oxidase pathway also had modulations under metal(iod) stress, and it was analyzed in barley (*Hordeum vulgare*) plants exposed to Cd stress which had an increase in activity (Garmash and Golovko 2009).

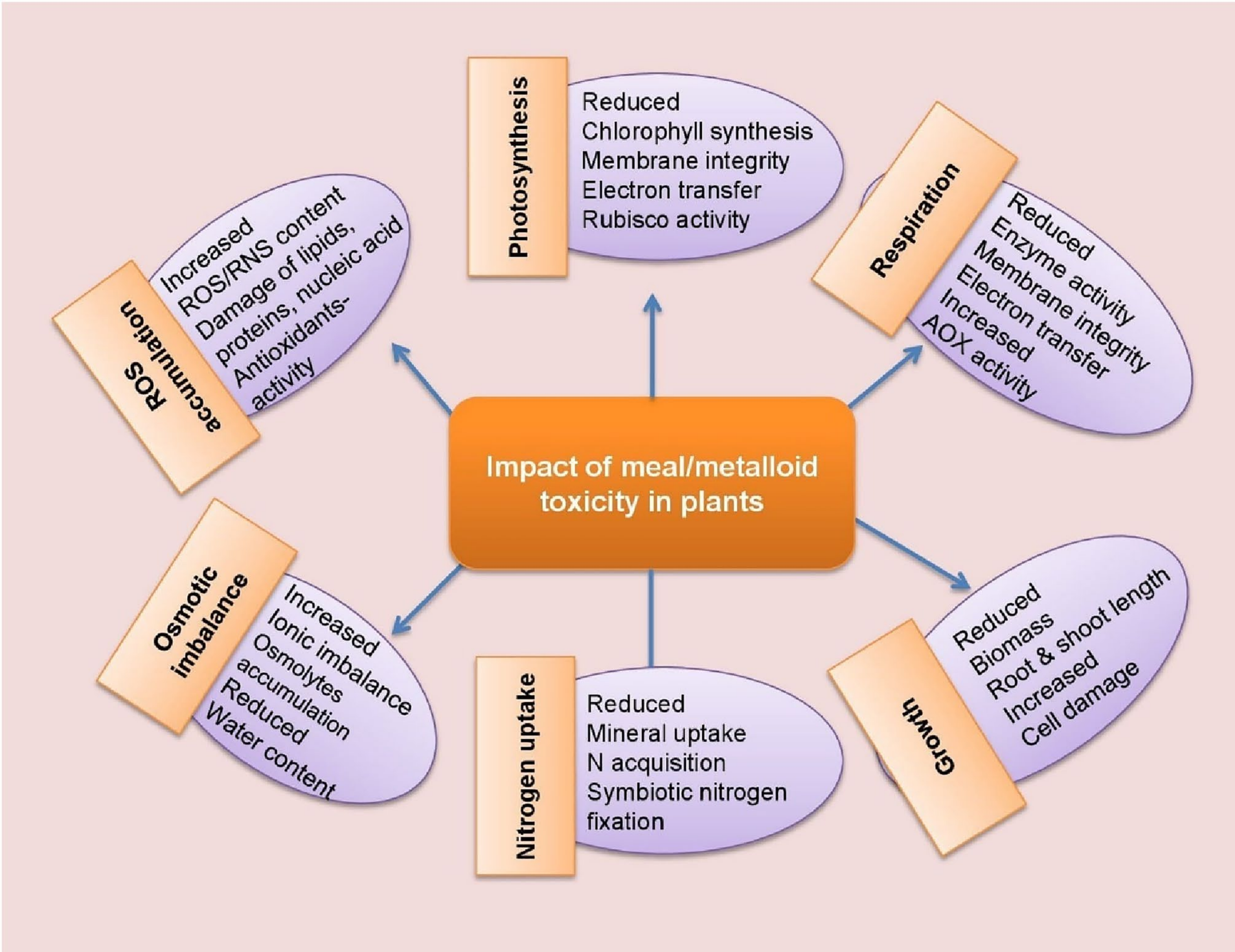

Fig. 1 Impact of metal(iod) toxicity on the metabolic and physiological responses of plants

Effects of Metal(loid) Stress on Plant Redox Homeostasis

The most common symptom of metal(iod) toxicity is the induction of oxidative stress in plants by the generation of reactive oxygen/nitrogen species (ROS and RNS), which induces cellular damage as well as the signaling cascades for different tolerance functions. ROS such as superoxide ($O_2^{\cdot -}$) and hydroxyl radicals ($^{\bullet}OH$), as well as non-radicals, such as hydrogen peroxide (H_2O_2) and singlet oxygen ($^1O_2$), are dangerous to plants. Moreover, the excess accumulation of nitric oxide (NO), *S*-nitrosothiols (SNOs), higher nitrogen oxides (NO_x), dinitrosyl iron complexes, and peroxynitrite ($ONOO^-$) are toxic to plants and all of these radicles are grouped as RNS. ROS and RNS cause damage to cellular lipids, proteins and nucleic acids, membrane leakage, enzyme inactivation and DNA damage or mutation, which can severely damage a cell (Romero-Puertas et al. 2019). Under metal and metalloid stress, it is essential to scavenge the reactive molecules and a dual cellular system based on both enzymatic and non-enzymatic biomolecules effectively operating this (Bhaduri and Fulekar 2012). Major antioxidant enzymes such as superoxide dismutase (SOD), ascorbate/guaiacol peroxidase (APX/GPX), glutathione *S*-transferases (GST) and catalase (CAT), and non-enzymatic molecules such as polyamines, glutathione (GSH), ascorbic acid, α-tocopherol, proline, and metallothionein participating in the scavenging of reactive oxygen/nitrogen molecules (Berni et al. 2019). Metal(iod) significantly interfere with the uptake and transport of macro and microelements essential for the growth and development of plants, especially N acquisition (Sjøgren et al. 2023).

Effect of Metal(loid)s on Mineral Assimilation by Plants

Most of the macro and micro minerals have the same translocation pathway of metal(iod)s. This creates a competition in the translocation of essential mineral ions and metal ions which inhibit transporters functional in the plant system for mineral uptake. Nickel (Ni)-induced reduction in the N accumulation was detected in tomato leaves and roots by reducing its absorption (Gajewska and Skłodowska 2009). Normally, some plants have the biological N fixation ability by maintaining symbiotic association with cyanobacteria or N fixing bacteria, but metal(iod) toxicity severely affects the microbial population and reduces the N fixation ability (Arnao and Hernández-Ruiz 2019). But different symbiotic association can maintain the N accumulation potential of plants even under the exposure of metal(iod) stresses. *Azotobacter chroococcum* maintained the N assimilation and protein production in maize plants under metal(iod)s contamination as compared to the plants under optimal Cu and Pb availability (Rizvi and Khan 2018). The major metabolic pathways such as photosynthesis and respiration get impaired under metal(iod)s stress.

Biochar: The Black Gold for Soil

Biochar is a product formed under oxygen-free environments and high temperatures (Ji et al. 2022). The production condition and structural framework of the substrate directly depend on the properties of BC (Kamali et al. 2022). These properties of BC influence the efficiency of soil amendment. The soil modification based on BC application depends on other factors such as soil characteristics as well as soil management targets (He et al. 2021). Soil pH, soil aggregate stability, soil organic matter, erosion rate, crop productivity, and ecotoxicity are different indicators to evaluate the impact of BC on soil (He et al. 2021). Different studies noted that BC can sequester pollutants in soils (Tan et al. 2022). The application of BC is beneficial to the soil as it is helpful in maintaining the moisture status, fertility, and cation exchange capacity. Remediation of soil xenobiotics, prevention of soil erosion, and modification in soil pH are the other important beneficial contribution of BC (Chagas et al. 2022). The effect of BC on soil can be extended to the modifications in microbial communality. The soil C content, mineralization, nutrient cycling, and enzyme activities are the factors that influence the microbial population and all these four factors can be altered with the help of BC application (Palansooriya et al. 2019). Biochar with high lignin content increased the density of negative bacteria in soil, but BC with high P, K, Mg, and other nutrients induced microbial enzyme activity (Ji et al. 2022).

Additionally, the application of BC aids the plants in improving their performance under metal(loids) stress. Biochar significantly modifies the ROS scavenging enzymes and provides an efficient electron-transferring mechanism to tackle the toxic effects of ROS in plants. Biochar is an efficient tool for the effective management of crop productivity and various environmental stresses (Yang et al. 2022).

Biochar for Limiting Plant Metal/Metalloid Uptake

Accumulation of metals and metalloids such as arsenic (As) antimony (Sb), Pb, Zn, Ni, Mn, mercury (Hg), chromium (Cr), Cu, and Cd (Asad et al. 2019) in agricultural land is one of the major issues for several decades. The presence of its high concentration impacts soil fertility which cause multiple hindrances of plant growth parameters (Sandeep et al. 2019; Yadav et al. 2021). The risk associated with metal(iod)s toxicity majorly affects human health and environmental stability by deteriorating the food chain (Mtemi et al. 2023). However, the use of carbonaceous material such as BC has emerged as a promising tool for soil amendments with the potential to restrict metal(iod) uptake in plants (Radziemska et al. 2022). The potential of BC on restricting metal availability depends its features such as the capacity to alter soil pH (Wei et al. 2023), highly porous structure (Tomczyk et al. 2020), active functional groups for sorption of ions and fixation of metal(loid)s (Wang et al. 2022), ability to improve soil fertility, better water-holding capacity (Alghamdi et al. 2020), and maximal carbon sequestration power (Mansoor et al. 2021). Here are some mechanisms depicting the relation of BC with the metal(iod) uptake.

pH Adjustment and Ion Exchange

Plants uptake and accumulate metal(iod)s from soil through roots (Feng et al. 2021). Therefore, the main role of BC is to limit the metal(loid) concentration in soil to reduce uptake and availability for plants and to increase crop yields (Haider et al. 2022). Changes pertaining to BC's effect on plant metal uptake depend on soil pH and have differential responses for different metal(iod)s present in soil (Masud et al. 2020; Kannan et al. 2021; Zhang et al. 2021a). Jing et al. (2020) reported that wheat straw-derived BC application increased soil pH, reducing cadmium uptake and accumulation by *O. sativa*. The CEC of BC also plays a crucial role in modifying soil pH, influencing metal(iod) speciation and availability (Kannan et al. 2021). Further research suggests that adding BC to soil decreases the concentration of Cd and Pb in plant tissues (Xu et al. 2018). The decrease in the uptake and transportation of metal(iod) to the plant is linked to the high amount of BC (10 mg kg^{-1}) (Bian et al. 2016). According to a study done by Wang et al. (2017), manure-derived BC often includes more Ca than plant-derived BC; therefore, they can attract metal(loid)s such as Cd^{2+} and Cu^{2+} through ion exchange. Another successful experiment conducted by Meier et al. (2021) specifies that in soil polluted by Cu mines, BC made from chicken manure can reduce the uptake of Cu in the aerial part of *Oenothera picensis*. In acidic soil, BC increases soil pH and restricts aluminum (Al) and other metal uptake by plant root (Bian et al. 2016; Wang et al. 2017; Meier et al. 2021; Qian et al. 2023). Reportedly, BC enhances the mobility of anionic metalloids (AsO_4^{3-}, AsO_3^{3-}) by reducing positively charged sites responsible for lowering the binding sites for As as soil pH increases (Igalavithana et al. 2017). A meta-analysis established that BC decreases the average amount of metals (Cd, Pb, Cu and Zn) in plant tissues under metal-contaminated soil by affecting the soil pH. Metal(iod)s present in soil either make bonds with clay particles or iron oxide or are free as ligand cations. Biochar immobilizes cationic metal by increasing the negatively charged exchange sites on clay particles through the action of liming effect (alkalinity) which raises pH of acidic soils (Bolan et al. 2022). While, on the contrary, a recent study demonstrated that on a condition where changes in soil pH remained negligible, BC effectively reduced extractability and metal uptake in plant by lowering the availability of Cu, Zn, and Pb except Cd in the rhizospheric region (Medyńska-Juraszek et al. 2020). This study has impacted well because limiting metal uptake without increasing pH is important, as high pH is linked with minimum availability of plant nutrients, thus may hamper growth and nutritious quality of plant. Moreover, another study, reported decreased concentration of Cd in plant responding to BC application in both acid and alkaline soils as well as during neutral pH condition (Chen et al. 2020). Depending on many factors, structural, chemical, and electrochemical changes occur between particles of BC and soil; therefore, water-soluble organic compounds (K, Na, Ca and P, N, S, and Cl) get dissolved in the soil results in change in pH (Qin et al. 2020; Rombolà et al. 2022).

Nutrients Regulation and Adsorption Mechanism

On the soil surface, metal(loid) immobilization occurs through different mechanisms such as ion exchange, precipitation, reduction, electron shuttling, and physio-sorption with O-functional groups available on BC (Singh 2021; Sun et al. 2022; Sha et al. 2023). The high surface area and porous structure of BC provide abundant active sites for metal(iod) binding (Gupta et al. 2021). Research by Deng et al. (2022) found that BC derived from bamboo residues effectively adsorbed Cr, reducing their availability to wheat plants. The aromatic C structure and functional groups present in BC, such as carboxylic and phenolic groups, contribute to strong electrostatic interactions and complexation with metal(iod) ions (Quan et al. 2020; Deng et al. 2022). Engineered BC such as nano-BC with special characteristics such as nano-sized pores, surface oxygen functional groups, and high surface reactivity triggers rapid metal immobilization in the soil altogether restricting metal(iod) uptake in plant cells (Shahcheraghi et al. 2022). Moreover, unsaturated bonds, radicals, lattice vacancies, and other defect structures become preferential reaction sites for binding and absorption or locking of metals into the C lattice. Biochar also enhances plants productivity by introducing organic matter and essential minerals (N, P, K, Ca, Mg) in the soil so as to increase the soil water retention, saturated hydraulic conductivity, enzymes, and microbial activity and thereby limit the plant metal uptake (Tanure et al. 2019; Toková et al. 2020; Lopes et al. 2021; Aon et al. 2023). Results of numerous studies show that, on average, BC decreases the concentration of metal(loid)s in plant tissues and increases soil minerals, particularly P availability (Yang et al. 2021; Lai et al. 2022; Mihoub et al. 2022). Consecutively, a 3-year period study on BC application showed reduced Cd and Pb content in *O. sativa* fields by increasing soil pH, organic supply, and immobilization of metal(loid)s present in the soil through precipitation, surface adsorption, and increasing level of soil-available minerals such as; Si, P, and K (Bian et al. 2014). A decrease in metal(iod) bioavailability is directly linked with the presence of a high concentration of mineral availability as evidenced by a reduction in Pb toxicity through C coated mineral particles found on BC surfaces (Kiran and Prasad 2019). The toxic Cr(VI) availability to plants can be reduced to Cr(III) by the inclusion of organo-mineral micro-agglomerates through the interaction of BC that reduced Fe, organic compounds, and free radicals (Kumar et al. 2020; Joseph et al. 2021). Uchimiya et al. (2011) found that the release of K, Na, Mg, and Ca from BC could be correlated with the adsorption of Cu on BC particles. Xing et al. (2020) reported that the Hg content in rice grain decreased after adding rice-husk-derived BC to soil with high Hg input through increasing mineral uptake and acclimatization. Similarly, Zhang et al. (2013) also found the lowered translocation of Cd in *Juncus subsecundus* when BC was added to the soil by increasing Si concentration in soil (Chen et al. 2016). Similarly, Li et al. (2020) used BC derived from soybean straw and added it to the soil contaminated with Cd and As. The results showed a reduction in the bioaccumulation of As and Cd in *O. sativa* which is related to the enhanced mineral availability to plants.

Biochar for Enhancing Plant Defense Against Metal/Metalloid Stress

Modulation of Antioxidant Defense

The presence of metal(loid)s in soil triggers ROS and causes oxidative damage to plant cellular organelles (proteins, DNA, lipids, etc.), and it further causes necrosis and therefore diminishes the survival capacity of the plant (Sachdev et al. 2021; Thakur et al. 2022). Biochar, due to its unique surface area, defective sites, and the presence of functional groups, is reported to expedite the radical oxidation process in which ·OH, H_2O_2, $SO_4^{\cdot-}$, and $O_2^{\cdot-}$ participate (Ren et al. 2021; Shi et al. 2022; Fig. 2). Further BC has been found to enhance the antioxidant defense systems in plants, enabling them to cope with metal(iod)-induced oxidative stress (Mehmood et al. 2020). Wang et al. (2021) reported that BC application increases the activities of antioxidant enzymes such as SOD and CAT, thereby reducing oxidative damage in plants exposed to metal(loid)s. The presence of BC in the soil matrix can stimulate the synthesis of phytochelatins and metal-binding peptides that help sequester metal(loid) toxicity (Shi et al. 2022). Further, a study done by Gong et al. (2019) shows that Cd-induced growth inhibition of ramie (*Boehmeria nivea* (L.) Gaudich.) seedlings was countered by BC through reverting oxidative damage (lipid peroxidation and H_2O_2 accumulation) in plants. Biochar releases functional groups and free radicals that participate in ROS scavenging in plants against metal(loid)s stress (Rashid et al. 2023). Studies on *Spinacia oleracea* (Qayyum et al. 2019) and *Triticum aestivum* (Abbas et al. 2017) showed similar results against Cd tolerance, where BC decreased malondialdehyde (MDA) and H_2O_2 content by up-regulating the level of protein. It has also been proven that BC application enhances antioxidative enzymes in plants under Cr stress (Naveed et al. 2021), and similar observation was also recorded in *Zea mays* (Bashir et al. 2020), *S. oleracea* (Sehrish et al. 2019), and *Brassica rapa* through increase in CAT, GSH, GR, GP, GPX, SOD, APX, and GST (Ali et al. 2018). Biochar application reportedly improves the proline and other metabolites with similar capabilities such as phenolic compounds, soluble sugars, and total soluble proteins (TSP) (Rohani et al. 2019; Mehdizadeh et al. 2020; Hussain et al. 2022; Tang et al. 2022; Meihana et al. 2023). Phenolic compound and protein content enhanced under BC application and was reported against Cd toxicity in radish (*Raphanus sativus*) plants (Dad et al. 2021). A stress regulator proline has a variety of roles in plants, including protecting enzymes, adjusting osmotic pressure,

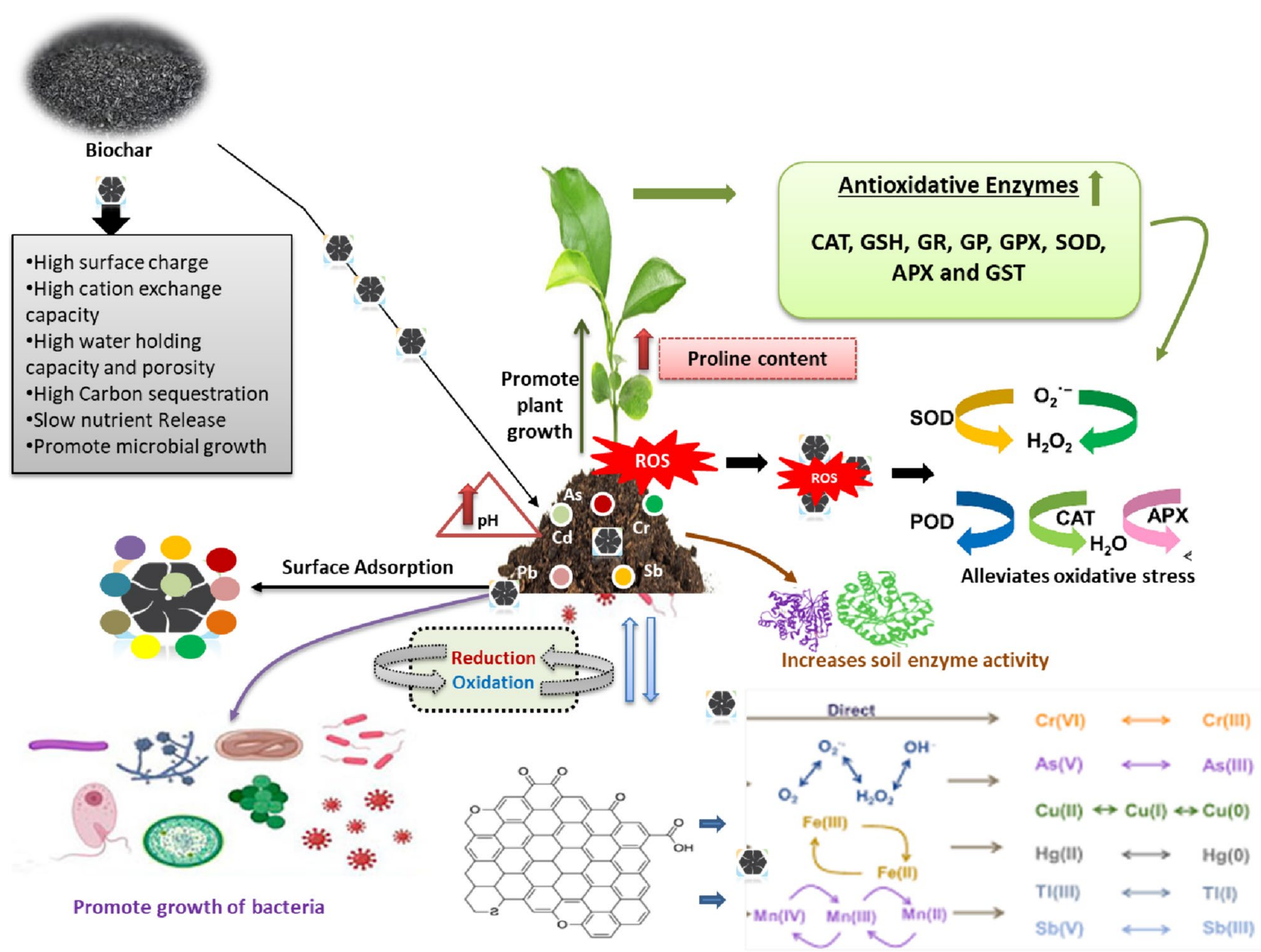

Fig. 2 Biochar and plants against metal(iod) stress

removing ROS, and maintaining protein synthesis (Hayat et al. 2012), thereby it participates in enhancing the antioxidative machinery of the plant by reducing oxidative stress (Mazhar et al. 2023). For instance, the high level of antioxidative enzymes improves the CMP (sialic acid transporter-like protein) and decreases MDA and H_2O_2 accumulation under Cd stress in radish (Dad et al. 2021) and in cotton by increasing the activities of CuZn-SOD, Mn-SOD, and Fe-SOD (Zhu et al. 2020).

Moreover, Khan et al. (2022) demonstrated that BC treatment up-regulated the expression of genes involved in metal(loid)s detoxification, antioxidative defense, and ion homeostasis in plants exposed to metals. This genetic regulation can improve plant resilience and reduce metal(iod) accumulation in tissues. It has been acknowledged that plants primed with BC in the initial stage induce stronger up-regulation of defense-related genes (Viger et al. 2015; Kolton et al. 2017) which helps in the activation of cellular oxidative defense reaction against metal(iod) stress in plants (Khan et al. 2022). Therefore, BC intervene plant resistant develops due to the involvement of the expression of defense-related gene, as evidenced by study on tomato plant against metal(loid)s-induced oxidative damage (Mehari et al. 2015). It has been also suggested that the suppression of toxicity is concentration dependent, as BC at low concentration proved to reduce Cd and Zn-induced oxidative stress in plants more effectively (Kang et al. 2022). Moreover, BC also enhances stress resistance of plants under metal(loid)s stress by intervening signaling pathways of jasmonic acid and H_2O_2 by gene expression regulation (Mehari et al. 2015). The up-regulation of the genes associated with antioxidative enzymes such as SOD, peroxidase (POD), ascorbate peroxidase (APX), glutathione s-transferase (GST), superoxide dismutase (SOD), catalase (CAT) and metal-tolerant conferring gene (*OsFSD1*) were observed and linked to vanadium toxicity tolerance in *O. sativa* (Mehmood et al. 2021). Similar observations were recorded in muskmelon against Cd toxicity (Cheng et al. 2023). Moreover, Kang et al. (2022) observed that BC application enhanced Mn-SOD, CAT, and glutathione reductase (GR) activities to suppress oxidative stress and increase Cd and Zn tolerance in foxtail millet (*Setaira italica* L.).

Biochar and Microbial Interaction Under Metal(iod)-Polluted Sites

Biochar-rhizosphere mechanism causes systematic resistance in plants against various biotic and abiotic stresses (Li et al. 2022). It enhances plant defense against metal(iod) through persuading change in microbial activity (Gong et al. 2019). Numerous proven records are available showing the positive impact of BC on soil bacteria for catalyzing excessive metal (Cd, Zn, Pb, Cr) concentration in soil (Andrey et al. 2019; Liu et al. 2020a; Wei et al. 2022; Ali et al. 2022; Shi et al. 2023). Biochar stimulates the activity of defensive bacterial reaction through different processes such as adsorption, adhesion, electron transport, and ion exchange (Ghassemi-Golezani et al. 2023; Nawaz e al. 2023). Proteobacteria are also more prevalent as a result of the application of BC which decreases metal(loid) toxicity through their special metabolic and ecological capacity to adapt to metal(iod)-contaminated soils (Awasthi et al. 2020). Biochar regulates the level of enzymes which indicates the health of microbial activity in soil. Several studies have been conducted proving its potential to regulate microbial activity by modulating plant enzymes (Shen et al. 2019; Ibrahim et al. 2020; Lin et al. 2021). Furthermore, BC at low availability is linked with high activity of dehydrogenase and phosphatase enzymes (Pokharel et al. 2020), while at high level, it creates unfavorable conditions for microbial activity (Zhang et al. 2021b). Lu et al. (2014) worked on bamboo and rice straw-derived BC and observed an increased number of microbial activities that participated in enhancing the tolerance level of *Sedum plumbizincicola* plant in Cd, Cu, Pb, and Zn-contaminated soil. Furthermore, Ahmad et al. (2016) also observed that soybean stover and pine needle-derived BCs stimulated a higher accumulation of microbial community in Pb and As-contaminated agricultural soil. Biochar provides better habitat for the growth of microbial communities because of high surface area reactivity, secretion from microbes modulates metal concentration and create favorable condition for plant growth by enhancing its tolerance (Andrey et al. 2019).

Molecular Insights into Biochar-Mediated Metal/Metalloid Tolerance

Different BC soil amendments effectively attenuate metal(iod) toxicity by up-regulating and downregulating genes involved in stress tolerance, for instance, Mehmood et al. (2021) reported that HNO_3-modified BC (3%) derived from rice straw plays a crucial role in improving phytoremediation capacity and vanadium tolerance (60 mg L^{-1}) by modulating antioxidant activity and genetic expression of genes encoding antioxidant enzymes (*OsSOD*, *OsPOD*, *OsCAT*, and *OsAPX*) and regulating a metal confronting gene (*OsFSD1*). They noted that the application of HNO_3-modified BC increased antioxidant activities, and the percent change for *OsSOD*, *OsPOD*, *OsCAT*, *OsAPX*, and *OsFSD1* was 5.57-, 5.04-, 4.97-, 5.25-, and 4.80-fold change, respectively, as compared with relative control plants (Fig. 3), suggesting that oxidative BC mitigates the detrimental effect of vanadium stress by enhancing plant defense mechanisms. In contrast, Kang et al. (2022) found non-significant differences in CAT in Foxtail millet with the application of corn straw BC (2%, pyrolyzed at 300 °C, 400 °C, and

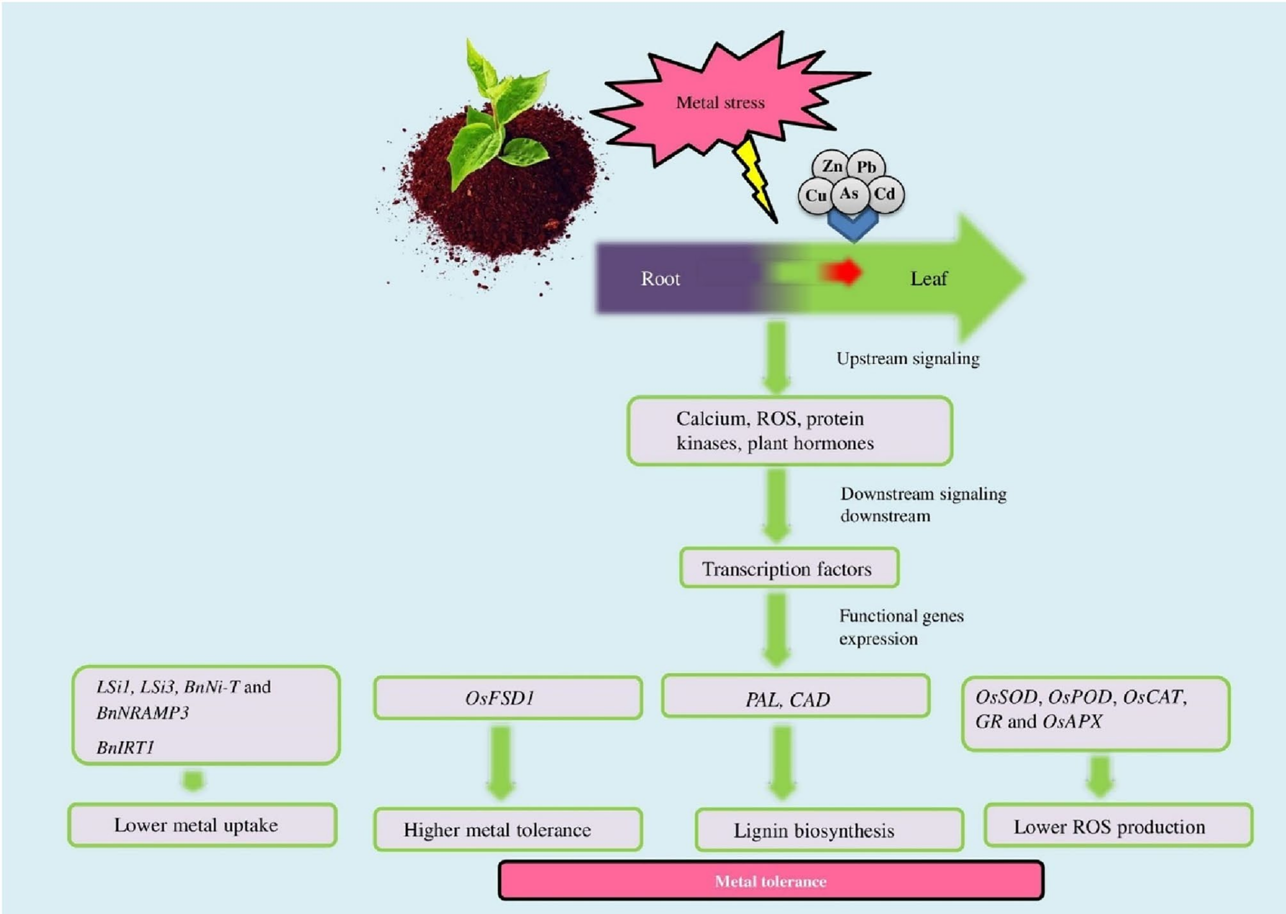

Fig. 3 Effect of biochar soil amendments on gene regulation of molecular basis of plants under metal(iod) stress

500 °C) under Zn (407 mg kg^{-1}), Cd (0.83 mg kg^{-1}), DTPA (diethylenetriamine pentaacetic acid)-Zn (9.32 mg kg^{-1}), and DTPA-Cd (0.18 mg kg^{-1}). However, Mn-SOD and GR expression decreased following the application of BC with increased pyrolysis temperature. Moreover, Hannan et al. (2021) reported that bamboo BC (3%) and their connections significantly reduced the transcript level of SOD-related gene in brassica (*Brassica napus* L.) under Ni stress (100 mg kg^{-1}), which show mitigation of Ni stress in the presence of BC amendments. They noted higher levels of CAT, APX, and GR-related genes with the addition of BC. Moreover, BC soil amendment significantly drops the Ni transporter expression (*BnNi-T* and *BnNRAMP3*) and iron-regulated transporter 1 (*BnIRT1*) involved in Ni transport. The results of gene expression related to secondary metabolites revealed significant up-regulation of cinnamyl alcohol dehydrogenase and phenylalanine ammonia-lyase with the addition of BC, suggesting that soil amendment reduces the expression of Ni transport genes and increases stress-tolerant genes in brassica. In another study, Wang et al. (2020a) used rice husk as the precursor of silicon (Si)-rich BCs (RH-300, RH-700) and wood sawdust (WB) as a precursor of Si-deficient BCs (WB300 and WB700) at 2% to attenuated Cd stress (50 mg kg^{-1}) toxicity. They noted that Si-rich BC amendment immobilizes Cd in soil inhibits root transport of Cd via Si gene regulation and prevents its translocation via Si-Cd composite formation. The effect of Si-rich BC (RH-300) was more pronounced as compared with Si-deficient BC and Si-rich (RH-700) treatments. Their findings suggested that Si-rich BC treatments reduce the gene expression of Si transporter (*LSi1* and *LSi3*) channel in rice roots thereby inhibiting Cd uptake in plants and its grain parts, probably due to the utilization of the same channel for Cd and Si transport. Contrarily, Ma et al. (2021) reported that the reduced uptake of Cd in different parts of the strictly controlled by plant genetics as compared to BC application. Moreover, Cheng et al. (2023) reported the alleviating effect of wood BC (1%, 3%, and 5%) on Cd stress (400 mg kg^{-1}) by studying muskmelon (*Cucumis melo*) as a model plant. They noted that BC application at 1%, 3%, and 5% downregulates the expression of genes related to stress tolerance (17, 5, and 16 genes) and phenylpropanoid pathway (3, 0, and 7 genes) as compared to Cd-exposed plants. Moreover, genes related

to the WRKY transcription factor, annexin, and P450 protein family were also downregulated with the application of BC under Cd stress. This indicates that muskmelons with the addition of BC are less susceptible to Cd stress.

In addition, Zhang et al. (2023) reported that As(III) proportion decreased significantly along with an increase in As(V) proportion after rice straw BC addition (3%). They suggested that BC addition mitigates As(III) toxicity (102 μg/g) by lowering its uptake and proportion which may plausibly be attributed to the contribution of As functional genes. According to Herath et al. (2020), rice husk BC decreased the abundance of *arsC* gene responsible for reducing As(V) to As(III) and increased the abundance of *aioA* gene capable of As(III) oxidation. In conclusion, published works are inconsistent, which may reflect the absence of a “one-size-fits-all” model for BC effect on genetic regulation, with differences in BC type, species, and environment. PAL: phenylalanine amonia-lyase, CAD: cinnamyl alcohol dehydrogenase.

Biochar Enhances Phytoremediation of Metal/Metalloids

The restoration of contaminated soil for healthy and safe food production can be achieved by reducing the phytoavailability of metal(loid)s (Yan et al. 2020). Traditional remediation techniques often have limitations and can be expensive, leading researchers to explore more sustainable and cost-effective alternatives. Among these innovative approaches, the combination of BC with phytoremediation has emerged as a promising solution.

Biochar is one of the organic materials that efficiently used for the management of metal(iod)s, which absorbs metal(iod)s and reduces its potential bioavailability and accumulation in plants (Alkharabsheh et al. 2021; Rajput et al. 2022). Biochar chemically stabilizes the metal(iod)s due to its highly porous structure, reactivity, active functional groups, and generally high pH and CEC (Bian et al. 2014; Liu et al. 2020b), whereas phytoremediation is a multidisciplinary field that uses to mobilize and immobilize contaminants, either by facilitating their uptake and storage in plant tissues or by enhancing their availability for removal from the environment (Shah and Daverey 2020). Phytoremediation encompasses phytostabilization, rhizoremediation, phytoextraction, phytodegradation, and phytovolatilization in general (Shah and Daverey 2020; Fig. 4). Phytoextraction is a soil remediation method that uses accumulators/hyperaccumulators, which are plants capable of absorbing and storing pollutants like metalloids from contaminated soil (Rezania et al. 2016). The combination of BC’s sorption capabilities heightened reactivity, and phytoremediation’s inherent ecological benefits synergistically enhance the remediation process. So far, many research findings have shown that the application of BC to plants considerably reduces metal and metalloid bioavailability. Gu et al. (2020) reported that cornstalk BC amendment reduced the DTPA-extractable Cd concentration and stimulated the root growth of *Beta vulgaris*. Furthermore, the BC amendment led to increased levels of soil-available phosphorus, labile organic carbon, total N, and total organic carbon, these improvements in soil fertility and organic matter content are favorable for plant growth and microbial activity. The enhanced microbial activity can contribute to the breakdown of organic matter and nutrient cycling, supporting root biomass production and overall plant growth. Correspondingly, Zanganeh et al. (2022) also reported the combined application of BC and cyanobacteria effectively immobilized the metals (Cr(III), Cr(VI), Fe, Al, and Zn) in the soil, reducing their bioavailability by enhancing the S3 fraction (bound to organic matter and sulfides) of all metal(iod)s. Biochar and bioaugmentation with cyanobacteria alter the solubility and binding properties of metal(iod)s to the soil matrix and making them less accessible to plants and reducing their potential toxic impacts on *Portulaca oleracea*. Likewise, Kiran and Prasad (2019) studied the phytoremediation of Pb-contaminated soils using rice husk BC and reported the declining Pb accumulation in plants due to the phytoremediation potential of rice husk BC. Several studies also reported the role of BC with hyperaccumulators, for instance, *B. napus* (hyperaccumulator) in conjunction with BC to retrieve Cd from the contaminated agricultural soil (Houben and Sonnet 2015; Narayanan and Ma 2022). Similarly, *Amaranthus tricolor* (hyperaccummulator) along with BC for phytoextraction to treat Cd-polluted agricultural soils (Lu et al. 2015; Narayanan and Ma 2022). While hardwood BC, combined with *B. campestris*, was also found to be effective in reducing the phytoavailable contents of Cu, Pb, Ni, and Zn in mine degraded soil (Forján et al. 2017). Moreover, supplementation of rice husk and groundnut shell BC was found to enhance the Pb accumulation potentials of *Moringa oleifera* (Ogundiran et al. 2018).

Scope of Using Biochar for Next-Generation Agriculture in Contaminated Areas

In the current scenario, agriculture area faces several issues like climatic change and technogenic issues which are combined with unbalanced use of resources and environmental problems like eutrophication, surface runoff, use of conventional fertilizers, and industrial waste emission (De Salvo et al. 2013; Withers et al. 2014; Rajput et al. 2022). Biochar offers promising solutions for mitigating agricultural issues, and it effectively reduces the biological availability of environmental contaminants, thereby improving soil quality

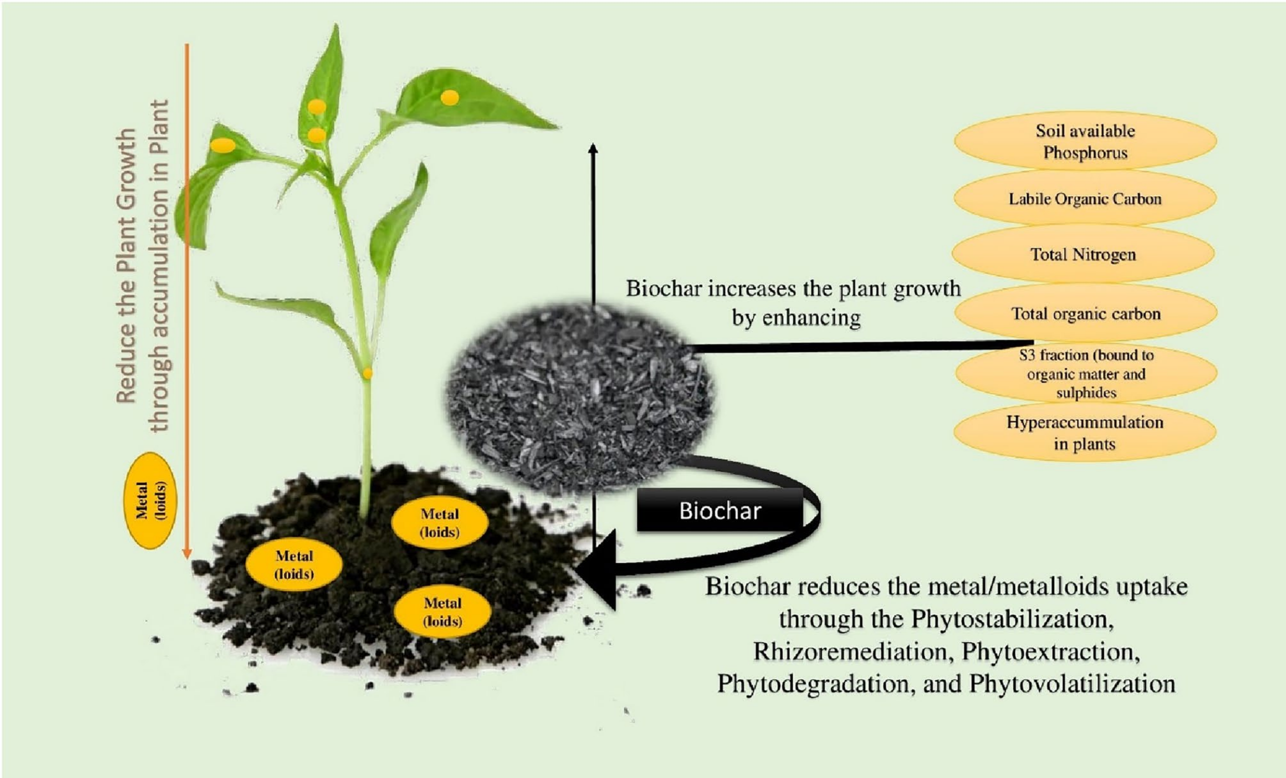

Fig. 4 Biochar lessens the uptake and availability of metal(iod) through the phytostabilization, rhizoremediation, phytoextraction, phytodegradation, and phytovolatilization as well as maintain the plant growth by increasing the levels of soil-available phosphorus, labile organic carbon, total N, and total organic carbon

and enhancing its suitability for plant growth and development (Oni et al. 2019). Presently, BC, as a soil supplement, significantly enhances soil fertility by positively modifying the chemical, biological, and physical properties of the soil (Awad et al. 2018; Xiao et al. 2018). Biochar is an organic material that has been accepted for several positive interactions in agriculture fields such as plant growth and development, disease management, pesticide remediation, soil fertility, and increased microbial growth (Rawat et al. 2019; Zhang et al. 2022). So, its use in agriculture, particularly in contaminated areas, has gained interest due to its potential to address soil degradation, improve fertility, and mitigate certain environmental issues. Biochar can be used to remediate contaminated soils by adsorbing or binding certain contaminants, such as metals, pesticides, and organic pollutants. Its porous structure and high surface area provide ample binding sites for these contaminants, effectively reducing their mobility and availability to plants and the environment (Wang et al. 2020b). In contaminated areas, the soil's fertility is often compromised. Biochar application can enhance soil fertility by providing a stable source of organic C and essential plant nutrients. It helps to retain nutrients like N, P, and K, reducing nutrient leaching and making them more available to plants over time (Rawat et al. 2019). Contaminated soils may have extreme pH levels, which can adversely affect plant growth (Kicińska et al. 2022). Biochar has a buffering effect on soil pH, which can help to neutralize acidic or alkaline soils and create a more favorable environment for plants. Contaminated soils are often less capable of retaining water, leading to drought stress for plants (Murtaza et al. 2021). Biochar's porous structure can help retain moisture in the soil, making water more available to plants and reducing the frequency of irrigation. Biochar can serve as a habitat for beneficial soil microorganisms, promoting their growth and activity. These microbes contribute to soil health, nutrient cycling, and overall plant growth.

Conclusion and Future Perspectives

Metal(iod)s are the dominant constraint to successful crop production and develop a range of nefarious responses in plants due to intensive industrialization in the modern era, so, the development of effective control and remediation has become imperative. Biochar soil amendment is a cost-effective, eco-friendly, and easy-to-obtain remediation material that offers efficient metal(iod)s removal through adsorption, electrostatic attraction, ion exchange, pH modification, precipitation, complexation, surface oxidation and reduction, CO_2 sequestration, slow release of nutrients, and soil microbial activities that reduce metals bioavailability and mobility in soils. Metal(iod) stress-relieving role of BC in plants includes the restriction of metal(iod)s uptake, rampaging of ROS, nutrient management, enhanced microbial activities, and induced genetic regulation to combat the stress responses. However, BC feedstock, designer BC nanomaterials, and pyrolysis temperature affect the mechanisms that are tweaked to deal with metal(iod)s and plant tolerance responses. In addition, the adsorption characteristics of BCs, and their dosage, soil pH, microbes, initial concentration of soil nutrients, and types of metal(iod)s depend on remediation efficiency. Further research directions and BC standardization for long-term field trials will also be proposed to enable large-scale applications for metal(iod)remediation from contaminated soil and decelerate the close-range transfer of these metals in our food chain. Moreover, corresponding monitoring before and after the remediation of soil with BC will also be needed for effective follow-up checking of metal bioactivity and environmental protections.

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