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REVIEW ARTICLE

Pros and Cons of Biochar to Soil Potentially Toxic Element Mobilization and Phytoavailability: Environmental Implications

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Abstract
While the potential of biochar (BC) to immobilize potentially toxic elements (PTEs) in contaminated soils has been studied and reviewed, no review has focused on the potential use of BC for enhancing the phytoremediation efficacy of PTE-contaminated soils. Consequently, the overarching purpose in this study is to critically review the effects of BC on the mobilization, phytoextraction, phytostabilization, and bioremediation of PTEs in contaminated soils. Potential mechanisms of the interactions between BC and PTEs in soils are also reviewed in detail. We discuss the promises and challenges of various approaches, including potential environmental implications, of BC application to PTE-contaminated soils. The properties of BC (e.g., surface functional groups, mineral content, ionic content, and π-electrons) govern its impact on the (im)mobilization of PTEs, which is complex and highly element-specific. This review demonstrates the contrary effects of BC on PTE mobilization and highlights possible opportunities for using BC as a mobilizing agent for enhancing phytoremediation of PTEs-contaminated soils.

Keywords Potentially toxic metal(loid)s · Contaminated soils · Phytoremediation · Biochars · Environmental implications

Abbreviations

PTE	Potentially toxic elements
BC	Biochar
UN	United Nation
FAO	Food and Agriculture Organization
EDTA	Ethylenediamine- tetra-acetic acid
CEC	Cation Exchange Capacity
SAR	Systemic acquired resistance
ISR	Induced systemic resistance

1 Introduction

Soil is a basic resource, essential for the survival of humans and also the source of their wealth. Soils provide humanity with 98.8% of its food; therefore, global food security and safety are strongly affected by soil agriculture policies (Kopittke et al. 2019). The rapid growth of human population (from ca. 250 million in the year AD 1000, to ca. 7.7 billion in 2020-it may reach 9.8 billion by 2050 and 11.6 billion in 2100; UN 2017) and increasing food consumption are placing unprecedented pressure on soil resources. For example, food production needs to increase by up to 70% by 2050, to achieve global food security (ELD 2015). This requirement implies more intensive agricultural production, because soil is a finite resource (Tilman et al. 2011; FAO et al. 2017; Hunter et al. 2017; Ickowitz et al. 2019). The current intensification of agricultural practices—including the over-application of inorganic fertilizers may cause degradation of soils and ecosystem, as depicted in Fig. 1 (Kopittke et al. 2019).

Soil contamination is one of the major forms of soil degradation, which can adversely affect food safety and security and thus human health (Antoniadis et al. 2022). Soils are being increasingly exposed to potentially toxic element (PTE) pollution due to various industrialization, modernization, and other anthropogenic activities. Contamination of soils with PTEs such as As, Cd, Cr, Co, Cu, Hg, Sb, Se, Sn,

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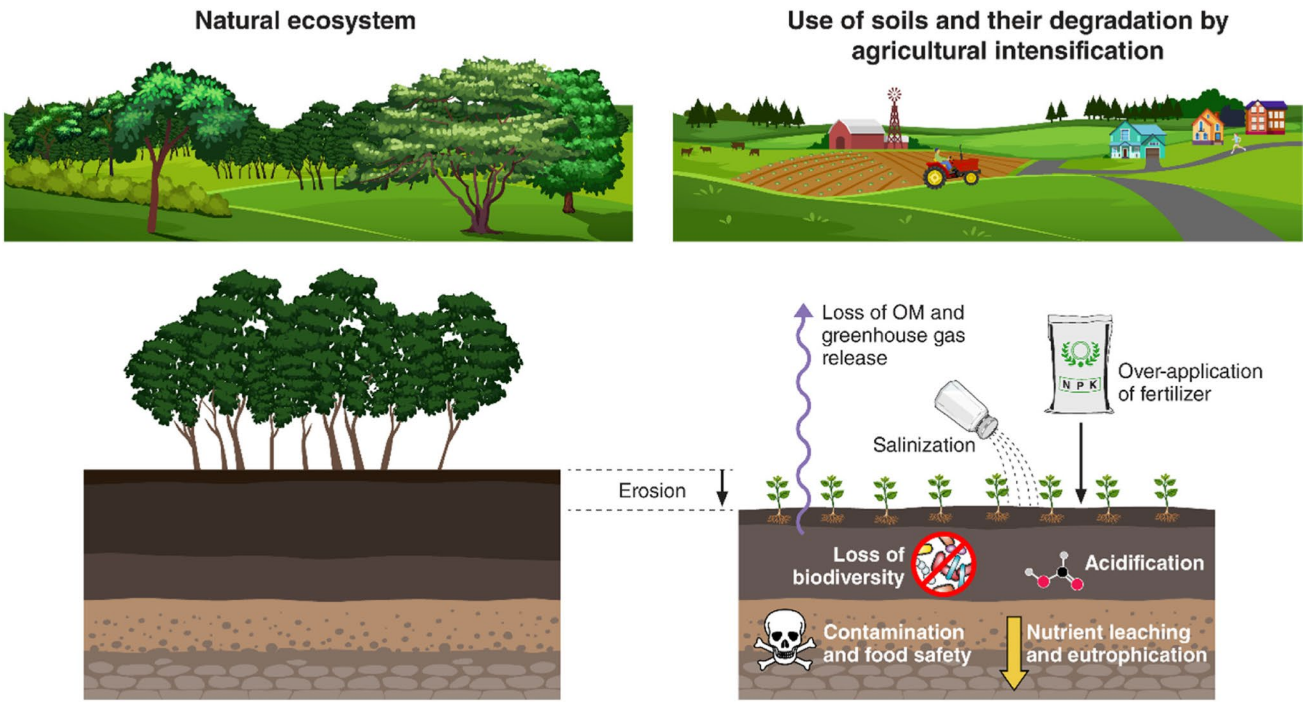


Fig. 1 Impact of agricultural intensification on soils, including degradation by loss of soil organic matter and the release of greenhouse gasses, over-application of fertilizers, erosion, soil contamination, acidification, salinization, and loss of soil genetic diversity (Reproduced from Kopittke et al. 2019, with permission of the publisher)

Tl, V, and Zn represents a health risk to humans (Antoniadis et al. 2022). Therefore, remediation of PTE-contaminated soils has received considerable attention over the past few years. Among the different remediation approaches for the sustainable management of contaminated soils, green remediation is one of the cheapest and most environmentally friendly (Jeyasundar et al. 2021). Green remediation of PTE-contaminated soils can be achieved with various methods including metal immobilization, phytostabilization, and/or phytoextraction (e.g., Shaheen and Rinklebe 2015; Antoniadis et al. 2017, 2021; Ali et al. 2020a; Hou et al. 2020; Palansooriya et al. 2020). The combination of soil amendments with hyperaccumulators is an effective method for increasing the efficiency of green remediation of PTE-contaminated soils. Among the soil amendments, BC has received significant attention in the last fifteen years (since 2007; Lehmann 2007). The focus on BC as a soil amendment for management of degraded soils is likely due to the fact that its feedstocks are locally available and potentially recyclable or renewable (El-Naggar et al. 2019a).

Research on BC as promising materials for remediation of degraded soils and water has grown rapidly since 2007 (e.g., Bolan et al. 2014, 2022; El-Naggar et al. 2019a; Bandara et al. 2020; Ali et al. 2020a; Shaheen et al. 2019a, b, 2022a, b). Many studies have concluded that BC has viable potential for the immobilization of some PTEs in soils and for reducing their phytoavailability (Shaheen et al. 2022c; Yang et al. 2023a,b). However, other studies have reported that BC can rather increase the mobilization and uptake of some PTEs (Yang et al. 2023a,b). These paradoxical findings depend mainly on the types and properties of the studied element, BC, and soils, which are discussed in the subsequent sections.

The potential of BC for PTEs immobilization in soils has been studied, but no review has focused on the potential use of BC for enhancing the phytoremediation efficacy of PTE-contaminated soils. Here, we review the effects of BC on PTE mobilization, phytoextraction, phytostabilization, and bioremediation in contaminated soils. We also summarize potential mechanisms of the interactions between BC and PTEs in soils in in detail. The pros and cons of BC application to PTE-contaminated soils and the potential environmental implications are also reviewed and summarized.

2 Soil PTEs: Sources, Mobilization, and Potential Risks

Potentially toxic elements can be interred into soils from geogenic and/or anthropogenic sources (Fig. 2; Palansooriya et al. 2020). Metals sources govern their mobilization in soils; for example, the mobilization of PTEs in soils contaminated with anthropogenic sources is higher than that in geogenically contaminated soils (Khan et al. 2021; Shaheen

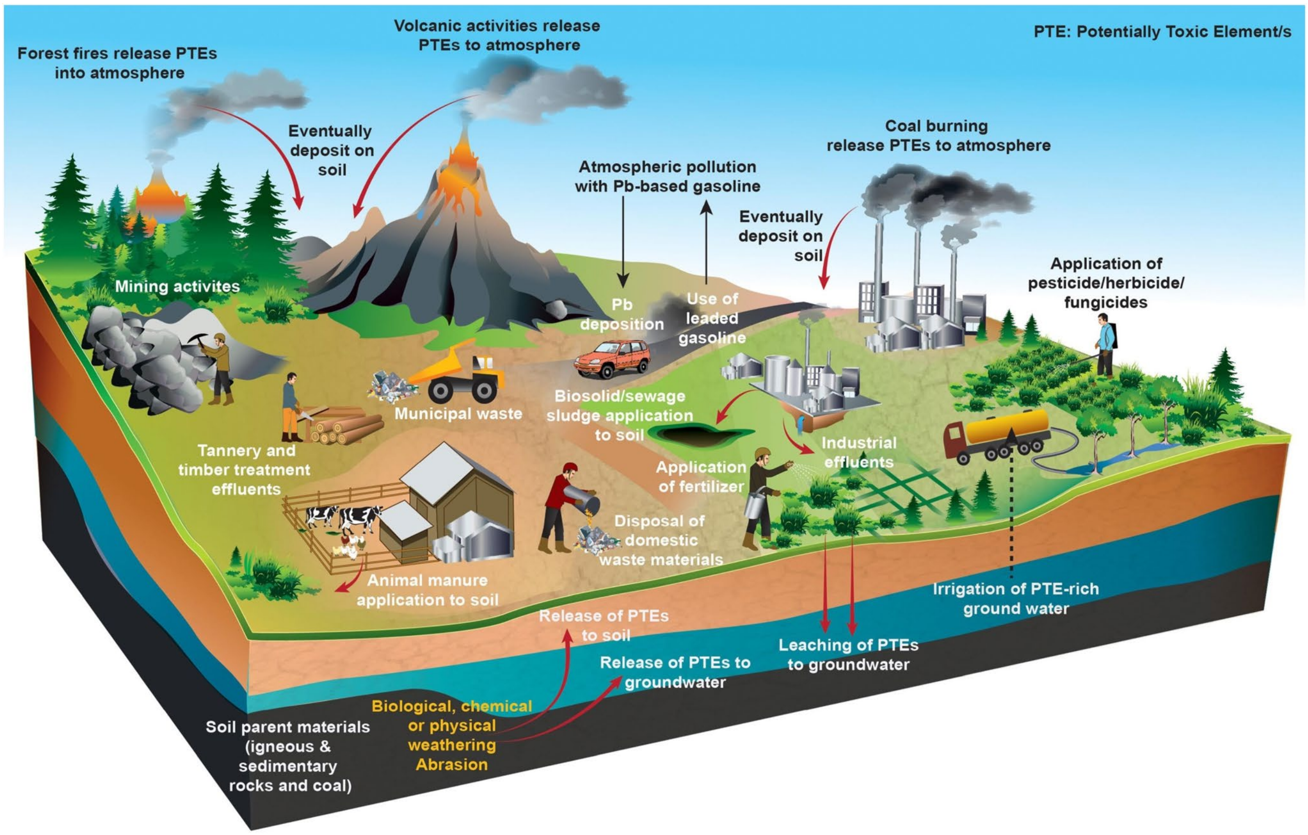


Fig. 2 Sources of toxic elements (TEs) in soil ecosystems (Reproduced from Palansooriya et al. 2020, with a permission of the publisher)

et al. 2022a). Soil properties affect PTE sorption/availability and thus affect their mobilization (Shaheen et al. 2013; Antoniadis et al. 2017; Rinklebe et al. 2020). Moreover, the fractions and speciation of PTEs in soils affect their solubilization (Rinklebe and Shaheen 2017; Kumar et al. 2022). Therefore, understanding the soil and PTE properties is necessary before selecting appropriate soil amendments (Palansooriya et al. 2020; Kumar et al. 2022). Soil PTEs can be bio-accumulated by plants, thus entering the food chain and raising serious concerns over adverse risks to human health (Fig. 3; Ali et al. 2020b; Antoniadis et al. 2017; Isinkaye 2018; Ekoa Bessa et al. 2021). The toxicity of PTEs depends on an element's speciation and corresponding bioavailability, which are governed by environmental conditions such as redox potential, soil minerals, soil solution chemistry, and soil microorganism communities (Palansooriya et al. 2020; Khan et al. 2021; Antoniadis et al. 2022). Therefore, it is important to understand soil PTE behavior and bioavailability to determine relevant environmental risks and adopt appropriate monitoring or remediation methods, as discussed in the following sections.

3 Remediation of PTE-Contaminated Soils

Different physical, chemical, and biological ex situ and in situ trials can be employed for the remediation of PTE-contaminated soils (Fig. 4), which have been reported in previous studies (e.g., Ali et al. 2020a, b; Palansooriya et al. 2020; Khan et al. 2021; Kumar et al. 2022). The PTE clean-up techniques are categorized into containment-based (e.g., capping/encapsulation), transformation-based (e.g., stabilization/immobilization), and transport-based (e.g., extraction/removal), all employing various physical, chemical, electrical, thermal and biological methods (Khan et al. 2021; Kumar et al. 2022). However, each method has different preference criteria, since an intensive analysis of specific field conditions is required. In general, different polluted soils require different treatment methods (Khan et al. 2021). For instance, surface capping is only viable to prevent PTEs from infiltrating vertically through the soil profile; nevertheless, the capped area may lose its natural soil functions. Similarly, the main challenge for encapsulation is to construct impermeable walls at contaminated

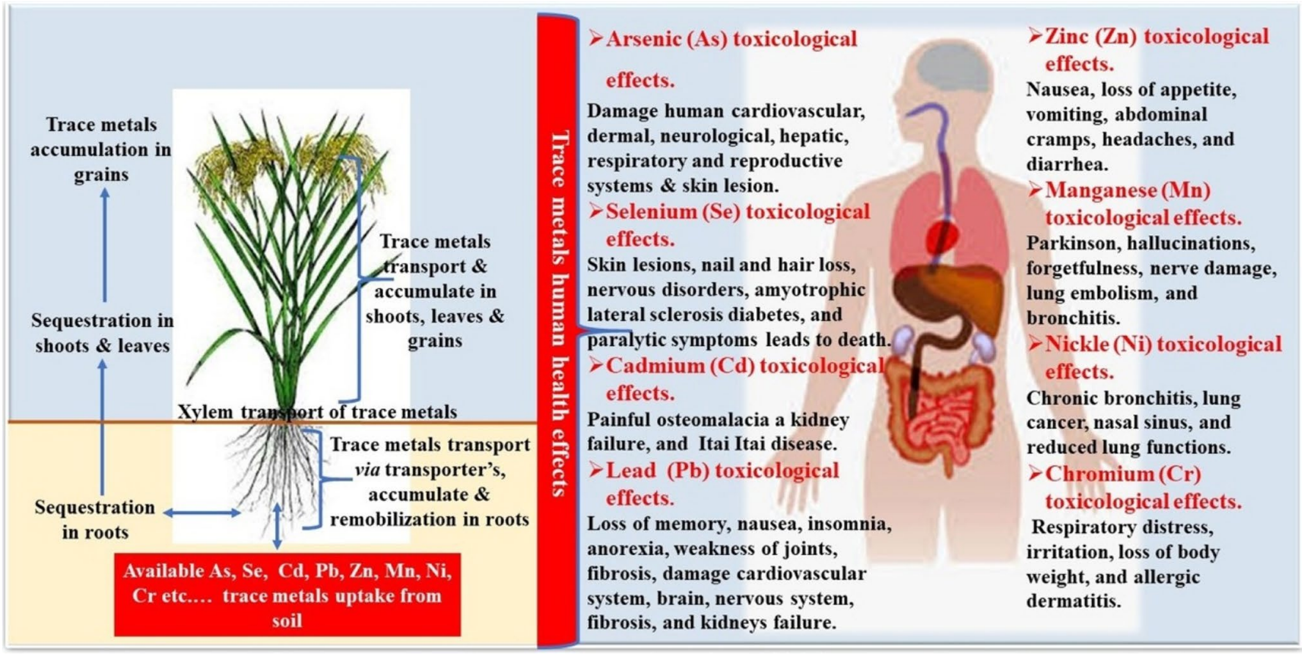


Fig. 3 A general overview of natural and anthropogenic sources of trace elements in environmental matrices, and associated human health toxicities (Reproduced from Ali et al. 2020b, with a permission of the publisher)

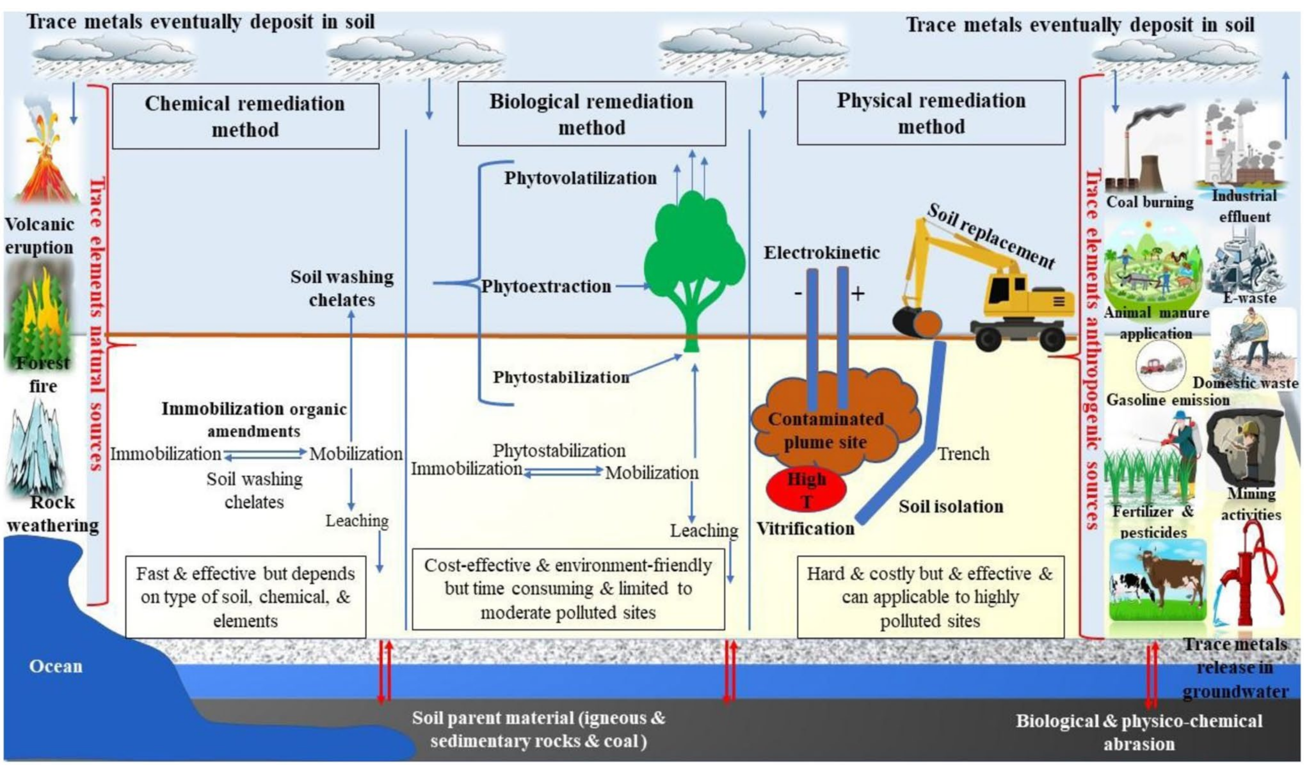


Fig. 4 Comparison of soil management/remediation methods for trace elements-contaminated soil (Reproduced from Ali et al. 2020b, with a permission of the publisher)

sites. Therefore, several well-established conventional methods for PTE remediation have often failed due to their high cost, technical complexity and the release of secondary pollutants.

Among remediation methods, bioremediation is a green strategy that recruits the biological mechanisms that are inherent in microbes, plants and other biological substances to clean-up PTE-polluted environments, rendering contaminated soil less polluted and free of recalcitrant and secondary pollutants (Singh and Gupta 2016; Nedjimi 2021; Zhang et al. 2023). It is operationally simple, esthetically non-destructive, solar energy-driven, economically viable and widely accepted; it also improves the physical, chemical and biological qualities of the contaminated site offering ecological restoration (Sarwar et al. 2017). Microbes may use PTEs as a source of nutrition and also can cause the oxidation, reduction and transition of PTEs; therefore, they do not incur any additional expense in meeting their nutritional demands (Verma and Kuila 2019). There are several advantages to adopting bioremediation strategies for PTE clean-up. They can enhance revenue while an ecosystem is being restored, a benefit which cannot be realized with any other method. The produced biomass may be considered as an alternative feedstock for sustainable biofuel production without affecting food security (Dastyar et al. 2019). Tailoring of microbes and plants may, therefore, add value of an ecosystem while simultaneously achieving enhanced decontamination efficiencies.

The efficiency of the remediation of PTE-contaminated soils depends on the type and properties of the soils and elements involved. The mobilization of PTEs in soil significantly affects the remediation process efficiency (Palansooriya et al. 2020). For example, increasing the PTE mobilization in soil may increase their absorption by hyperaccumulator plants and may thus enhance the rate of PTE phytoremediation or phytoextraction processes (Amin et al. 2018; Shaheen et al. 2019a, b; Wang et al. 2019). On the other hand, the immobilization of PTEs in soils aims to reduce their mobility via sorption, precipitation, and/or stabilization with various soil amendments (Fig. 4), to minimize ecosystem and human health risks.

Among the (im)mobilizing agents, BC has been used successfully for PTEs immobilization and reducing their phytoavailability; however, in some cases BC mobilized the PTEs and enhanced their phytoavailability, as discussed in details in the following sections. Therefore, understanding the factors and processes which govern PTE mobilization in BC-treated soils is necessary to develop an effective remediation plan.

4 Biochars for the Remediation of PTE-Contaminated Soils

4.1 Biochars for PTE Immobilization

4.1.1 Biochars and PTE Immobilization Efficiency

Biochar can be used effectively for PTE immobilization in soils. The efficiency of the immobilization is highly dependent upon multiple BC-related factors, including its application rate, source of feedstock, pyrolysis temperature, pyrolysis gas, ash content, and particle size. The physicochemical properties of BC derived from different feedstocks under varying pyrolysis temperatures are summarized in Table 1. Additionally, several indirect factors related to soil characteristics (e.g., soil pH, redox potential and particle size distribution) control how effectively BC can mitigate PTE phytotoxicity.

Several attempts have been made to identify the optimum application rate of BC in soil, which nevertheless remains uncertain. We extracted data from recent published investigations (36 studies, comprising 315 observations) to evaluate the most important factors underlying PTE immobilization in soil with emphasis on the most widely studied elements (As, Cd, Cr, Cu, Pb and Zn) (Fig. 5). Among the studied factors, there seems to be a consensus that application rate of BC is the most crucial factor for enhancing the immobilization efficiency of PTEs. According to the obtained data, immobilization efficiency of PTEs averaged 30.8% (i.e., if a 100 mg PTE L^{-1}-solution was added to a soil-BC mixture, 30.8 mg L^{-1} was retained by the mixture and 69.2 mg L^{-1} remained in solution) when the application rate was < 2%. The retention rate rose to 44.6% at a dose of 2–5%, and to 48.1% at a dose of > 5.0% (Fig. 6a). Highly polluted sites (e.g., mining areas) might need even higher application rates of BC to achieve an optimal safeguard effect (Khan et al. 2020).

The effect of BC feedstock on its properties and on the ability of BC to immobilize PTE has also been widely investigated (Table 1). Data extracted from recent literature show that the immobilization efficiency of PTEs (As, Cd, Cr, Cu, Pb and Zn) as a function of feedstock type can be ranked as follows: weeds (49.6%) > sludge (37.8%) > crop residues (32.7%) > woods (29.2%) > bones (20.3%) (Fig. 6b). Pyrolysis temperature also has a pivotal role in controlling the functionality of BC and its stabilization capacity. Analysis of recent published data demonstrates that BC produced at high pyrolysis temperatures are more efficient in immobilizing PTEs than those produced at low temperatures. For instance, 32.57% immobilization was achieved when BC were produced at 300–499 °C, but 36.17% and 36.51% were achieved

Table 1 Physiochemical properties of biochar derived from different feedstocks under different pyrolysis temperatures

Feedstock	Pyrolysis condition (°C)	SA ($m^2 g^{-1}$)	Pore size (mm)	Pore volume ($cm^3 g^{-1}$)	CEC (cmolc kg^{-1})	C (%)	*N* (%)	C/N	Ash content (%)	References
Coconut shell	800	486	–	–	95	93	–	–	7 g/kg	Pračke et al. (2021)
Miscanthus	600	50.1	–	–	188	5.82	0.03	41.9	–	Drzewiecka et al. (2021)
Apple pruning	500	–	–	–	24.94	68.9	0.75	91.8	14.68	Moradi et al. (2021)
Grape pruning	500	–	–	–	34.43	71.5	0.87	82.2	11.18	Moradi et al. (2021)
Wheat straw	500	–	–	–	50.1	64.3	0.22	292	22.98	Moradi et al. (2021)
Acacia wood	450	90.51	2.56	0.036	14.54	9.77	0.8	–	–	Kowitwiwat and Sampanpanish (2020)
Wood	450	–	–	–	5	1.18	0.11	–	–	Rees et al. 2020)
Wood	–	–	–	–	–	–	4.45 g/kg	–	–	Ali et al. (2019)
Cattle manure	500	–	–	–	–	13.8	1	–	83.1	Sigua et al. (2019)
Pine	500	–	–	–	–	90.5	0.7	–	3.2	Sigua et al. (2019)
Poultry manure	500	–	–	–	–	37.4	4.2	–	42.5	Sigua et al. (2019)
Rabbit manure	450	5.677	–	0.0236	148	28.52	1.47	–	–	Gascó et al. 2019)
Wood	650	–	–	–	3.2	685	5.25	131	–	Rue et al. (2019)
Wood	650	–	–	–	3.2	685	5.25	131	–	Rue et al. (2019)
Wheat straw	550	350	–	–	78.3	–	–	–	–	Zhang et al. (2019)
Rabbit manure	600	35.97	–	0.0942	132	24.99	0.38	–	–	Gascó et al. (2019)
Maize stalks	400	–	–	–	520 g/kg	5 g/kg	–	–	–	Eissa (2019)
Rice straw, bone ash and fly ash	600	–	–	–	–	–	0.81 g/kg	–	–	Li et al. (2019)
Wood chips	500	223	2.16	0.12	–	–	–	–	–	Lebrun et al. (2018a)
Lightwood	500	267.3	2.6	0.175	–	–	–	–	–	Lebrun et al. (2018b)
Pine wood	500	234.8	2.1	0.122	–	–	–	–	–	Lebrun et al. (2018b)
Eucalyptus	600	334.56	<0.5	0.1612	–	81.03	1.07	78.7	1.74	Lu et al. (2015)
Poultry manure	400	7.418	<1	0.0286	–	16.77	1.37	8.9	74.95	Lu et al. (2015)
coconut shells	–	486	4	–	73	–	–	–	12	Břendová et al. (2015)
Eucalyptus	600	334.56	<0.5	0.1612	–	81.03	1.07	78.7	1.74	Lu et al. (2014)
Poultry manure	400	7.418	<1	0.0286	–	16.77	1.37	8.9	74.95	Lu et al. (2014)

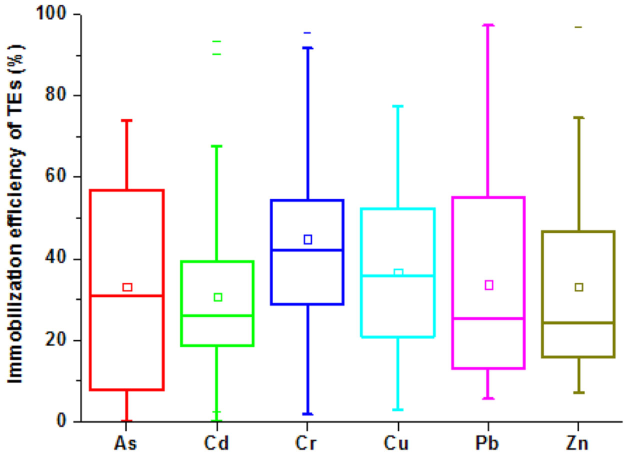


Fig. 5 Effect of biochar application on immobilization efficiency of TEs (%). Data are extracted from 315 observations comprising 36 recent studies. The box chart presents median (centerline), mean (dot), lower quartiles (lower border of the box), upper quartiles (upper border of the box) and whiskers-error bars (the minimum and maximum observations)

when BC were produced at 500–599 °C and 600–800 °C, respectively (Fig. 6c).

A possible explanation for this could be that BC produced at high pyrolysis temperature have higher persistence in soil as well as higher pH values, total carbon, specific surface area and porosity relative to those produced at low pyrolysis temperatures (El-Naggar et al. 2022; Tomczyk et al. 2020).

The ash content of BC depends not only on the feedstock type (Table 1), but also on the details of the thermochemical conversion process. From recently published data we found that the average efficiency of PTE immobilization increased slightly as the ash content increased from < 10 to 20% (with immobilization increased from 36 to 37.7%, respectively). This immobilization efficiency decreased sharply to 29.4% with ash contents above 20% (Fig. 6d). The particle size of BC often depends on the feedstock particle size, but it is likely smaller than the precursor due to shrinkage and attrition during pyrolysis (Panahi et al. 2020). Few investigations have studied the effect of particle size of BC on its stabilization efficiency. It is hypothesized that the efficiency of BC in stabilizing PTEs increases when size is decreased due to enhanced available surface area. In the view of this, Fahmi et al. (2018) recommended using fine particles of BC derived from empty fruit bunch oil palm (< 50 µm) to achieve the highest in situ immobilization of Cd^{2+} and Pb^{2+}. They reported that such fine particles were more efficient compared to coarse particles of > 2 mm.

Several factors related to soil physicochemical properties underly the efficiency of BC in immobilizing PTEs. It is generally agreed that the value of soil pH is a crucial criterion for controlling the ability of BC to safeguard against the phytotoxicity of PTEs. Meta-analysis of PTE stabilization indicates that soil pH is the most important factor (Yuan et al. 2021). These authors showed that the bioavailability of PTEs decreased by about 28.7% in weakly acid coarse-textured soils and by 6.4% in medium-textured soils. This reduction in PTE bioavailability reached 149% and 121% in soils with a highly alkaline nature (pH > 8.0).

Soil texture can also play a pivotal role in controlling the mobility/accessibility of PTEs, since fine-textured soils possess high clay content that improves PTEs retention in the soil matrix (Mosa et al. 2021, 2022; Yin et al. 2019). Meta-analysis of PTE bioavailability in response to BC aging illustrated that the contribution of soil texture (18.6%) was the second most influential criterion, after soil pH (Yuan et al. 2021). In this regard, BC exhibits a remarkable effect in fine-textured soils relative to coarse-textured soils. For example, a sandy soil was more responsive to the lowest application rate (1%) of a 620 °C-wood BC; however, BC addition to a sandy loam soil only started to show a significant response at a 5% application rate (Verheijen et al. 2019).

Unlike most soil characteristics, the mutual interactions between BC and soil redox conditions have rarely been studied in respect to PTE decontamination. The effect of pig carcass-derived BC at 650 °C was studied for As immobilization in a contaminated paddy soil using an automated biogeochemical microcosm apparatus to control the redox potential (E_H) (Yang et al. 2022a). The authors concluded that BC reduced the phytoavailability of As under moderately reducing conditions (38.7 and 35.4% reduction at $E_H = +100$ and $+200$ mV, respectively). Meanwhile, BC application maximized the phytotoxic effect of As under oxidized (317.6% increment at $E_H = +250$ mV) and highly reducing conditions (13.5% increment at $E_H = -300$ mV). The interactions between BC and PTEs in soils can be happen via different potential mechanisms as disused in detail in the following section.

4.1.2 Mechanistic Insights into the Role of BC in PTE Immobilization in Soil

The immobilization of PTEs in soil by the addition of BC depends on a variety of complex and intertwined mechanisms. Direct mechanisms include the interaction between biochar and PTEs, while indirect mechanisms include the modulation of soil physicochemical properties (Fig. 7).

Physisorption is a weak secondary mechanism, which depends mainly on the porosity of BC (Yang et al. 2019). Physisorption often relies on the porosity of BC through Van der Waals forces, which increase with increasing specific surface area and BC pore size (Salam et al. 2019; Ahmad et al. 2021; El-Naggar et al. 2021; Shaheen et al. 2022a). As such, the higher specific surface area and pore volume of two phosphorus-supported BC were found to stimulate the physisorption mechanism for the effective amelioration

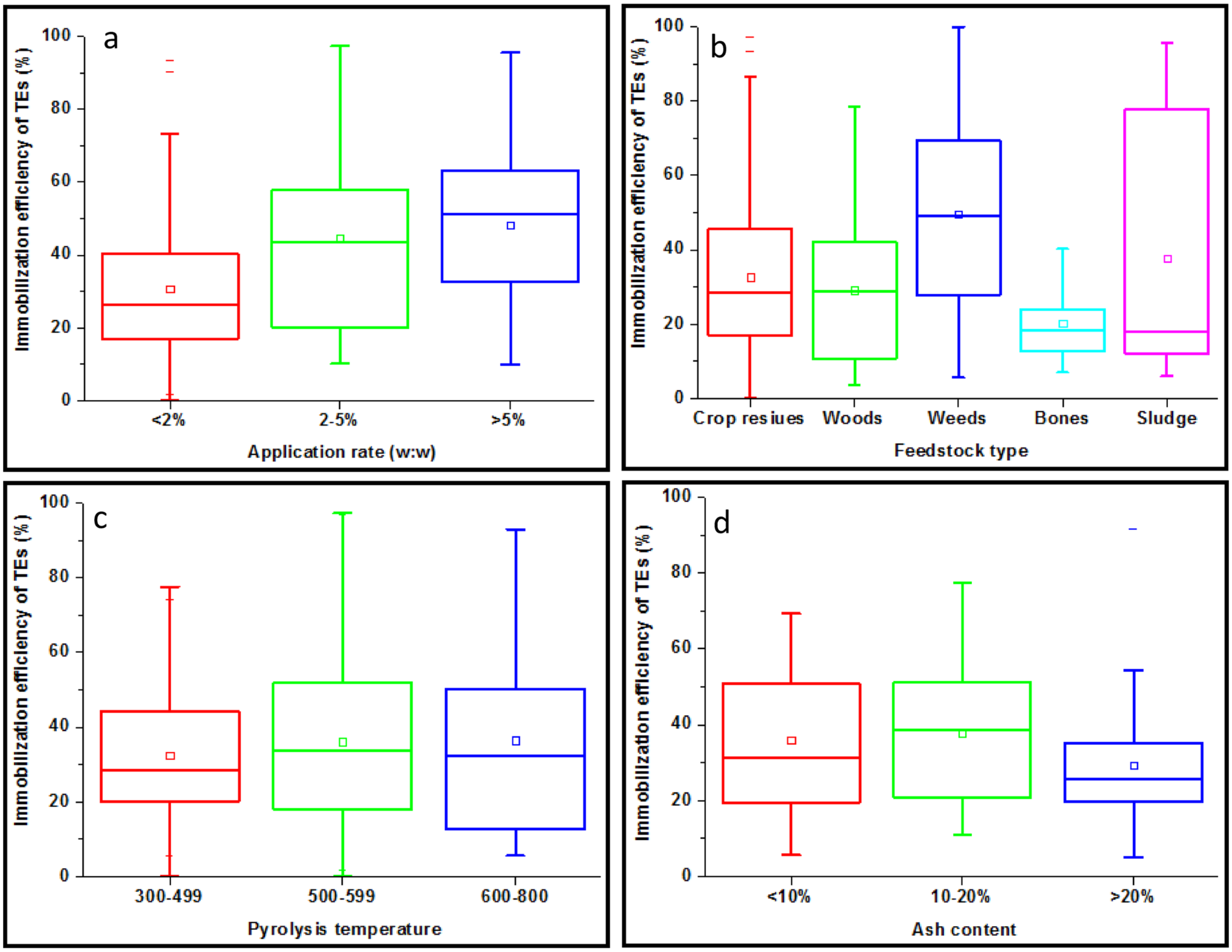


Fig. 6 Effect of biochar application rate (**a**), feedstock type (**b**), pyrolysis temperature (**c**) and ash content (**d**) on immobilization efficiency of TEs (%). Data are extracted from 315 observations comprising 36 recent studies. The box chart presents median (centerline), mean (dot), lower quartiles (lower border of the box), upper quartiles (upper border of the box) and whiskers-error bars (the minimum and maximum observations)

of Pb-contaminated *Udic ferrosols* (Cui et al. 2022). Physical adsorption via pore filling onto modified BC (EDTA crosslinked β-cyclodextrin at 300 °C corn stalks) was also tested for the remediation of a Cd/Pb-contaminated soil (Qu et al. 2022). The involvement of cation-π electron interaction mechanisms in PTE sorption upon remediation of polluted soils has also been reported (Yi et al. 2022; Zhou et al. 2022). The electron-rich domains of S/Fe-modified corncob BC were found to have enhanced the active contribution of the cation-π interaction mechanism for Cd^{2+} and Pb^{2+} stabilization in a contaminated soil, as revealed by Shen et al. (2019). However, the elements sorbed by this mechanism could be exposed to leaching at low values of soil pH levels. Electrostatic interaction is another physisorption mechanism, which could function as the spark for PTE immobilization in contaminated soils (Sun et al. 2022).

On the other hand, several chemisorption mechanisms contribute mutually toward PTE immobilization. Among them, ion exchange involves the replacement of labile PTEs with similarly charged ion exchangers of BC. Metal cations initially on BC surfaces (e.g., Na^+, K^+, Ca^{2+} and Mg^{2+}) could be exchanged with PTEs (Qi et al. 2022). Ion exchange might also occur between PTEs and oxygen-containing functional groups (Wu et al. 2021b). According to Cui et al. (2022), a gradual reduction in the pH value of the soil solution occurred during ion exchange with soil Pb^{2+} in Udic ferrosols according to the following reactions:

$$-\mathrm{COOH} + \mathrm{Pb}^{2+} = -\mathrm{COOPb}^{+} + \mathrm{H}^{+} \quad (1)$$

$$-\mathrm{OH} + \mathrm{Pb}^{2+} = -\mathrm{OHPb}^{+} + \mathrm{H}^{+} \quad (2)$$

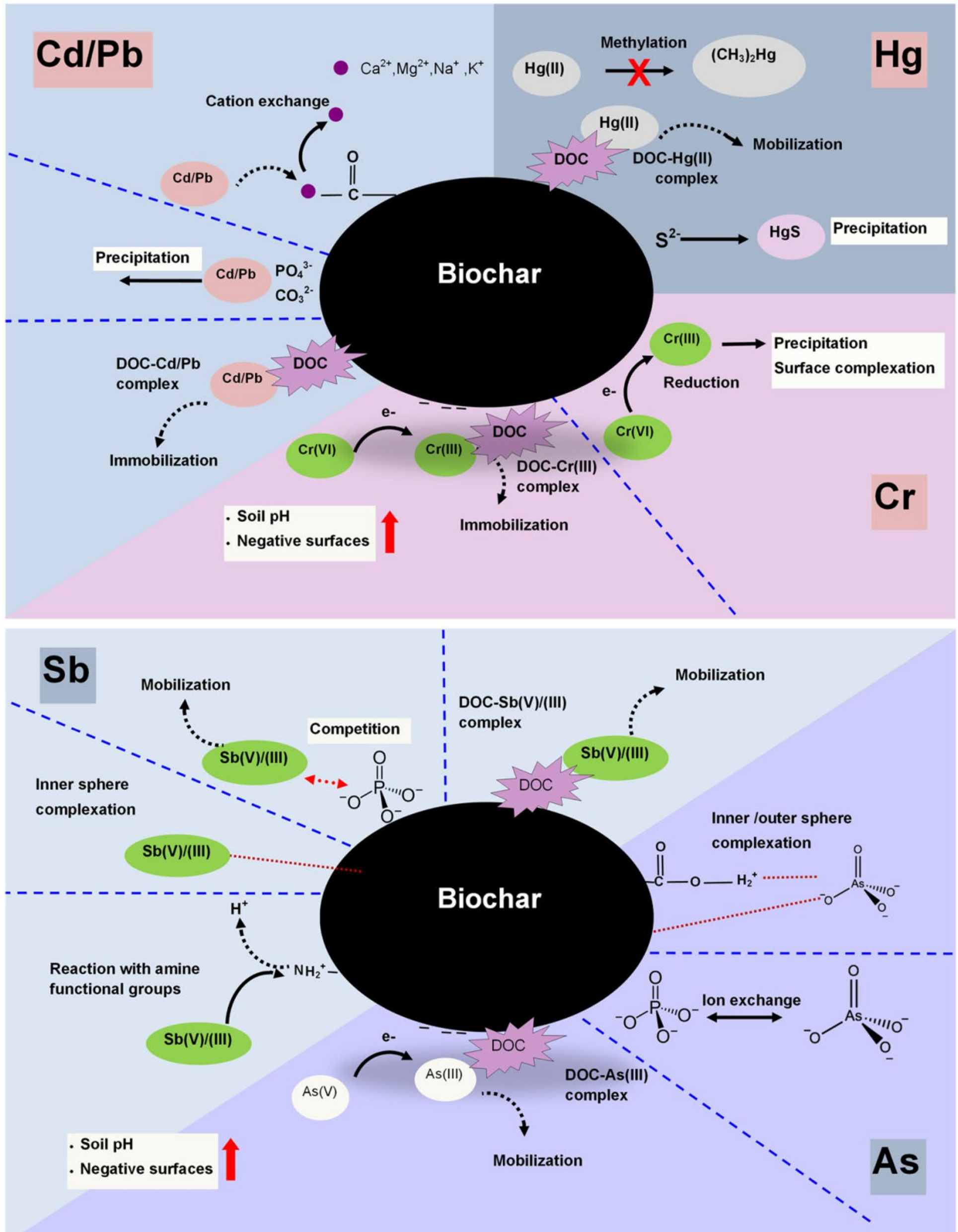


Fig. 7 Mechanistic illustration of Cd, Cr, Hg, and Pb sorption (**A**) and As and Sb sorption (**B**) by biochars in soil. DOC: dissolved organic C (Reproduced from Bandara et al. (2020), with a permission of the publisher)

The active surfaces functional groups on BC can also bind PTEs to create multi-atom structures. For example, the grafting of thiol functional groups onto a 500 °C-pyrolyzed rice straw BC was the predominant mechanism for the remediation of a Pb-contaminated soil (Fan et al. 2020). The tendency to form surface complexes containing active functional groups differs among PTEs. As an example, the higher affinity of alcoholic, hydroxylic and carboxylic functional groups to Pb^{2+} than Zn^{2+} ions was found to be the main reason for the wide variation in their stabilization efficiency in a contaminated paddy soil (Chao et al. 2018).

Precipitation is another important chemisorption mechanism for the stabilization of PTEs into mineral formations in the charosphere. The high ash and total phosphorus contents in reed straw BC-supported phosphate composite stimulated the remediation of a Pb-contaminated soil via the formation of insoluble cerussite, hydrocerussite and hydroxylpyromorphite precipitates (Cui et al. 2022). In yet in another study, the release of high concentrations of OH^-, CO_3^{2-}, and PO_4^{3-} anions from a 500 °C-pyrolyzed rice straw BC was found to have promoted the formation of stable $Zn(OH)_2$, $ZnCO_3$ and $Zn_3(PO_4)_2$ precipitates (Li et al. 2022a).

Biochar application as a green oxidant/reductant has been widely explored for the decontamination of redox elements [e.g., Cr(VI) and As(III)] by enhancing electron transfer between oxidants and reductants in soil (Ambika et al. 2022;

Rafique et al. 2021; Shaheen et al. 2022b; Wang et al. 2022; Yang et al. 2022b) (Fig. 7). Sulfurization of a 700 °C-*Eichhornia crassipes* BC using sulfide Fe_3O_4 coating triggered As(III) redox conversion through the generation of dissolved O_2 and Fe^{2+} ions (Wang et al. 2022). On the other hand, utilization of sewage sludge BC supported the action of ferrous sulfate as a green reductant for a Cr(VI)-contaminated soil, where passivation was considered from a mechanistic point of view (Li et al. 2020). Alterations in leachability/bioaccessibility of Cr(VI) in the soil matrix could be mainly attributed to its reduction into less soluble and toxic Cr(III) with the help of active functional groups of BC (OH, C=O, C–H and C–O), as well as the concurrent oxidation of grafted Fe^{2+} ions to their trivalent species. The description of the Cr reduction mechanism can be summarized as follows:

$$3Fe^{2+} + CrO_4^{\ 2-} + 8H_2O \rightarrow 4Fe_{0.75}Cr_{0.25}(OH)_3 + 4H^+ \quad (3)$$

$$\begin{aligned} &HCrO_4^{\ -} + Fe - BC + 7H^+ \rightarrow Cr(III) \\ &+ \text{Partially oxidized Fe} - BC + CO_2 + 4H_2O \end{aligned} \quad (4)$$

$$\begin{aligned} &HCrO_4^{\ -} + 7H^+ + \text{Reductive functional groups} \\ &\rightarrow Cr(III) - \text{complexes} + CO_2 + 4H_2O \end{aligned} \quad (5)$$

Note that BC plays roles in modulating soil physicochemical properties and regulating the phytotoxicity of PTEs. The liming effect of BC to raise the pH of acidic soil has been acknowledged as an indirect mechanism for PTE decontamination given the alkaline nature and high ash content of BC (Xu et al. 2022a). Biochar application often increases soil pH, which in turn helps to stabilize PTEs by accelerating the formation of precipitated hydroxide species (Chao et al. 2018). The applicability of BC for mitigating PTE phytotoxicity remains challenging when both cationic and anionic elements are involved. Nevertheless, the addition of a 500 °C-wood BC increased the pH value of soil, promoted the phytoavailability of Cr(VI) and enhanced the immobilization of Cd^{2+} and Pb^{2+} by 85.14% and 28.68%, respectively (Gong et al. 2022).

In addition, the phytoavailability of PTEs can be mitigated indirectly by BC through modulation of the redox state of soil. Yang et al. (Yang et al. 2022b) reported that original (650 °C *Platanus orientalis* L. branches) and Fe-modified BC were highly suitable for mitigating environmental risk of As in paddy soils. The plentiful redox-active moieties (O-containing functional groups and condensed aromatics) improved BC redox buffering capacity, changed soil E_H and thus immobilized As by about 16.0–41.3% at $E_H < -100$ mV. A Fe-modified BC immobilized As to a higher extent, by 32.6–81.1% at $E_H < 0$ mV due to the transformation of As-bound Fe (hydr)oxides into complexes (e.g., ternary As-Fe-DOC). In addition, the redox activity of dissolved organic substances derived from BC could also reduce the phytotoxicity of Cr and As [oxidation of As(III) and reduction of Cr(VI)] (Wu et al. 2021a) (Fig. 7).

The beneficial effect of BC application on soil fertility and buffering capacity can be expressed by increases in CEC (Cation Exchange Capacity), which improves the PTE immobilization efficiency in soil. For example, the addition of 5% and 10% sludge BC (400 °C) to soil collected from a mining area had a significant effect on its CEC (Kong et al. 2021): The CEC value of the untreated soil increased from 9.2 to 12.86 (at 5% of application) and to 13.04 $cmol_c\ kg^{-1}$ (at 10%). The beneficial effect of BC in regulating soil biological properties is another indirect mechanism for enhancing PTE remediation, since bacteria can adhere better to the charosphere instead of being leached out from the unamended rhizospheric layer (Lehmann et al. 2011). The significant contribution of active functional groups (i.e., –OH, –COOH, –NH– and $PO_4^{\ 3-}$) that exist on PTE-tolerant bacterial cells (*Pseudomonas* sp. NT-2) might be the predominant mechanism for immobilizing Cd^{2+} and Cu^{2+} in Cd- and Pb-contaminated soils (Tu et al. 2020). The enhancement of soil bacteria following BC application might also promote the swift reduction of phytoavailable Cr(IV) by accelerating extracellular electron transfer (Zheng et al. 2021). Biochar can also immobilize Hg and reduce its accumulation in rice plants by binding with thiols (e.g., cysteine), which are either BC- or soil-borne (Fig. 8; Xing et al. 2020).

4.1.3 Designer/Functionalized BC for the Stabilization of PTEs in Soil

Recently, BC functionalization (or specialization) has shown a progressively increased effectiveness in the remediation of PTE-contaminated soils (Yang et al. 2023a,b). Analysis of recent literature shows enhancement in the immobilization efficiency of Cd by 2.38%, Cr by 19.27%, Cu by 24.47%, and Pb by 7.22%, following the functionalization process (Fig. 9). Acid and alkali treatments of pristine BC have been widely investigated to maximize their functionality. Alkali-treated BC (KOH-modified rice straw BC at 500 °C) exhibited higher efficiency than the pristine form for reducing Cd^{2+} solubility (30.3 *vs.* 27.4%) and biocaccesability (32.4 vs. 25.2%) in Cd-contaminated red acidic soils (Bashir et al. 2018; 2020). On the other hand, the modulating effect of vinegar residue BC (pH = 5.47) on a Pb-contaminated alkaline soil was studied by Li et al. (2022b). The authors reported that acidic BC reduced exchangeable & carbonate-bound Pb fractions and increased the residual and Fe/Mn–bound fractions.

Experiments have also been performed in an attempt to graft active functional groups (e.g., –OH, –C=O and $–NH_2$) onto BC surfaces to improve its complexation potential. For instance, a cetyltrimethylammonium bromide-modified

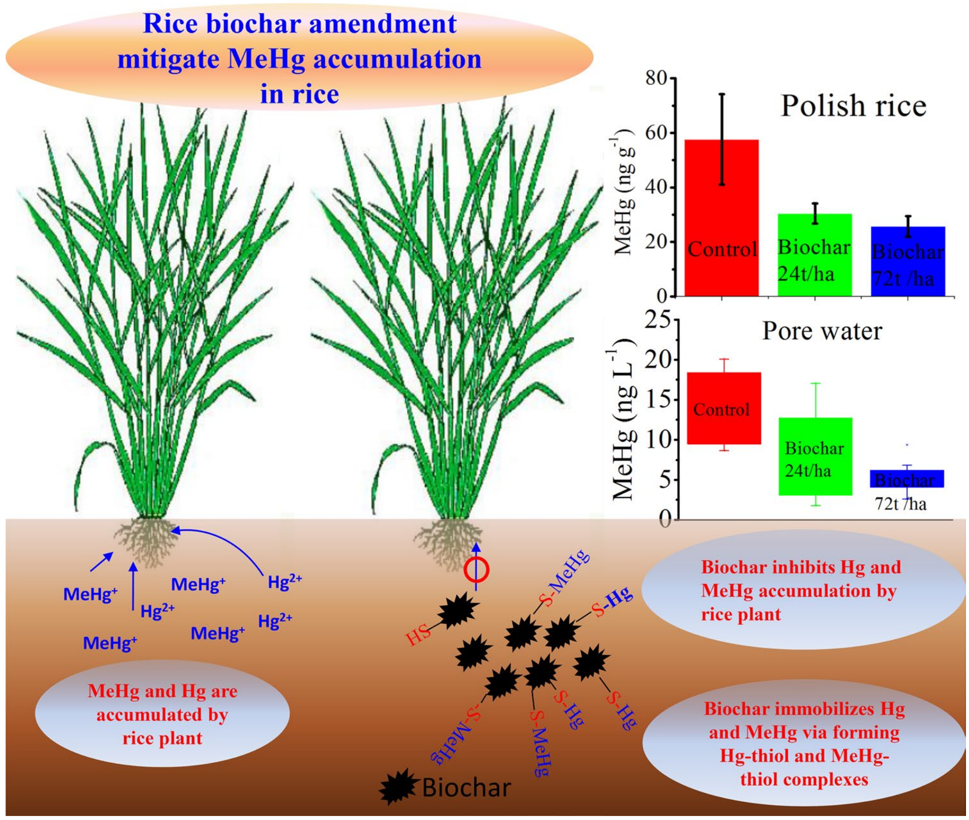


Fig. 8 Effects of the application of rice hull-derived biochar (RHB) at 24 t ha^{-1} and 72 t ha^{-1} on total Hg (THg) and methylHg (MeHg) immobilization in a paddy field and their accumulation by rice plants (Reproduced from Xing et al. (2020), with a permission of the publisher

peanut-shell BC showed outstanding capacity for decreasing the bioavailability of Cr(VI) by 92%, its leachability by 100%, and its bioaccessibility by 97% compared to the untreated form (Murad et al. 2022). The authors argued that this greater passivation efficiency of the engineered BC was due to the grafting of carbonyl functional groups, which served as proton donors for the reduction of Cr(VI) ions. Gholami and Rahimi (2021) synthesized a modified thiourea-potato peel BC for the immobilization of Cd^{2+}, Cu^{2+} and Zn^{2+} in an acidic contaminated soil. The application of the modified BC at a dose of 8% maximized the solidifying efficiency of Cd^{2+} (5142.63 mg kg^{-1}), Cu^{2+} (4993.12 mg kg^{-1}) and Zn^{2+} (3508.44 mg kg^{-1}) due to the enrichment of BC surfaces with –OH, –C=O, –COOH and –C–O groups. Recent results about the impacts of functionalized BC on the mobilization and phytoavailability of As, Cd, and Pb in a paddy soil are published in Yang et al. (2023a,b).

Nano-scale fabricated BC have recently been tested for their ability to improve TE immobilization in soil. In this regard, ball milled BC-supported nanoscale red P particles were investigated for the immobilization of Cd^{2+} and Pb^{2+} in an alkaline soil (Zhang et al. 2022). The nano-sized BC showed outstanding performance for the decontamination of PTEs in soil by accelerating the conversion of red P into phosphorus oxides, (hydro)phosphates and phosphoric acid, following the interaction with alkaline minerals, carbonates and O-containing functional groups of ball milled-BC. Another study used a 700 °C-pine BC as a carrier for nano zirconia (ZrO_2) for solidifying an As(V)-contaminated brown soil (Liu et al. 2021). Application of 2 wt% of a nano zirconia-loaded BC recorded outstanding stabilization efficiency (retaining 99.3% of the amount added) due to the abundance of –Zr–O functional groups that produce tetranuclear ions, which are rich in –OH ligands.

Biological activation of raw BC was also investigated by Ji et al. (2022). Several bacterial strains (*Bacillus velezensis*, *Bacillus cereus* and *Bacillus amyloliquefaciens*) were loaded onto a 500 °C-corn stalks BC and exploited for the decontamination of a polluted soil system. Results pointed to a mutual synergistic effect between bacterial strains and BC with a long-lasting passivation of PTEs into precipitated forms [i.e., $Pb_5(PO_4)_3OH$, $Ca_2As_2O_7$, $CdCO_3$ and $Cd_3(AsO_4)_2$]. Interestingly, application of BC-immobilized Cd-resistant bacteria (*Arthrobacter* sp. and *Micrococcus* sp.) significanly increased the accumulation of Cd in *Chlorophytum laxum* grown in a highly contaminated agricultural soil in Thailand (Chuaphasuk and Prapagdee 2019). Those authors explained this trend as being the result of the accumulation of Cd in tolerant bacterial strains (bacterial cell walls and exopolymers), leading to maximized Cd^{2+} bioavailability in the soil. This type of functionalized BC, therefore,

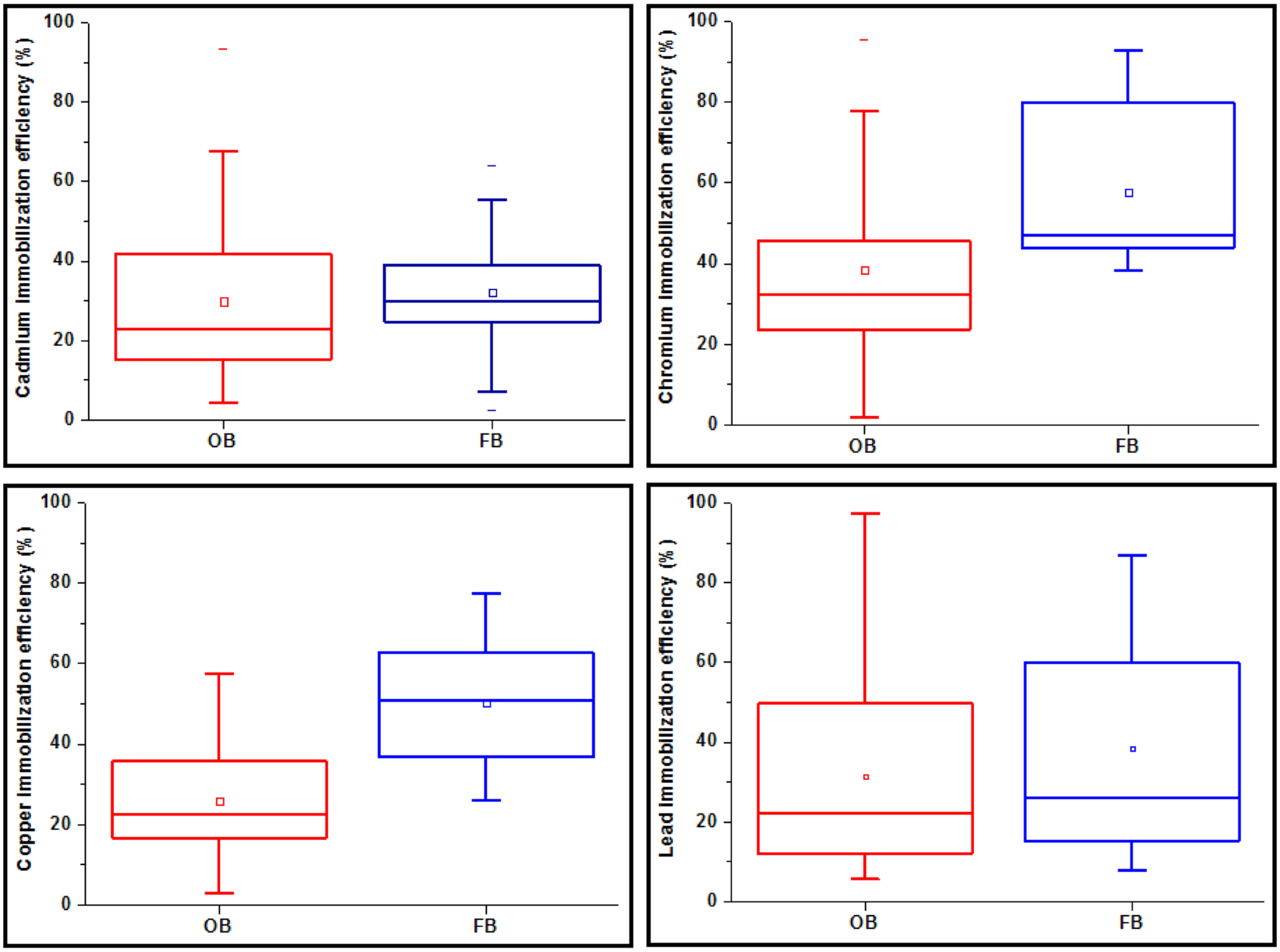


Fig. 9 Effect of biochar functionalization on immobilization efficiency of TEs (%). Data are extracted from 315 observations comprising 36 recent studies. The box chart presents median (centerline), mean (dot), lower quartiles (lower border of the box), upper quartiles (upper border of the box) and whiskers-error bars (the minimum and maximum observations)

can effectively promote Cd^{2+}-phytoextraction efficiency by metallophytes.

Doping heteroatoms (e.g., P, N, S and Ni) into BC showed promising results for the PTE decontamination, owing to the electron-withdrawal effect. Phosphorus-based BC (reed straw-supported potassium dihydrogen phosphate or hydroxyapatite) showed higher Pb^{2+} stabilization than the original form (400 °C) through the active transformation of labile Pb^{2+} into Fe/Mn oxides and residual fractions (Cui et al. 2022). Similar observations were also reported by Ren et al. (2020) in stabilization of Cd and Pb in soils using pristine swine manure BC and P-enhanced engineered BC. Moreover, Luo et al. (2022) attributed the beneficial effect of incorporating P into BC to the enhancement of BC stability in soil by the chemical formation of C–O–P, $C–PO_3$ and $C_2–PO_2$, thereby maximizing the immobilization of Pb^{2+} and Cd^{2+}. Sulfur doping into a 550 °C-bamboo hardwoods BC greatly increased the formation of Fe plaque on the surfaces of rice roots and decreased the accumulation of Cd in grains below the standard soil maximum allowable limits (0.2 mg kg^{-1} as recommenended by the China National Standard) (Rajendran et al. 2019).

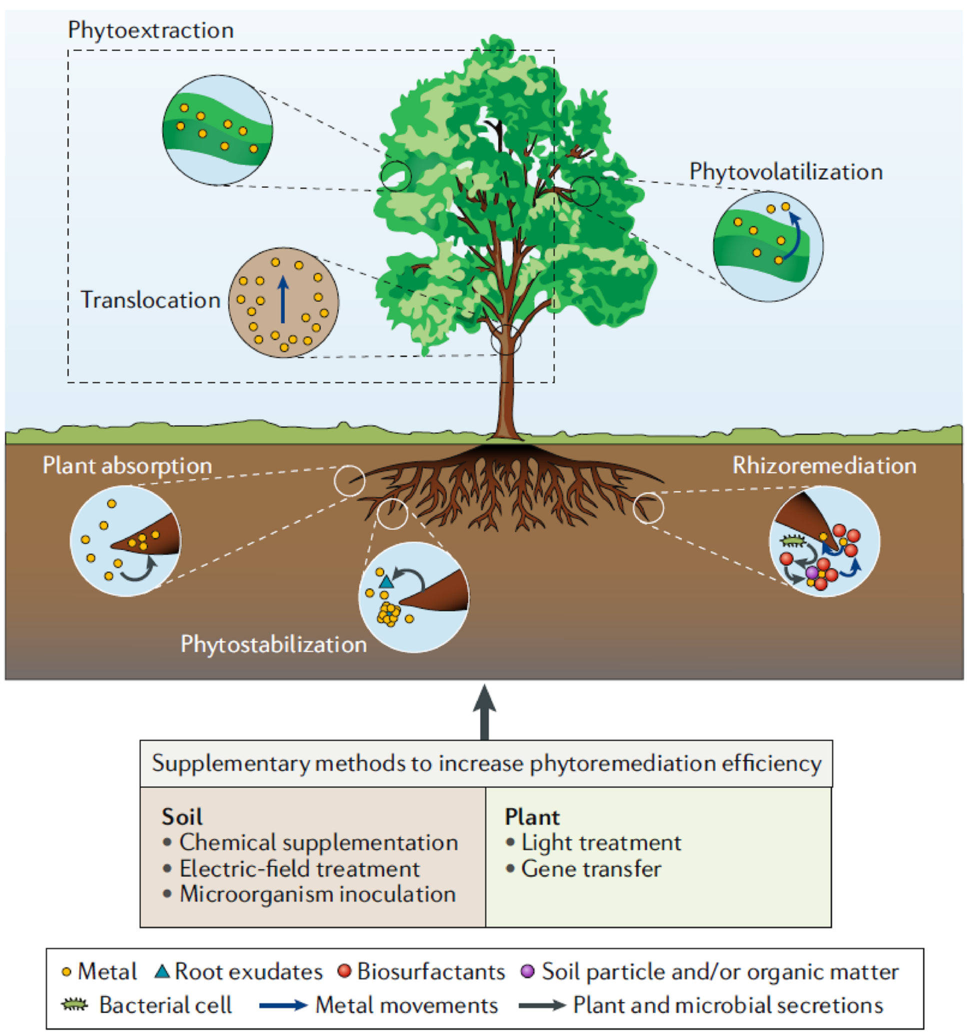
It is believed that BC have a greater capacity to stabilize PTEs after aging. The effect of dry–wet and freeze–thaw aging on the phytoavailability of Cd^{2+} and Cu^{2+} was studied in a contaminated soil near a Cu smelter in Jiangxi Province, China (Cui et al. 2021). Biochar aging resulted in the reduction of Cu^{2+} and Cd^{2+} phytoavailability; however, the ecotoxicological risk could be increased by aged BC rich in endogenous PTEs. The effect of three aging methods on the stabilization performance in a Pb-contaminated soil by BC was found to be significant; these methods were high-temperature, freeze–thaw, and natural aging, in order of decreasing effectiveness (Chen et al. 2022). In a study conducted by Rathnayake et al. (2021), it was found that when H_2O_2-aged BC (equivalent to a naturally aged BC of 100 years) was applied at 2 wt%, it resulted a higher Cd decontamination efficiency when compared to fresh BC; aged BC produced at high temperatures (500 and 600 °C) were superior to those produced at low temperature (400 °C).

Recent attempts at BC activation have also been directed toward generating hybrid magnetized forms through grafting ferromagnetic oxides into the carbonaceous matrix of the pristine BC (Shaheen et al. 2022a, b, c. For example, an Fe–Zn oxide-modified corn straw BC (at 500 °C) was more effective than its pristine form for reducing the extractability of Cd in both acidic and alkaline soils: the modified BC retained 35.1% of the initially added amount vs. 17.0% for the pristine BC in the acidic soil, while in the alkaline soil the modified BC retained 38.1 vs. 12.0% for the pristine BC (Yang et al. 2021a). The prominent safeguarding effect of the functionalized BC is related mainly to the incorporation of exchangeable Cd^{2+} into its Fe/Mn oxyhydroxide-bound fraction. The abundance and diversity of bacterial communities in the soil was significantly stimulated as well. To date, functionalization of effective BC composites for simultaneous immobilization of cationic and anionic pollutants remains challenging. In this regard, a novel sulfide Fe_3O_4 coated BC composite (derived at 700 °C from *Eichhornia crassipes*) was fabricated for the simultaneous removal of As(III) and Pb(II) (Wang et al. 2022). The excellent stabilization performance of the designed dual-purpose BC was attributed to the maximized BC functionality (specific surface area and anionic exchange capacity) followed by the stimulation of As(III) oxidation and Pb(II) precipitation.

4.2 Biochars for Enhancing PTE Phytoremediation

Phytoremediation is a green, ecofriendly, and low-cost method for the remediation of PTE-contaminated soils (Fig. 10). Many hyperaccumulators such as *Pteris vittata*, *Zea mays*, and Brassica species have been employed for the phytoextraction of PTEs (Khalid et al. 2017). Plant growth in highly contaminated soils is severely affected, and biochar application in combination with phytoextractors can be an

Fig. 10 Schematic representation of phytoremediation strategies (adapted from Favas et al. 2014 and Reproduced from Huo et al. 2021, with a permission of the publisher)



effective method for PTE remediation in such soils (Khalid et al. 2017; Pračke et al. 2021).

4.2.1 Biochars for Enhancing PTE Mobilization and Phytoextraction

Phytoextraction is a widely applied method for the reclamation of contaminated soils using hyperaccumulator plants to absorb PTEs. Phytoextraction is often used in agricultural soils to lower the concentrations of PTEs to ensure sustainable crop production. Preferably, plant species used for phytoextraction not only accumulate high concentrations of targeted PTEs but also exhibit high biomass yield, high tolerance capacity, resistant to pests and diseases, and are easy to cultivate (Khalid et al. 2017; Yadav et al. 2018). Although hyperaccumulators absorb high PTE concentrations, they are often characterized by slow growth, which may limit their efficiency. If this is the case, then in highly contaminated soils phytoextraction could last for hundreds of years. There is a considerable and ever-increasing bibliography regarding the use of BC for the immobilization of PTEs (El-Naggar et al. 2021). However, there are only few studies available focusing on the effect of BC on the phytoextraction of PTEs (Uchimiya et al. 2011).

PTEs mobility and bioavailability are dependent on the characteristics of both BC and the contaminated soil (Ghosh and Maiti 2021). The addition of BC to soil can affect soil pH and dissolved organic matter. Consequently, its application to soil influences the mobility and phytoextraction of PTEs (Fig. 11). Some studies have shown that in BC-amended soils the mobility of PTEs such as As, Cu, and Sb may increase (Beesley et al. 2010; Uchimiya et al. 2011). The possible mechanism for such mobilization is the electrostatic repulsion between anionic PTEs species and negatively charged BC surfaces, resulting in the desorption of PTEs (Sun et al. 2022). The resulting increase in phytoavailable PTEs results in high uptake by plants (Fig. 11). Although most research findings indicate that the addition of BC reduces the bioavailability of PTEs, little is known about the use of BC to phytoremediate PTE-contaminated soils by increasing their bioavailability. Plants require high concentrations of soluble PTEs and any change of the added BC to this effect could accelerate phytoextraction, an approach not widely studied yet.

BC was indeed found to increase the dissolved concentrations of Cu, Cd, Ni, and Zn, especially the former, under oxic conditions was reported by El-Naggar et al. (2018). In another work, El-Naggar et al. (2019b) found that BC increased the dissolved and colloidal concentrations of As, Co, and Mo under oxidizing conditions. In the same soil, Rinklebe et al. (2020) found that BC mitigated Ag release, but promoted Sb, Sn, and Tl mobilization under a wide range of redox changes. In three studies (El-Naggar et al. 2018, 2019b; Rinklebe et al. 2020), the changes in soil redox potential (E_H) affected the release of the studied PTEs, particularly the anions As and Mo. Oxic conditions can stimulate the formation of mobile pentavalent As species such as $H_2As^VO_4^-$ and $HAs^VO_4^{2-}$, as reported by Takeno (2005). Also, the BC surface functional groups may act as electron donors for PTE reduction reactions. For example, BC may play an important role in reducing Tl^{III} to Tl^I, Sb^V to Sb^{III}, and Sn^{IV} to Sn^{II}. During all these processes, the reduced state is more mobile than the oxidized, and so PTE availability increases.

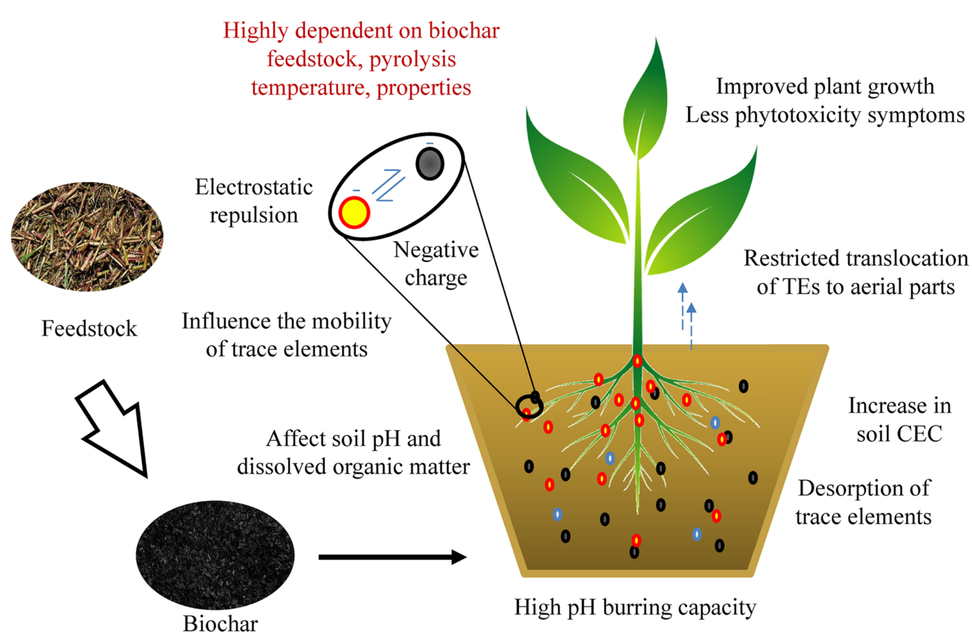


Fig. 11 Potential effects of biochar on phytoextraction of trace element contaminated soils (adapted from Ghosh and Maiti 2021)

The changes in soil E_H may also cause changes in soil pH, which can affect the solubility of PTEs. For example, the E_H-induced decrease in pH of BC-treated soils was found to increase the mobilization of metallic cations such as Cd, Cu, and Zn, while E_H-induced increases in pH caused the mobilization of the metal anions As, Mo, and V (Shaheen et al. 2019a, b; El-Naggar et al. 2019b). Soil E_H and pH may also affect the BC surface activity, which might decrease the original alkaline sites on BC surfaces and form new acidic functional groups; these may increase the dissolved concentration of the anionic PTEs like As in BC-treated soils. Hence the surface functionality of BC plays a vital role in its effects on PTE mobilization in soils. For example, El-Naggar et al. (2021) concluded that the application of rice-hull BC, which has a low density of oxygen-containing functional groups, increased V solubility and uptake. They also found that a BC with a high density of oxygen-containing functional groups immobilized V and reduced its solubility by 46% and its uptake by corn and sorghum by up to 86% as compared to the control. This can be attributed to the high reactive surface area, the acidity, the abundance of various oxygen-containing functional groups, and the hydrophilicity of the former BC.

4.2.2 Designer/Functionalized BC for Enhancing PTE Mobilization and Phytoextraction

Previous studies have reported the production and use of designer/functionalized (i.e., specialized) BC with superior functions to achieve an improved performance in reducing the mobilization and bioavailability of PTEs in soils (Chen et al. 2021; Sornhiran et al. 2022; Yang et al. 2022b). However, phytoremediation, including phytostabilization, phytoextraction, and phytostimulation (Antoniadis et al. 2017; Zhang et al. 2021), is generally restricted due to the bioavailability of PTEs. On the other hand, designer/functionalized BC could also assist in phytoremediation by enhancing the mobility and bioavailability of PTEs (Wang et al. 2019), being at the same time a source of both carbon and nutrients (Khudzari et al. 2019), improving microbial activity (Natasha et al. 2021), and regulating soil reaction (e.g., pH and redox potential; Yang et al. 2021b).

Several recent studies have proved the potential of designer/functionalized BC for the mobilization of PTEs in soils, as well as the enhancement of their uptake and translocation within plants (Abd El-Mageed et al. 2020; Zhang et al. 2020; Wen et al. 2021). For instance, Abd El-Mageed et al. (2020) reported that the uptake of Cu, Fe, Mn, and Zn by *Capsicum annum* increased by 6%, 16%, 8%, and 18%, respectively, following the application of a residual sulfur-enhanced citrus wood BC. Wen et al. (2021) conducted a rice cultivation experiment, where they found that the application of an iron-modified green waste BC alleviated As, while elevating Cd and Pb accumulation in rice plants (*Oryza sativa* L.), under both continuously flooded and alternatively wet and dry water management regimes. This could have been caused by the BC-induced change in soil pH. However, Zhang et al. (2020) reported that tripotassium phosphate-impregnated BC, regardless of feedstocks (i.e., bamboo offcuts, camphorwood chips, cornstalks, and rice husks), immobilized Cd(II) and Cu(II) through precipitation and complexation, while increasing the mobilization of As(V), because of the competition between phosphate and arsenate for the same binding sites. Similarly, through a redox incubation experiment, Yang et al. (2022a) found an increase of As mobilization after the addition of a phosphorus-rich BC derived from pig carcasses, under both strongly reducing and oxidizing conditions. Guo and Li (2019) observed an enhanced uptake of Cr (by 16%) and Pb (by 2%) by *Senna occidentalis* after the incorporation of an iron-modified coconut husk BC into the soil. It is well-know that PTE accumulators/hyperaccumulators are capable of absorbing higher-than-normal concentrations of PTEs from soils and can readily transport and accumulate those PTEs in their above-ground tissues (Antoniadis et al. 2017). Although many studies have paid attention to the bioremediation of PTE-contaminated soils using hyperaccumulators assisted with pristine BC (Gu et al. 2020; Ghosh and Maiti 2021; Rathika et al. 2021; Zhang et al. 2023), the role of designer/functionalized BC is scarcely studied. A schematic of phytoremediation mechanisms of designer/functionalized BC in PTE-contaminated soils is shown in Fig. 12, as a recommendation for future studies.

4.2.3 Biochars for Enhancing PTE Phytostabilization

Phytostabilization is another process widely used for decelerating the mobility of soil contaminants. Vegetative cover diminishes eolian dispersion and water erosion, while roots prevent leaching and contribute to the immobilization of PTEs (Sun et al. 2022). The mechanisms involved in phytostabilization include precipitation, root sorption, complexation, and metal valence reduction (Shahid 2021). Unlike phytoextraction, phytostabilization primarily focuses on PTE sequestration within the rhizosphere or sometimes in the roots. The low transfer of PTE in the aerial parts can be considered as a major plant defense mechanism that contributes to their phytostabilization efficiency (Ogundiran et al. 2018).

The primary mechanism of stabilization in soil is related to pH: soils with high pH keep PTs relatively immobilized and thus stabilized. However, changes to soil pH in the rhizosphere can potentially affect the effectiveness of BC to immobilize PTEs in soils (Wang et al. 2022). The immobilization of PTEs takes place through multiple ractions of BC with soil PTEs, including precipitation, complexation, electrostatic interaction, and ion exchange. However, some

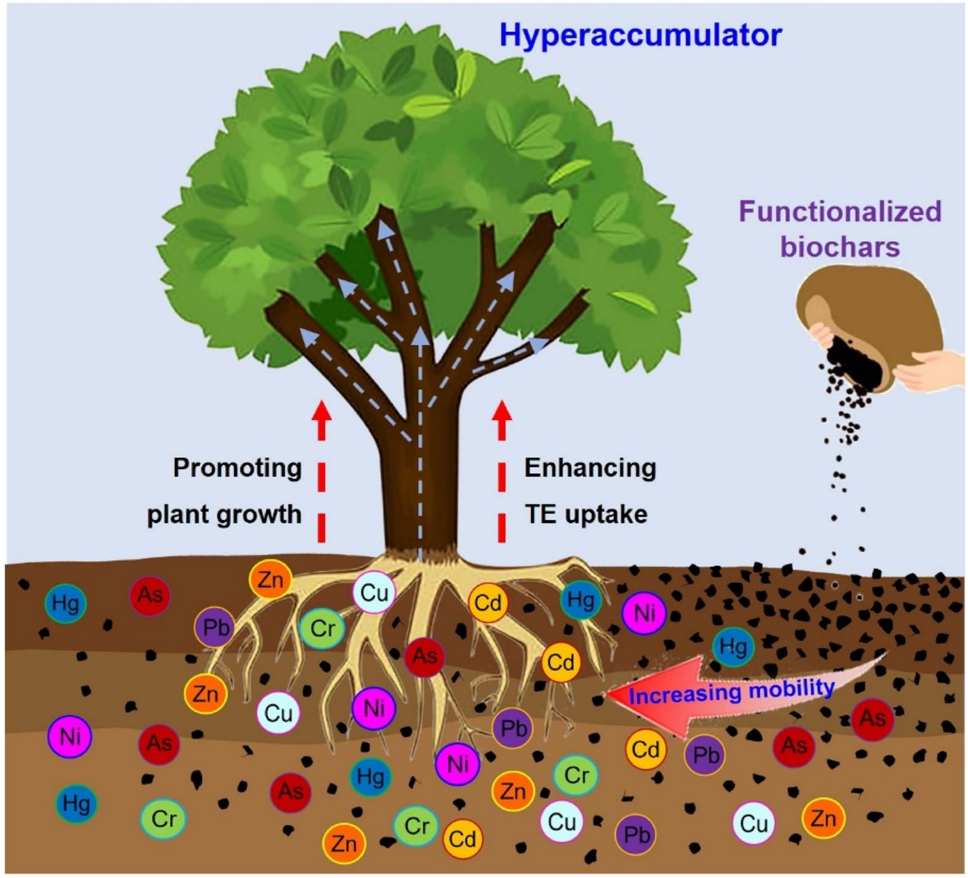


Fig. 12 Schematic of the mechanisms of the designer/functionalized biochars assisting in phytoremediation of soils contaminated with PTEs

changes in physicochemical soil properties (pH, CEC, water retention) can also lead toward the immobilization of PTEs in soils (Ghosh and Maiti 2021; Natasha et al. 2021). A wide range of different studies have unanimously reported that BC can stabilize contaminants in soils to reduce their bioavailability and thus their concentrations in plants [e.g., (Visconti et al. 2020)].

4.2.4 Biochars for Enhancing PTE Bioremediation

Microbial bioremediation is the processes by which soil microbes can govern the amelioration of PTEs in soils (Tsezos 2009; Ahemad 2019; Huo et al. 2021; Zhang et al. 2023; Fig. 13). Microbes can affect PTEs mobilization in soils via different mechanisms including biosorption, biosynthesis or biodegradation, bioleaching, bioprecipitation, bioaccumulation, and bioassimilation (Fig. 13; Hou et al. 2020). Details about the microbe-PTE interactions can be found in other articles (e.g., Tsezos 2009; Ahemad 2019; Hou et al. 2020; Zhang et al. 2023).

Adding BC to soil strongly influences soil physiochemical and biological properties (Azeem et al. 2023). This is largely because BC is stable under microbial decomposition, which is mainly a consequence of the presence of aromatic carbons in its macromolecular structure (Yang et al. 2022a,b; Tomczyk et al. 2020). Biochar offers a wide range of environmental services, especially with respect to phytoremediation, by directly or indirectly shaping the microbial community structures (Xu et al. 2022a). Stimulations of plant potential primarily take place through changes in the BC-microbe-plant interface (Andrey et al. 2019).

Biochar can influence the microbially mediated phytoremediation in many ways (Fig. 14). A few notable interactions are: (i) enhancing the key soil factors shaping the rhizosphere; (ii) acting as a niche or microhabitat preventing predation; and (iii) impacting chemical signals to accelerate soil decontamination (Zhu et al. 2017). Many of these functional alterations induced by BC probably occur at a micron scale and thus only the immediate vicinity of BC is predominantly influenced (Gundale and DeLuca 2006; Azeem et al. 2023).

The modification of nutrient availability is a prerequisite for alleviating the inhibitions to microbial and plant growth in a highly stressed environment (Olmo et al. 2016; Azeem et al. 2023). Primarily, BC elevates the quantity of bioavailable nutrients, base cations and minerals (metallic and non-metallic alike) by altering soil pH and increasing cation exchange capacity (Hossain et al. 2020). Biochar also makes microbial mobility easier by decreasing the soil bulk density due to increased macroporosity, an effect that also improves

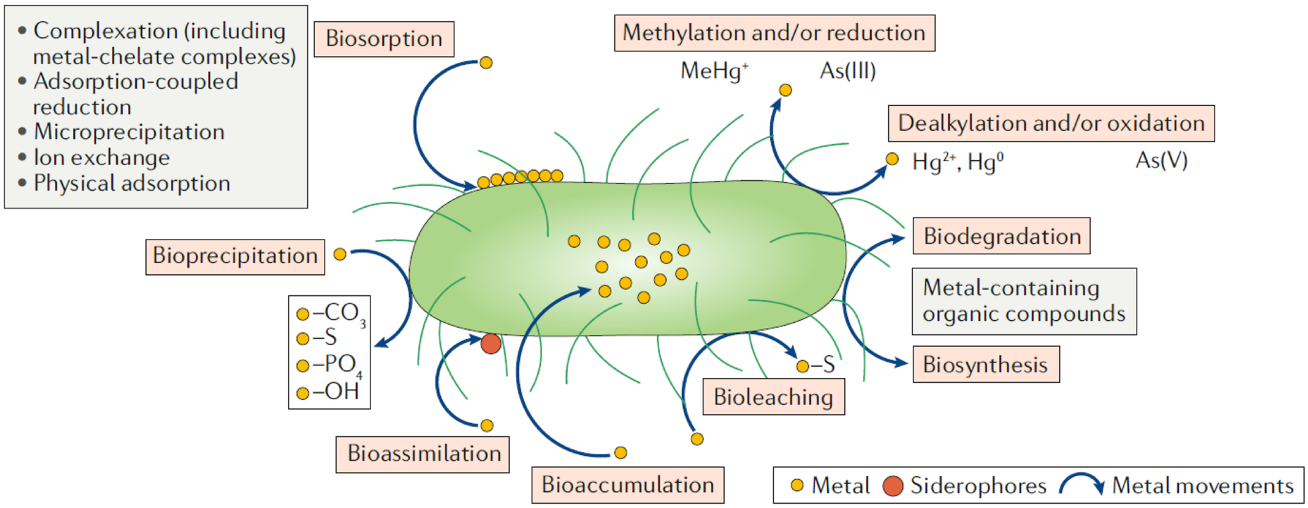


Fig. 13 Microbial bioremediation: depiction of various types of bacterial interaction with heavy metals in metal polluted soils (Adapted from Tsezos 2009; Ahemad 2019 and Reproduced from Hou et al. 2020, with a permission of the publisher)

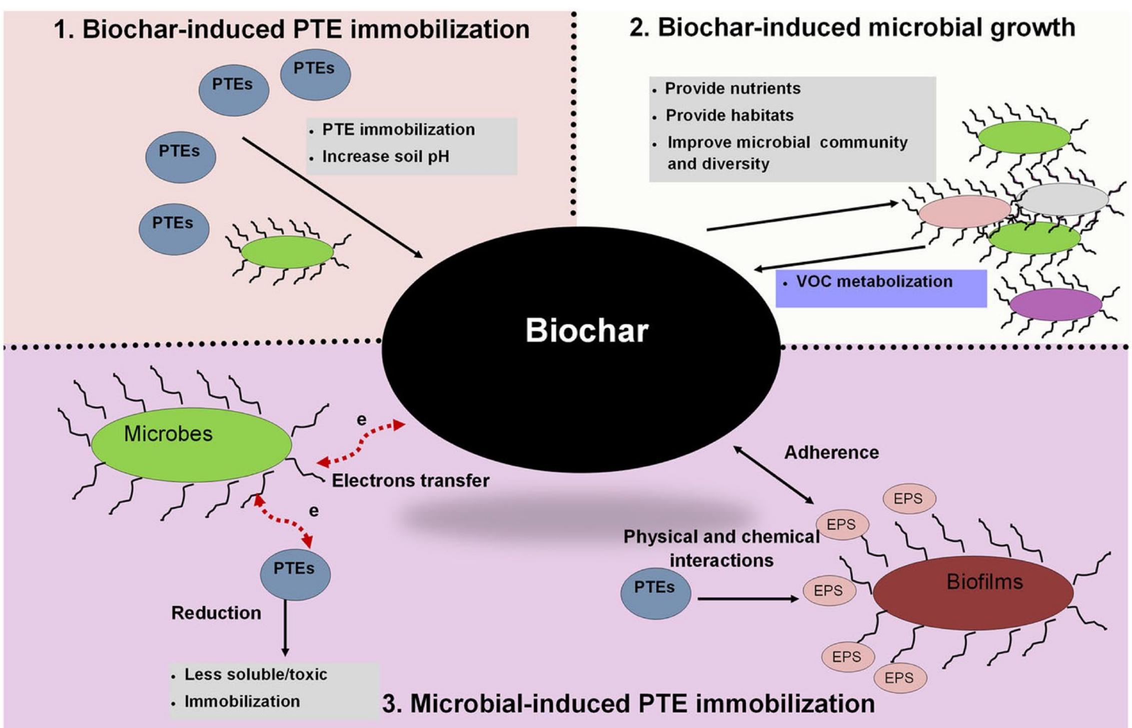


Fig. 14 Proposed immobilization mechanisms of potentially toxic elements (PTEs) by soil microorganisms in biocharamended soil. EPS, Extracellular polymeric substances (Reproduced from Bandara et al. (2020), with a permission of the publisher)

soil aeration and water retention (Chang et al. 2021). Other BC components such as minerals, free radicals and volatile organic matters strongly controlmicrobial abundances (Spokas et al. 2011; Paz-Ferreiro et al. 2014).

By enhancing beneficial plant genera, including *Pseudomonas*, *Bacillus, Rhizobia*, and *Trichoderma*, BC stimulates plant performance by enhancing growth hormones, including IAA, ethylene, cytokinin and gibberellins (Jaiswal et al. 2020). This boost helps to alleviate growth restrictions and achieve a higher biomass, all of which are indispensable for phytoremediation (Kocsis et al. 2020). Biochar helps in reversible nutrient retention via sorption, either of cations or inorganic anions, onto its surface functional groups. It can thus act as a slow-release fertilizer in its own right, boosting overall nutrients efficiency (Mukherjee and Zimmerman 2013). By promoting soil fertility as well as by acting as a carbon source, BC also promotes plant growth-promoting rhizobacteria (PGPR) that are crucial for transforming sulfur, phosphorous and other such metallic and non-metallic minerals into phyto-available forms (Wu et al. 2019).

Plant growth-promoting microbes can resist metal pollutants and this reduces PTE availability to plants. This is achieved by various interactions, including secretion of metal-binding proteins (phytochelatins and metallothioneins), chelation, complexation, mobilization, and translocation (Wiangkham and Prapagdee 2018). Plant pathogens generally degrade plant health and reduce plant phytoextraction potential. However, by controlling the hormonal and nutrient equilibrium, PGPR can inhibit attacks by pathogens (Spence and Bais 2015). Biochar may even become toxic toward pathogens, due to the fact that it possesses microbial inhibitors in its structure, such as benzene, phenols, furans, VOCs (volatile organic carbons), and persistent free radicals (Truong et al. 2010). The inhibition is not species-specific, but at higher concentrations, these substances can cause toxic effects on pathogenic microbes.

Due to its porous nature, BC can provide more habitable pore volume per unit volume than soil (Quilliam et al. 2013). The porosity determines its surface activity; macro-pores can act as a habitat accommodating microbes, protecting them from predation, while capillary pores are mostly involved in molecule adsorption and transport (Atkinson et al. 2010). Moreover, BC provides a surface for microbial attachment by promoting niches. Recent studies (e.g., Hill et al. 2019) reported that smooth-surfaced BC may act as a substrate for the formation of microbial biofilm. Smooth surfaces (BC as well as plant roots) and quorum sensing molecules are the prerequisites for such biofilm establishment. Biofilms are dense communities composed of polymeric matrices, mostly of polysaccharides, protein complexes and extracellular DNA (Limoli et al. 2015). They thus offer protection to beneficial microbes against various stresses, toxins and pollutants. Biofilms can act as biosorbents or exopolymeric substances, due to their surfactant and emulsifying properties, to mitigate the toxic effects of metal ions (Ugya et al. 2021). Such natural transformation and/or protein interaction of BC is responsible for changes in the bioavailability of metal ions to plants, enhancing their phytoremediation potential (Sharma 2021).

The rhizosphere accommodates numerous interactions, secretions and signaling between plant roots and microbial biota (Li et al. 2022a, b, c). Biochar, by adsorbing the inhibitory phenolic contents of soil, promotes the beneficial microbial biomass in the rhizosphere, which may then actively take part in metallic mineral solubilization (Liu et al. 2022). The sorptive capacity of BC could act as signaling interference in the rhizosphere and could serve as a signal reservoir or sink. Due to the sorption capacity of BC, it may also inhibit certain components, including allelochemicals (Oni et al. 2019). For instance, Akiyama et al. (2005) demonstrated the ability of BC to adsorb and desorb strigolactone, a signaling compound that promotes arbuscular mycorrhizal colonization in plant roots. The adsorbed signaling molecules can thus act as a secondary source, which can easily be desorbed back into solution, making them available to stimulate microbe-plant interactions (Ding et al. 2016).

Biochar is also recognized for adsorbing and protecting chemical signaling molecules that are derived from plants, such as the *nod* factor; this is responsible for enhancing root nodulation by rhizhobia, a major determining factor for enhancing plant biomass (Thies and Rillig 2012). Biochar can alter signaling-dependent protein expression and can also modify microbe-plant interactions especially in the rhizosphere, diminishing pathogen attacks as well as triggering systemic plant defenses, including both SAR (systemic acquired resistance) and ISR (induced systemic resistance) systems (Harel et al. 2012). The SAR is related to the pathogenic protein-mediated salicylic response and the ISR occurs through plant beneficial microbial colonization (Elad et al. 2010). Apart from inducing systemic plant defense mechanisms, BC has priming effects on gene expression in plants once they become infected (Jaiswal et al. 2020). BC also promotes the colonization of arbuscular mycorrhizal fungi, some of which are known to be involved in interplant signaling in pathogen resistance through interconnected hyphal networks (Johnson and Gilbert 2015). By conferring resistance to plant pathogens and enhancing microbial abundance, BC stimulates biomass as well as the microbial-assisted metal uptake by plants (Zhang et al. 2017).

5 Conclusions

The pros and cons of the addition of BC to PTEs contaminated soils are reviewed in this article. In particular, BC-induced changes on the mobilization, phytoextraction, phytostabilization, and bioremediation of PTEs in contaminated soils have been discussed and summarized. We conclude that addition of BC to metal(loid)s polluted soils affect both their mobilization and phytoavailability, which mainly depends on the type and properties of the elements, soils, and feedstocks. The chemical and surface properties of BC strongly control their ability to (im)mobilize PTEs in soils. The addition alkaline BC to contaminated acidic soils can increase soil pH, and thus may increase the sorption and immobilization of metal cations (e.g., Cd, Cu, Zn); however, it may increase the mobilization of metal anions such as As, V, and Cr. The associated increase of soil alkalinity after addition of alkaline BC to soils can cause a competition between OH^- and $HAsO_4^{2-}$ and thus increase As release and mobilization. The BC-induced increase of dissolved organic carbon may increase the mobilization of some PTEs including Cu, and the redox-mediated interactions between BC and PTEs greatly impact their mobilization. Biochar can donate or accept electrons via functional groups and thus can reduce or oxidize the soil environment, which impacts the reduction or oxidation of redox sensate PTEs such as As and Cr, changing their speciation and mobilization potential. Biochar may enhance the PTEs mobilization and thus increase phytoremediation efficiency. The BC induced enhances in roots growth may increase the roots ability for PTEs absorption (rhizoremediation). Addition of BC can also enhance the PTEs translocation from the roots to the above-ground biomass, where they can be lost by transpiration (phytovolatilization) or be removed from the field by harvesting the plant. Moreover, BC-induced changes on the microbial community and activity can affect the mobilization and bioremediation of PTEs in polluted soils. In turn, increasing the mobilization of PTEs using BC can enhance phytoextraction of these PTEs in soils and shorten the phytoremediation period, which is recommended from agro-environmental and economic points of view. This review demonstrates the potentiality of using BC as a promising effective material for the green remediation of PTEs contaminated soils. However, more attention is needed to verify the potentiality of engineered/designer BC as a mobilizing agent for enhancing the phytoavailability and phytoextraction of PTEs in soils. Also, more future research is needed to investigate the interactions between PTEs with BC using advanced spectroscopic techniques.

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