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Impact of Biochar on the Bioremediation and Phytoremediation of Heavy Metal(loid)s in Soil

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Abstract

Anthropogenic activities, such as mining/smelting, result in the release and accumulation of heavy metal(loid)s in soil, posing serious human health and ecological risks. Due to the persistence of metal(loid)s, not undergoing any chemical and biological degradation, they can only be either immobilized or removed by, bioremediation and phytoremediation. Biochar is increasingly being recognized as a promising, effective material that can be used to remediate various contaminations including excessive heavy metals in soil. This chapter provides an overview of the state of the art on biochar resources, production processes and result of pyrolysis, surface characteristics of biochar, interactions of biochar with soil, and associated biota (microbes and plant). Furthermore, the understanding of characteristics of biochar and the interactions of biochar with soil and biota is necessary to assess the impacts of biochar on bioremediation and phytoremediation of heavy metal contaminated soil.

Keywords: biochar, heavy metal(loid)s, soil contamination, bioremediation, phytoremediation

1. Introduction

Soil contamination with heavy metal(loid)s can be attributed to many different sources such as agricultural and mining activities, industrial and residential release, which pose serious risks to environmental safety and human health. Various remediation techniques, based on either mobilization or immobilization processes, have been developed to solve

these challenges. Of those methods, bioremediation, especially biochar amended phytoremediation, is increasingly being recognized as a promising technology that can be used to remediate various contaminations in soil. Many studies have reported that biochar has been effectively used to immobilize the metal(loid)s in contaminated soils and influence the bioavailability and bioaccessibility of metal(loid)s. Bioremediation, especially phytoremediation of metal(loid)s, has been extensively studied. Biochar, the carbon-rich product, is perceived to play significant roles on the bioaccessibility and bioavailability, hence biotransformation and bioremediation of heavy metal(loid) contaminated soil. However, biochar is often prepared from a variety of feedstocks under different pyrolysis systems, and thus, the surface properties could be varying significantly. It is urgent to address some key areas of research in order to ensure a safe and sustainable use of biochar. In particular, understanding the characteristics of various biochar, illustrating the effects of biochar properties on heavy metal(loid) behavior and transport, evaluating the influence of biochar on soil structure and nutrients, microbial community, plant growth, and consequently the effectiveness of bioremediation and phytoremediation are some of the areas that require attention.

This chapter provides an up-to-date review on the state of the art of environmental impacts and applications of biochar amended bioremediation and phytoremediation of heavy metal(loid) contaminated soil. In addition, the discussion will focus on the remediation of highly toxic metal(loid)s such as arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), and lead (Pb) and different land-use scenarios that can potentially cause human health and phytotoxicity problems.

2. Characteristics of biochar

2.1. Physiochemical properties

Biochar is generally obtained from the low-temperature (e.g., 400–700°C) pyrolysis of various biomass such as manure [1], agricultural residues [2], bamboos [3], and biosolids in the absence of oxygen and is often used as a soil amendment [10], which is therefore distinguished from fuel charcoal. **Table 1** summarizes the physiochemical properties of biochar that is derived from wood material, agricultural by products, poultry litter, or sludge under different pyrolysis temperatures.

As shown in **Table 1**, although the physiochemical properties of biochar varied significantly due to the production from a variety of feedstocks under different pyrolysis systems, biochar is generally alkaline and has high surface area with large porosity, variable charges, and various functional groups. These characteristics can further affect its pH, cation exchange capacity (CEC), and surface sorption capacity. The particle size of biochar depends on the initial particle size of the feedstock, but it is likely to be smaller than the feedstock due to shrinkage and attrition during pyrolysis. An increased pyrolysis temperature could result in smaller biochar particles due to the decreased tensile strength of the feedstock at higher pyrolysis temperature [9].

Feedstock	Pyrolysis temperature (°C)	pH	CEC (mmol kg ⁻¹)	C (%)	C/N ratio	Total P (mg kg ⁻¹)	Ash (%)	Volatiles (%)	Surface area (m ² g ⁻¹)
Oak wood [4, 5, 10]	60	3.7	182	47.1	444	5	0.3	88.6	n.d.
	350	4.8	294	74.9	455	12	1.1	60.8	450
	600	6.4	75.7	87.5	489	29	1.3	27.5	642
Pine needles [6]	300	6.4	n.d.	84.2	22	n.d.	7.2	38.6	4.1
	500	8.1	n.d.	90.1	22	n.d.	11.8	15.8	13.1
	700	10.6	n.d.	93.7	26	n.d.	18.7	6.2	391
Corn stover [4, 5, 10]	60	6.7	269	42.6	83	526	8.8	85.2	n.d.
	350	9.4	419	60.4	51	1889	11.4	48.8	293
	600	9.4	252	70.6	66	2114	16.7	23.5	527
Poultry litter [7]	0	8.2	n.d.	7.9	n.d.	n.d.	16.9	74.3	1
	350	8.7	n.d.	24	n.d.	n.d.	30.7	42.3	4
	700	10.3	n.d.	36	n.d.	n.d.	46.2	18.3	51
Poultry litter [10]	60	7.5	363	24.6	13	16,685	36.4	60.5	n.d.
	350	9.7	121	29.3	15	21,256	51.2	47.2	47
	600	10.3	58.7	23.6	25	23,596	55.8	44.1	94
Poultry litter [8]	450	9.9	n.d.	38	19	11,600	n.d.	n.d.	n.d.
	550	13.1	n.d.	33	39	1800	n.d.	n.d.	n.d.
	300	5.3	n.d.	25.6	7.7	493	52.8	33.8	n.d.
Sludge [9]	400	4.9	n.d.	20.2	8.4	740	63.3	25.7	n.d.
	500	7.3	n.d.	20.3	10	568	68.2	20.7	n.d.
	700	12	n.d.	20.4	17	528	72.5	15.8	n.d.

Note: n.d. means not detected.

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

2.1.1. Alkalinity

The alkalinity of biochar is greatly affected by the type of feedstocks and pyrolysis temperature. It seems that biochar, derived from agricultural residuals and poultry letter in particular, is alkaline even at low pyrolysis temperature (<300°C), whereas biochar that derived from wood

material is acid under low pyrolysis temperature [6, 8, 10]. The content of the carbonates are considered as the main alkaline components in biochar [11]. During the pyrolysis process, functional groups such as carboxyl and hydroxyl molecules on the surface of biochar are formed and also greatly contribute to the alkalinity of biochar. In general, biochar alkalinity increases with the increase in pyrolysis temperature [7, 11, 12] as shown in **Table 1**.

2.1.2. Nutrient

Biochar contains various nutrients such as P, K, Ca, and Mg, which are concentrated from the pyrolysis feedstock. Additionally, dissolved organic matter is formed during the pyrolysis process. Thus, the addition of biochar could provide a source of bioavailable nutrients to plants and microorganisms. However, the type and amount of bioavailable nutrients in biochar significantly depend on the feedstock type and pyrolysis conditions. When biochar is produced from poultry manure, peanut husk, and pine tree at 400 and 500°C, respectively, the contents of C and N varied greatly in biochar. In addition, the exchangeable P, K, Ca, and Mg were much higher in biochar obtained at 500°C than that at 400°C [13]. The difference was mainly attributed to the higher pyrolysis temperature that increased the mineralization of feedstocks, but decreased the CEC. From this perspective, it is most important to obtain nutrient-rich biochar from nutrient-rich feedstock under proper pyrolysis conditions. Generally speaking, plant-derived biochar has a relatively lower nutrient content than manure-derived biochar [14].

2.1.3. Stability

When biochar is added into the soil, it will present as isolated particulates, which distinguish from other forms of stable organic matter, either entrapped in soil pores and adsorbed to mineral surfaces or occluded in aggregates. Biochar containing more aromatic black carbons onto the surface is more persistent in the soil than any other form of organic carbon [15] and thus could enhance carbon sequestration in soils [2]. A previous study showed that the mineralization rate of biochar is very low, and the half-lives of carbon in biochar range from 102 to 107 years [16]. Another study has reported that fine biochar particles have remained in soils in humid tropical climates, such as in Amazon, for thousands of years [17].

2.2. Interactions between biochar and metal(loid)s

In the environment, biogeochemical reactions play important roles in influencing the fate, transport, and transformation of metal(loid)s. Since the ionic metal(loid)s may exist as cationic and anionic forms, the behavior of these ions will be affected through the interactions with positive and negative charges on the biochar surface. When mixed with topsoil, biochar with negative charges can tightly adsorb the cationic metal(loid)s such as Cd^{2+} and Pb^{2+} [18, 19], while biochar with positive charges can retain anionic metal(loid)s such as arsenite (H_2AsO_3^-) and arsenate ($\text{H}_2\text{AsO}_4^{3-}$). For cationic metal(loid)s such as Pb^{2+} , the physical adsorption, surface (co)precipitation, and surface/inner complexation with functional groups are considered as the major mechanism for the immobilization of Pb by biochar. Therefore, the biochar-induced changes in soils such as the increase of soil pH can further lower the solubility of cationic metal(loid)s. Because the physiochemical properties of biochar are a function of feedstock type and pyrolysis

conditions (e.g., temperature and rate of temperature increase), it is necessary to determine suitable feedstock for biochar production that have the potential to remediate different metal(loid) in particular soils. On the other hand, unlike cationic metal(loid)s, anionic forms of metal(loid)s such as As (H_2AsO_3^- and $\text{H}_2\text{AsO}_4^{3-}$), SeO_4^{2-} and Cr (CrO_4^{2-} or HCrO_4^-) are often dominant species in alkaline soils and weakly adsorbed by the negatively charged soil particles [20, 21].

It is well known that the oxidation state of metal(loid)s can affect the mobility in soil. For examples, the lower oxidation state of As (As(III) and As(V)) shows much higher mobility in soil, while the higher oxidation state of Cr (Cr(VI) and Cr(III)) presents much higher mobility in soils. Additionally, the redox potential in soils can alter the oxidation states of metal(loid)s. For instance, it was reported that biochar transformed Cr(VI) to the less mobile Cr(III) by continuously donating electrons, which may be associated with oxygen-containing functional groups on the surface of biochar [22]. Moreover, microbial metabolism by using biochar-derived organic carbon can also reduce Cr(VI) [16]. This reduction process resulted in the lower solubility of Cr and thus enhanced the immobilization of Cr in soil.

Soil pH and organic matter content also significantly control the adsorption/desorption processes of metal(loid)s in soils, where cationic metal concentrations are higher in acid soil solution. For example, Cr exists predominantly in the cationic form Cr^{3+} or $\text{Cr}(\text{OH})^{2+}$ in acid soils (e.g., pH 3.5–6.0). The addition of biochar to soil can affect the pH and dissolved organic matter (DOC), and as a consequence to influence the mobility of metal(loid)s. Some studies revealed that biochar amended soil may increase the mobility of metal(loid)s such as As, Cu, and Sb [23–25]. For instance, the mobility of As was enhanced by the increase of pH in biochar amended soil [23, 26]. The possible mechanism for the mobilization is the electrostatic repulsion between anionic As and Sb species and negatively charged biochar surfaces, resulting in the desorption of As and Sb. In the case of Cu, the mobility is strongly correlated with the level of DOC in biochar. High DOC contents in biochar (pyrolysis temperature $<500^\circ\text{C}$) can facilitate the organo-Cu complexes [27], but biochar with low DOC contents (e.g., pyrolysis temperature $>600^\circ\text{C}$) will immobilize Cu by surface adsorption [25].

3. Bioremediation and phytoremediation with biochar

3.1. Bioremediation

Biochar application facilitates bioremediation of organic compounds [28–30]. The main mechanism is the increase of petroleum hydrocarbon-degrading microbial populations in biochar-amended soils [28]. Heavy metal(loid)s cannot be degraded or completely eliminated from the environment, but can be changed from one form to another, from high concentration to low concentration. Heavy metal(loid)s can also be accumulated in the biota. Therefore, there are two commonly used strategies for bioremediation of heavy metal(loid)s: (1) the absorption and accumulation to heavy metal(loid)s in woody plants and bioenergy crops in contaminated farmlands, and the removal of heavy metal(loid)s by harvesting the metal(loid)s accumulated biomass; (2) the transformation of heavy metal(loid)s into lower toxic products (e.g., complex state), and the adsorption by microorganism to reduce their toxicity and migration.

The potential benefits of biochar application in phytostabilization can be summarized in **Figure 1**. The negative charged surface of biochar and the alkaline nature can adsorb and retain toxic metal ions by different mechanisms. Biochar, at the same time, also provides a more favorable soil environment for beneficial microorganism and the development of plant roots by slowly releasing nutrients and maintaining good soil structures.

Microorganisms have been known to develop the resistance to toxic metal(loid)s and even evolved metabolic pathways to transform the metal(loid)s using several mechanisms. There are many factors affecting the effectiveness of bioremediation of heavy metal(loid)s. It has been reported that the reduction of Hg by a thermophilic *Streptomyces* species was associated with a novel Fe²⁺-dependent mechanism in the membrane cytochrome c oxidase [31]. As we discussed before, the reductive precipitation of Cr(VI) to Cr(III) in soil was enhanced in the presence of biochar [22], which was due to the increased microbial activities promoted by the released carbon and nutrients from biochar [16]. In addition, dissimilative reduction may also facilitate immobilization of metal(loid)s such as Cr(VI) and U(VI) [32]; however, no reported evidences have illustrated the roles of biochar. Compared to the directly enhanced bioremediation, the presence of biochar could also provide indirect mechanism for the bioremediation of metal(loid)s. Microbial-induced calcite precipitation can strongly adsorb and/or coprecipitate the heavy metal(loid)s on its surfaces. During precipitation of calcite, heavy metal ions with ion radius close to Ca²⁺, such as Cd²⁺, Pb²⁺, and Cu²⁺, may be incorporated into the calcite crystal by substitution reaction [33]. Moreover, modern genetic engineering promotes the development of engineering microbes to remediation metal(loid) contaminated soils. For instances, genetically engineered *Ralstonia eutropha* has been reported to sequester Cd in soils and further reduce the availability of Cd [34]. Biochar facilitated

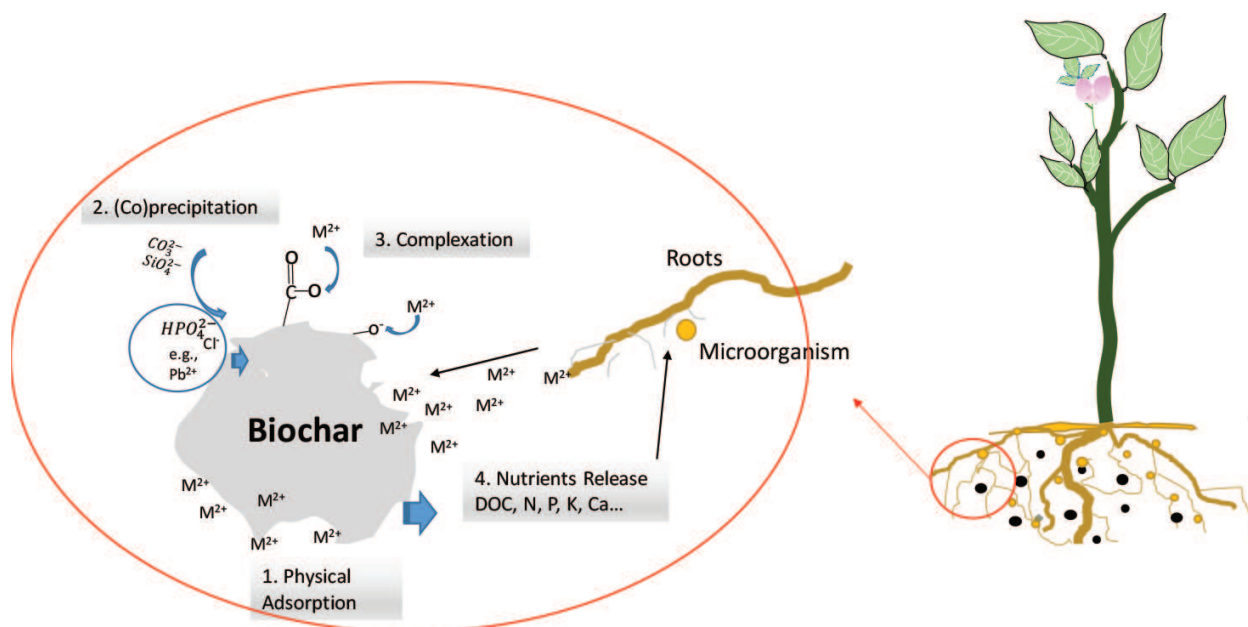


Figure 1. An overview of the potential positive effects attained by combining phytoremediation and biochar for bioremediation of heavy metal contaminated soil. Cationic metal ions expressed as M²⁺. The potential benefits of biochar to phytoremediation are (1) physical adsorption of cationic metal(loid)s from soil pore water; (2) (co) precipitation with phosphate, carbonates, silicate, and chloride, e.g., the formation of pyromorphite; (3) complexation with functional groups on the surface of biochar; and (4) nutrients release such as N, P, K, Ca, and DOC. The processes (1)–(3) can reduce the bioavailable metal concentrations in soil pore water and further reduce the phytotoxicity. The process (4) can produce nutrients to plant roots and microorganism in rhizosphere.

this process by creating a microbe-favorable soil environment in the presence of biochar and thus potentially increased the bioremediation efficiency. Recently, a bamboo biochar oxygen-releasing bead (ORB) was reported to be a potential oxygen-releasing material for use in soil and ground-water bioremediation [35]. This type of biochar can potentially promote dissimilative oxidation of metal(loid)s such as As(III) to less mobile form.

3.2. Phytoremediation

Phytoremediation is a combined multidiscipline consisting of soil chemistry, microbiology, and plant physiology, aiming to (im)mobilize pollutants from various environmental media [36]. In general, phytoremediation includes phytoextraction, phytostabilization, phytodegradation, phytovolatilization, and rhizoremediation. In this chapter, phytoextraction and phytostabilization are discussed in detail. Compared with other remedial practices for heavy metal(loid)s, digging and dumping or chemical immobilization, phytoremediation is attracting more attention because of the effectiveness and low cost. Other benefits such as prevention of erosion or contaminant leaching are also very important for further land management and development. **Table 2** summarizes some biochar amended phytoremediation for heavy metal(loid)s contaminated soils.

Feedstock	Dose	Metal(loid)s	Effects	Plant species
Wood [51]	1, 2.5, and 5 %w/w	Ni, Mn, and Cr	Decrease exchangeable Ni, Mn, and Cr; improved plant growth	<i>Lycopersicon esculentum</i> L.
Hardwoods [26]	20% v/v	As	Increased pore water As but no effect on As uptake	<i>Miscanthus x giganteus</i>
Miscanthus [52]	1, 5, and 10% w/w	Cd, Pb, Zn	Decreased bioavailable metal concentrations and that in shoots but the biomass tripled	<i>Brassica napus</i> L.
Pruning residues; fir tree pellets and manure [43]	0, 1.5, and 3% w/w	Cd, Cr, Cu, Fe, Ni, Pb, Tl, and Zn	Decreased water extractable Cd, Cr, Cu, and Zn due to increased pH; No effect on Pb and Ni	<i>Anthyllis vulneraria</i> , <i>Noccaea rotundifolium</i> and <i>Poa alpina</i>
Oka, Ash, Sycamore, and Birch [53]	20% v/v	Cu and Pb	Decreased pore water Cu and Pb concentration and that in shoots	<i>Lolium perenne</i> L. var. Cadix
Hardwood [18, 24, 26]	–	As, Cu, Cd, and Zn	Increased pore water As and Cu; immobilization of Cd and Zn due to enhanced pH and DOC	<i>Solanum lycopersicum</i> L.
Sewage sludge [54]	0, 5, and 10% w/w	As, Cd, Cr, Co, Cu, Ni, Pb, and Zn	Decreased pore water As, Cr, Co, Ni, and Pb due to increase soil pH; mobilization of Cu, Zn, and Cd due to high available concentrations in biochar	Rice plants
Chicken manure and green waste [27]	1, 5, and 15% w/w	Cd, Cu, and Pb	Reduced NH ₄ NO ₃ extractable Cd, Cu, and Pb; increased plant dry biomass by 353% for shoot; reduced Cd, Cu, and Pb accumulation by plants	Indian mustard (<i>Brassica juncea</i>)

Note: v/v means volume/volume and w/w means weight/weight.

Table 2. Biochar amended phytoremediation for heavy metal(loid) contaminated soils.

3.3. Phytoextraction

Phytoextraction, generally based on the hyper-accumulators or energy plants to uptake metal(loid)s, is the main method to remediate the metal(loid) contamination in soils. So far, hundreds of plant species have been used to accumulate As, Cu, Cd, Zn, Pb, Ni, Co, and Cr from soils. Ideally, plant species used for phytoextraction not only accumulate high amounts of the target metal(loid)s, but also have high biomass yield, tolerate the toxicity of the heavy metal(loid)s, be adaptive to soil and climate, be resistant to pests and diseases, and be easy to cultivate [37]. There are two factors as yield and the metal(loid) concentration determining the efficiency of phytoextraction. Hence, metal(loid) uptake, which is the product of these two parameters, can be either positive or null [38]. As far as we know, no studies meet all of the criteria mentioned above. However, there is a study reported that biochar-amended soil significantly improved the biomass of willow, yet the concentration of Cd and Zn in willow remained unchanged. Yet, phytoextraction is enhanced [39]. Phytoextraction in practice is often used in agricultural soils to lower the concentrations of toxic metal(loid)s below soil quality standards to improve soil environmental quality and to ensure food security. In highly contaminated soils, such as mine tailings, phytoextraction could cost hundreds of years. Thus, the contamination levels of the target agricultural soils should not be too high for phytoextraction. Although a hyper-accumulator could accumulate much higher metal(loid) concentrations, its slow growth rate often limits its application. Instead, energy plants such as sunflower and rapeseed plants are used to extract Cd from agricultural soils [40, 41]. Several studies have combined biochar and phytoextraction in practice. For instance, *Brassica napus* L. is used to extract Cd in the presence of biochar [42]. And different plant species and biochar have been also used in multicontaminated soils [43]. However, very few studies are available with a focus on the combination of biochar on phytoextraction of soil heavy metal(loid)s. For example, biochar amended phytoextraction was performed using *Amaranthus tricolor* L. to remediate the Cd contaminated soil [44]. Until now, most research results indicate that the addition of biochar reduces the bioavailability of heavy metal(loid)s, but plants require high concentrations of soluble metal(loid)s to extract and accumulate them. The benefits of biochar are to improve the characteristics of the polluted soil (water-holding capacity and nutrients) [45], enhance the soil microbial activity [10, 44–47], and have the potential to increase agricultural yields. Thus, using biochar to treat these soils not only immobilizes the heavy metal(loid)s but also increases the microbial biomass [48], which further lowers the ecological risk of heavy metal(loid)s in soil.

3.4. Phytostabilization

Phytostabilization is another phytoremediation process widely used for stabilization and containment of mine tailings [49]. The vegetative cover diminishes eolian dispersion and water erosion, while roots prevent leaching, which contribute to the immobilization of heavy metal(loid)s. The mechanisms involved in phytostabilization include precipitation, root sorption, complexation, or metal valence reduction. Phytostabilization, contrary to phytoextraction, primarily focuses on the heavy metal(loid) sequestration within the rhizosphere, but not in plant tissues. Metal(loid) stabilization is usually achieved through in situ application of soil amendments and microorganisms that effectively promote the metal immobilization and plant growth [42].

Most studies for biochar enhanced phytostabilization of metal(loid)s in soils include As, Cd, Cu, Cr, Ni, Zn, and Sb [25]. It is well known that As behaves differently from other metal(loid)s as a function of pH, since the As mobility can be reduced in acid soils due to increased adsorption on iron oxides under acidic conditions. Hartley et al. [26] showed that biochar can be used in combination with *Miscanthus* for phytostabilization. However, the results showed that the addition of hardwood biochar did not increase the As transfer to *Miscanthus* plants in three soils, whereas the alkaline biochar could mobilize As in soils. Cu and Pb were relatively easy to stabilize in biochar amended soil, while Cd and Ni varied greatly on the type of biochar added to soils [25]. The mechanism of stabilization is most likely due to the increase of soil pH. Extensive studies reported that soil amendments, such as lime, have the potential to be combined with phytoremediators so as to reduce the bioavailability of heavy metal(loid)s. By comparison, biochar seems to be more effective to regulating the availability of toxic elements and improving the biomass production of plants and remediation efficiency [39]. Improvements of plant yield with biochar addition are attributed to increased water and nutrient retention, improved biological properties and CEC, and buffered soil pH. Thus, biochar has a potential as an amendment for reducing metal uptake by plants. However, changes of soil pH in rhizosphere can potentially affect the effectiveness of biochar to immobilize metal(loid)s in soils and the acidification of the rhizosphere should be minimized [42].

It is perceived that biochar can interact with soil components for a prolonged period of time. As a result, the redox processes might result in the alteration of biochar, a process known as aging. The immobilization of heavy metal(loid)s by biochar was related to the metal lability (e.g., Pb^{2+} is prone to be immobilized first other than Cd^{2+}). During the aging process, a large variety of functional groups such as carboxylic, phenolic, and hydroxyl could be formed, and immobilization of cationic heavy metal(loid)s was not affected by biochar aging in soils with aged biochar [50].

4. Application of biochar to the bioremediation of mine area

Mining activities can cause the destruction of soil structure and change of soil biology and vegetation, resulting in extensive soil degradation. The contaminated soil after mining causes the devoid of vegetation due to metal toxicity and high acidity. Remediation and rehabilitation of these contaminated soils can be achieved via phytostabilization, a long-term and cost-effective rehabilitation strategy, promoting the revegetation to reduce the risk of pollutant transfer and ecological restoration [43], although these are difficult without proper soil amendments. The addition of biochar to contaminated soil may increase soil pH, water-holding capacity, and soil fertility, reduce the mobility of plant-available pollutant, and promote the revegetation [55]. Phytostabilization of mine tailings with biochar, produced from orchard prune residues and manure, at four different dosages (0, 1, 5, and 10%) showed the significant benefits of biochar to revegetate the plant species [43]. And the bioavailability of Cd, Pb, and Zn decreased proportionally with the increase of biochar content [43].

Biochar can reduce toxicity of heavy metal(loid)s and promote the plant growth in heavily contaminated soils [19, 56, 57], as shown in **Figure 1** (process 4). Soils with high available concentrations of toxic metal(loid)s are generally very acidic, unlikely supporting plant germination and growth.

4.1. Acid mine wastes

In highly multi-contaminants polluted soils, such as mine tailings, the phytoextraction process could take hundreds of years because of slow growth rate and low biomass of phytoextractors. Considering these limitations, revegetated phytostabilization, a long-term and cost-effective rehabilitation strategy, is one of the most promising remediation technologies to enhance metal stabilization in soils and reduce the risk of toxic metal(loid) transfer via leaching and water erosion [43]. However, when this technology is applied to mine tailings or contaminated soils, there are several issues that need to be addressed: (1) high metal(loid) contents cause high toxicity; (2) high acidity promotes metal release and enhances the toxicity; (3) the iron- and sulfur-oxidizing bacteria are dominated in acidic tailings that further increase acidity [58]; and (4) low nutrients cannot support plant growth. So far, no effective amendments have been developed to simultaneously fix these problems. Usually, the first step in practice is to add some liming materials such as limestone to increase alkalinity and increase the soil pH. Furthermore, the added alkalinity could be rapidly lost. And even if a higher soil pH is maintained, the lack of nutrients also makes the revegetation fail. However, the application of fertilizers to the lime-amended mine soils could further cause a higher acidity, which led to the rapid leaching out of added nutrients [59].

By comparison, biochar is one of the most relevant organic amendments. The addition of biochar to contaminated soil and waste rock piles can increase soil pH, water-holding capacity, and soil fertility, reduce the mobility of plant-available pollutants, and promote the revegetation [55]. Phytostabilization of mine tailings with biochar, produced from orchard prune residues and manure, at four different dosages (0, 1, 5, and 10%) exhibited the significant benefits to improve the revegetation of the plant species [43]. Additionally, the pH, nutrient retention, cation exchange capacity, and water-holding capacity of mine tailings increased, and the bioavailability of Cd, Pb, and Zn decreased proportionally with the increase of biochar content [43]. Soils developed on or around mine tailings are generally very acidic, with high available concentrations of dissolved toxic metal(loid)s, unlikely supporting plant germination and growth. Biochar is very stable with slow-releasing nutrients and readily reduces the plant-available concentrations of cationic metal(loid)s, resulting in the decrease of phytotoxicity of metal(loid)s to plants [19, 51, 56, 57], as the increase of the germination rate [60], root length, and better plant growth [51] are found in the presence of biochar.

4.2. Alkaline tailing soils

Alkaline tailing soils are another type of common metal(loid) contaminated soils, resulted from mining (e.g., Pb and Zn), smelting activities, or mining in arid regions [49]. These unclaimed or abandoned mining sites generally remain unvegetated for dozens or hundreds of years, and gradually, the contamination can greatly expand via eolian dispersion and water

erosion [49]. The main concerns of high alkaline tailings and soils are that tailings and mining/smelting-affected soils become a significant source of air pollution, due to the formation of tiny particulate matter (e.g., PM 10 and PM 2.5), and as a consequence, they increase the exposure of heavy metal(loid)s to local residents. Therefore, it is urgent to improve the vegetation in alkaline tailing sites so as to control the release of particulate matter. Phytostabilization of mine tailings can be a promising strategy for metal immobilization in a long run, since vegetation will reduce the tiny metal-containing particles, while roots will prevent water erosion and immobilize metal(loid)s by adsorption or accumulation.

Although total metal(loid) contents in soils are very high (e.g., total Pb over 6000 mg kg⁻¹ soil), the aqueous concentrations in soil solution (e.g., Pb below 10 µg l⁻¹) can be very low, due to the high soil alkalinity and the large fraction of nonchemical reactive metal(loid)s [61]. The addition of alkaline biochar will not improve the soil pH as it is already very high (e.g., 8), which reduce the solubility of metal(loid)s and prevent their bioavailability to plants.

However, because the replacement of topsoil with continuous addition of organic matter and nutrients is very expensive for extensive mine tailings sites, organic amendments such as biochar are commonly used as a substitute. Biochar can provide a slow-release fertilizer and serve as microbial carriers to improve soil quality, creating a favorable environment for further vegetation practices. In addition, biochar can improve soil structure, reduce erosion, and increase infiltration. Soil amendments such as biochar facilitate grassland recovery and revegetation in severely degraded habitats, such as mining waste and contaminated soils. For example, biochar reduced the toxicity of heavy metal(loid)s to plant growth in heavily contaminated soils [19, 56, 57]. Furthermore, biochar can improve soil structure and aeration and provide some necessary nutrients that promote microbial activity and diversity. Moreover, biochar can adsorb metal(loid)s on the surface and reduce the toxicity to microorganism. The improvement of soil enzymatic activities and microbial growth and diversities have been found in biochar-added soils [44, 46, 47, 51]. Biochar can alter soil microbial community, possibly including an increase in beneficial organisms that produce antibiotics, and can protect plants against pathogens [62]. However, some studies using wood-biochar as soil amendment do not show the same benefits [63].

5. Defects of biochar amended bioremediation

5.1. Phytoextraction of arsenic

From the perspectives of fate, transport, and transformation of the metal(loid)s, As behaves differently with other cationic metal(loid)s such as Cd. As exists predominantly as anionic form such as H₂AsO₃⁻ and H₂AsO₄³⁻ in soil solution. The mobility of As is pH-dependent and also greatly influenced by the biogeochemical interactions with soil minerals (e.g., iron oxides) in soils. The negatively charged As (As(III) and As(V)) are strongly adsorbed on iron oxides. However, when alkaline biochar is added to acidic or slightly acidic soils, the soil pH increased, which contributes to the increase of negative charges on the soil surface, promoting the release of adsorbed As into soil solution through charge repulsion. Several studies have

reported that the As concentration in soil pore water increased with the increase of soil pH, induced by the presence of biochar derived from hardwood- or *Eucalyptus saligna* [18, 23, 24, 26, 64, 65]. Another intriguing factor that potentially increases the mobility of As is the introduction of dissolved organic matter from biochar. It is well known that the mobility of As and Fe also is greatly affected by soil redox condition. An increase in dissolved organic matter can decrease the soil redox potential and enhance the reductive dissolution of solid iron oxides and release the adsorbed As to aqueous phase. In addition, the mobility of As(III) is higher than As(V). The reduction of As(V) to As(III) was predominantly (>83%) attributed to the biological reduction, stimulated by increased dissolved organic matter from biochar. The As(III) released from sediment upon biochar amendment ($656 \mu\text{g l}^{-1}$) was significantly higher than that from sediment without biochar addition ($98 \mu\text{g l}^{-1}$) after 49 days of cultivation [66]. Furthermore, the phosphate-extractable As in soil increased with biochar, because of the release of phosphate from biochar derived from hardwood [67]. Other anionic metal(loid)s, such as Sb, Cr, Mo, and Se, may also demonstrate the similar pattern as As in biochar-amended soils. To prevent the dissimilatory As reduction and mobility, a bamboo biochar oxygen-releasing bead (ORB) (104 days) was used to inhibit Fe(III) and As(V) reduction [35]. However, biochar derived from other feedstocks has not been well examined. Therefore, it is important to determine the impacts of biochar on the biogeochemical interactions that control the mobility of metal(loid)s in soil.

5.2. Phytoremediation of sewage sludge

Biochar seems to be very effective in controlling metal(loid) availability and facilitates the application of phytostabilization [68]. Sewage sludge, as an important feedstock for biochar production, is often used as soil amendments. However, there are concerns of pathogens and high available metal concentrations from sewage sludge and derived biochar. So far, the application of sludge-derived biochar is limited in both laboratory and field studies. The risk of using sludge in agricultural soils has still not been well evaluated, although there are reports that the concentrations of heavy metal(loid)s (i.e., Cu, Pb, Zn, Cd, and Cr) were concentrated in biochar, without increasing the metal uptake by Chinese cabbage [69].

Additional concerns raised for other metal(loid)-rich biochar, derived from plants used for phytoremediation or agricultural straw from contaminated soils. Although some studies claimed that metal(loid)s in feedstocks can mostly be fixed in biochar without the risk of leaching, the mechanism of fixation is still unclear. Pyrolysis temperature greatly affected the metal distribution in biochar product. With the increase of pyrolysis temperature, metal contents such as Zn and Pb decreased and perceived to form volatile metal chlorides [70]. However, the rest of metal(loid)s in biochar seem not increase the available metal(loid)s in soil in a 3-year field trails, even after repeated agricultural applications [71].

6. Future research

6.1. Characterization of biochar

Biochar has great potential as an amendment for phytoremediation, but its effect depends on the type of pyrolysis feedstock and temperature. Since most researches used different

biochar produced from various feedstock, the impacts on the bioremediation varied greatly. However, these results are not comparable, and thus, a systematic evaluation is urgently needed for biochar-making procedure. The characteristics of the feedstock and pyrolysis conditions are crucial for the biochar selection. If the characteristics of feedstock can be qualitatively and quantitatively correlated with the properties of biochar, the selection and optimization of biochar becomes more promising [72]. The characterization of a range of surface properties of biochar and its biological effects on bioremediation are essential in order to implement these approaches effectively in practice [73]. The biochar-assisted phytoremediator targeting at different heavy metal(loid)s is strongly dependent on the interactions between specific metal(loid)s and biochar. How these properties are relevant for the adsorption of heavy metal(loid)s and how they contribute to the different mechanisms of heavy metal(loid)s immobilization need further examination.

6.2. Evaluation of biochar stability

Until now, the stability of biochar is still not well understood. The effectiveness of biochar on the improvement of soil quality has not been examined on a large timescale. In a 3-year field trial, the alkalinity associated with the biochar had been fully neutralized and most of the cations (i.e., K, Na, and Ca) from the biochar had been lost, but microbial community had built up [74]. The addition of biochar to soil causes small and potentially transient changes in a temperate agroecosystem functioning. However, most of these experiments for biochar amended bioremediation of heavy metal(loid)s (both under laboratory conditions and in field scale) have been conducted in the short term, which poses an interrogation on the long-term effectiveness. In fact, it could be expected that, due to aging processes, the ability and capacity of biochar to sequester heavy metal(loid)s decreases with time. More research is needed to understand the aging process in biochar. In addition, the degradation of biochar may not be avoided, and the degradation rate may vary greatly depending on feedstocks and pyrolysis conditions. It is still unclear which factors, e.g., feedstock type, pyrolysis conditions, or soil properties, determine the long-term stability of biochar. Thus, well-designed, large-scale and long-term field trials will be essential to evaluating the feasibility and stability of biochar amended bioremediation.

6.3. Elucidation of the mechanisms of biochar-assisted bioremediation

It is urgent to explore and improve the understanding of mechanisms involved in the biochar amended bioremediation of heavy metal(loid) contaminated soils. Biochar-induced changes in the soil ecosystem must be clarified before broad application, including the interactions among biochar, soil components, and soil microbial communities and plant roots. Until now, very few studies have been reported to systematically evaluate the joint application of biochar with phytoremediators under laboratory conditions or in field scale. For examples, although various approaches have been developed to remediate Pb contaminated soil, in which soil amendments with biochar for phytoremediation are the most suitable, practicable, and publicly acceptable, but this practice still have some constraints due to the insufficient information to understand the immobilization processes. For other cationic metal(loid)s, biochar seem not work well in the phytoremediation of either acid or alkaline soils in some cases. In this case, without full understanding on the impacts of biochar on phytoremediators, this can result in an overestimation of heavy metal(loid) extraction and stabilization.

7. Conclusion

Biochar amended bioremediation is one of the important remedial technologies to remediate heavy metal(loid) contaminated soils. The biochar-enhanced phytoremediation has great potential to immobilize cationic heavy metal(loid)s in mine wastes and tailing soils, particularly those with high acidity. Biochar can reduce the bioavailability and leachability of cationic heavy metal(loid)s in soils, and improve the soil fertility and revegetation, and create a suitable environment for soil microbial diversity. However, the application of joint biochar and phytoextraction may be only capable of remediating the multicontaminated arable soils with low contamination levels, because biochar seems to be less effective to stabilize the potentially toxic cationic metal(loid)s such as Cd that have a high mobility in soils. In addition, it is important to select appropriate biochar so as to develop effective strategy to immobilize anionic metal(loid)s in situ. Furthermore, more thorough studies are needed to evaluate the efficiency of biochar amended bioremediation of highly contaminated alkaline soils. Future research should be performed with focuses on: illustrate the correlations among pyrolysis feedstocks, physic-chemical properties of biochar, and soil bioremediation; evaluate the biochar stability and its influence on fate and transport of metal(loid)s in mining tailings and soils on a large timescale; and understand the mechanisms of biochar-assisted bioremediation, especially involved in the interactions among biochar, soil particle, and soil microbial/plant roots, which is the key point for the development of cost-effective remediation strategies.

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