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REVIEW ARTICLE

Biological technologies for the remediation of co-contaminated soil

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ABSTRACT

Compound contamination in soil, caused by unreasonable waste disposal, has attracted increasing attention on a global scale, particularly since multiple heavy metals and/or organic pollutants are entering natural ecosystem through human activities, causing an enormous threat. The remediation of co-contaminated soil is more complicated and difficult than that of single contamination, due to the disparate remediation pathways utilized for different types of pollutants. Several modern remediation technologies have been developed for the treatment of co-contaminated soil. Biological remediation technologies, as the eco-friendly methods, have received widespread concern due to soil improvement besides remediation. This review summarizes the application of biological technologies, which contains microbial technologies (function microbial remediation and composting or compost addition), biochar, phytoremediation technologies, genetic engineering technologies and biochemical technologies, for the remediation of co-contaminated soil with heavy metals and organic pollutants. Mechanisms of these technologies and their remediation efficiencies are also reviewed. Based on this study, this review also identifies the future research required in this field.

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Soil remediation; co-contaminated soil; biological technologies; mechanisms; heavy metals; organic pollutants

Introduction

Soil contamination has caused great attention on a global scale, especially in slag disposal sites, specific industrial wasteland and farmland. The soil in most of these sites was contaminated by multiple pollutants rather than individual pollutants [1]. Also, the quantities of co-contaminated sites with multielements sharply increased [2], due to the anthropogenic activities such as rapid industrialization and urbanization [3,4]. In particular, heavy metal pollutions frequently occur with organic pollutions in different types involved in endocrine disruptors, pesticides, petroleum and their derivatives [5]. Heavy metals/metalloids and organic pollutants are carcinogenic and mutagenic [6,7], and they would arouse amplification effects through the food chain in organisms, causing great threats to human health and natural ecosystems [8].

Owing to the different physical and chemical properties of diverse pollutants, both the migration and transformation modes of pollutants in soil and their responses to the remediation technology are different. In addition, the interactions among multiple pollutants in soil make the remediation processes becoming more complicated. For example, the interaction between heavy metals and organic pollutants might change the speciation, solubility and bioavailability of pollutants, thereby mutual inhibiting or promoting the remediation efficiency of each other [9,10]. Furthermore, competition among different pollutants exist frequently for the binding sites of adsorbents and enzymes [11]. Microbial consortium and/or plants would suffer double pressure [12] and drastically reduce the biomass and biodegradability in co-contaminated soil [4]. High concentrations of heavy metals tend to inhibit the microbial metabolism and enzymatic activities thereby reducing the degradation efficiency of organic pollutants [13]. The uptake of metals may be enhanced due to the change in membrane permeability caused by the interaction between polycyclic aromatic hydrocarbons (PAHs) and the hydrophobic component of cell membrane [14]. The combined pollutants in soil show synergistic and antagonistic effects on the remediation results through intricate interactions.

Based on these conditions, considerable research work has been conducted to develop the technologies

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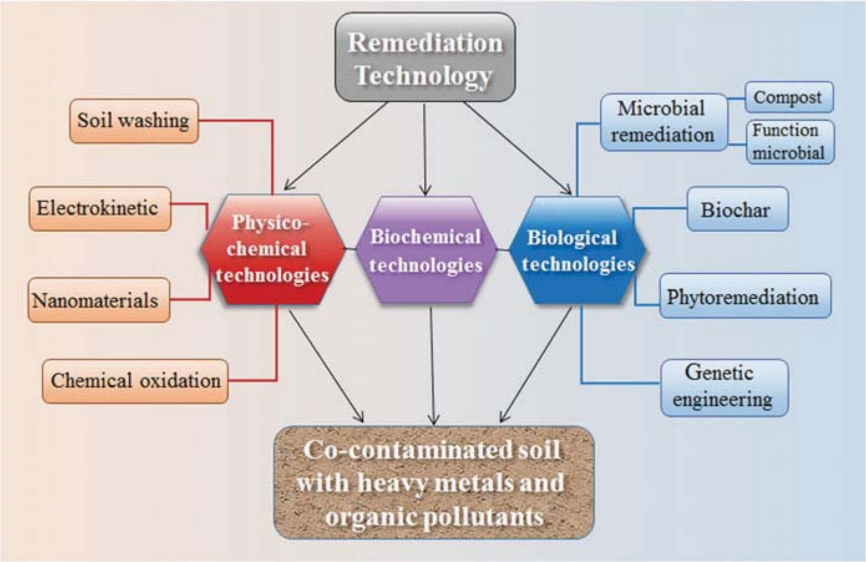

Figure 1. Technologies for remediation of co-contaminated soil.

for reducing multiple contaminants synchronously (Figure 1). The physicochemical remediation technologies in soil, including extracted washing [15], electrokinetic remediation [10], chemical oxidation [16] and nanomaterials remediation [17,18], are likely to damage the soil ecosystem via a wide range of changes in pH and the moisture content or higher oxidation potential [19,20]. Biological remediation technologies make use of the capacity of plants and/or microorganisms for the transformation of heavy metals (bioavailable state reduction and biological toxic forms transition) and metabolic decomposition of organic pollutants [21]. Compared with physicochemical technologies, biological technologies are more suitable and low-cost for large-scale *in situ* remediation. They keep ecological sustainability through the abilities of organisms to improve soil quality and restore soil function [22].

This review focuses on the diverse soil biological remediation technologies and their mechanisms about the synchronous degradation of refractory organic pollutants and passivation of heavy metals. Based on the increasing quantity of studies in this field, this paper is intended to: (1) elaborate the biological remediation technologies for decreasing multipollution; (2) discuss the mechanisms of technologies on the transformation of heavy metals and elimination of organic pollutants; and (3) determine the current needs and future research directions in the field.

Microbial remediation technologies

Microbial remediation, a kind of remediation technology that utilizes the role of microorganisms in soil to render the pollutants harmless, consisting of biostimulation and bioaugmentation. The indigenous microorganisms are always limited by the toxicity of pollutants in a co-contaminated site due to the small number and low degradation ability. Biostimulation improves soil quality by adding nutrients and growth hormone to meet the conditions for the growth of native microflora [23]. Bioaugmentation establishes a microbial formula by adding the obligate degrading bacteria with those strains that tolerate multiple heavy metals and remove target pollutants [24]. This review discusses the microbial technologies containing functioning microbes. Also, composting and compost addition for the remediation of co-contaminated soil is discussed.

Functioning microbial remediation

Microorganisms with a function in toxicity resistance, metal sorption and organic pollutant degradation have been reported for the remediation of co-contaminated soil [25]. Research by Thavamani et al. [26] showed the isolated bacteria with the ability for Cd-tolerance and PAHs-metabolism exhibited excellent remediation potential in soil contamination by a combination of different contaminants. Bacterial accumulation trials indicated Cd^{2+} (chemisorption) and Zn^{2+} (physisorption) were principally adsorbed onto the cell walls, instead of accumulation inside the bacteria [27]. Furthermore, some modification strategies (e.g. chelators, surfactants and organic acids) are evaluated to control the bioavailability of pollutants in the process of microbial remediation in co-contaminated soil [28,29].

Hoffman et al. [30] showed the carboxymethyl-β-cyclodextrin (CMCD) could alleviate the toxicity of metals (Cd, Co and Cu) depended on the multidentate and metal-binding capacity. Meanwhile, they also found CMCD had the potential to strengthen biodegradation rates by enhancing the solubility and bioavailability of naphthalene substrate [30]. Microbial consortiums, isolated from oil contaminated sludge, could produce biosurfactants to emulsify the hydrophobic organics significantly by reducing the surface tension, which makes it possible for microbes to have a high adsorption and degradation capacity to naphthalene, phenanthrene, pyrene and crude oil even in the co-contaminated soil containing Cu^{2+}, Zn^{2+} and Pb^{2+} (5). Also, the biodegradable surfactant can act as a substrate to support microbial growth [13]. A report confirmed that the uptake of Cd and Pb by endophytes *Bacillus* sp. L14 achieved up to 80.8% and 76.5%, respectively, and the metals were distributed in membrane fractions [31]. It was different from the tying up with cell wall, which is easily decomposed and caused secondary pollution [32]. Overall, the remediation mechanisms of microbes for combined pollutants involve intracellular and extracellular aspects (Figure 2), as the following: (1) accumulation by bacterial cells and then immobilization through bioprecipitation or store in lipid vesicles [32,33]; (2) uptake into cells, thereby transformation through combination with intracellular metallothionein and polypeptides or metabolic biodegradation by intracellular enzymes [5]; (3) selective adsorption by a living microbial consortium relies on the structure of the microbial surface and a concentration difference driving force of substrates [34,35]. The adsorption by killed microbes depends on the surface polarity or partition coefficient [36]; (4) transformation, immobilization and degradation by many kinds of extracellular substances (enzymes, surfactants and organic acids) secreted from microorganisms [37,38]; and (5) redox reaction between heavy metals, microbes and organic pollutants and serves bacteria as the electron transfer. A metal-reducing microorganism, *Geobacter matallreducens*, has the ability to transfer electrons from the toluene to solid-phase Fe (III). The reduction of iron oxide simultaneously liberated the adsorbed As and reduced As (V) toward As (III) during the oxidation processes of toluene [3]. Fungi have been found capable of secreting a series of extracellular enzymes in order to alleviate the oxidation stress caused by lipid peroxidation, and they show great mycoremediation potential in co-contaminated soil [39–41]. Liu et al. [42] performed pot experiments to investigate the potential of *Clitocybe maxima* on the bioremediation of soil contaminated with 2,4,5-trichlorophenol (TCP) and heavy metals. The increment of TCP removal was attributed to the enhancement of soil biological activities, and the higher proportion of acetic acid extractable Cd and Cu caused by *Clitocybe maxima* was beneficial to the metal uptake [42].

Composting or compost addition

Composting is a spontaneous process to stabilize the agricultural and municipal solid waste by microbial oxidation degradation, which also helps reduce the need

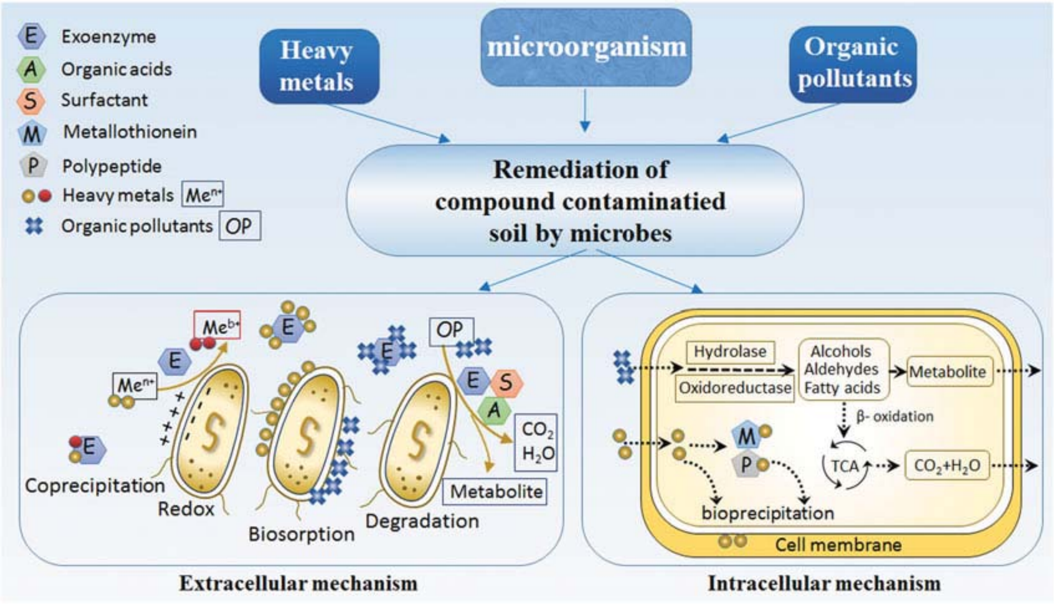

Figure 2. The mechanisms of microbial remediation used for reducing heavy metals and organic pollutants.

for waste storage and disposal. A great deal of research clarified, in detail, the composting or compost addition with a bulking agent and surfactant can effectively remediate the co-contaminated soil with a wide range of heavy metals and organic pollutants [43]. Compost can decrease the bioavailable heavy metals via complexation, absorption, redox reaction, (co)precipitation, (de)methylation etc., [44] by microbes or organic matter which is derived by microbial degradation. In the amended soil, the distribution of heavy metals (Cd, Pb, Zn, Cr and Cu) displayed a similar pattern. Namely, the residual portion was governing and followed by the Fe- and Mn-bound portion [45], different from Perez et al. [46] whose research confirmed that Cu mainly existed in the organic bound fraction. On the one hand, the mobility of heavy metals reduces significantly as a result of the promotion of soil organic matter, cation-exchange capacity and pH value. On the other hand, soluble organic matter performs ligand effects to strengthen the solubility of heavy metals [47,48]. In comparison with poultry manure and organic municipal solid waste (MSW), study found that composted crushed cotton contained greater humic substances which contained a variety of functional groups for binding with multiple heavy metals [49]. Compost can also affect the movement and bioavailability of organic pollutants due to the change of organic matter (especially the humic acid) content. The increase in water-extractable organic matter derived from cow manure compost, increased the solubility of phenanthrene, pyrene and benzo[a]pyrene for microbial metabolic degradation [50]. Reports claimed that the decrease in aliphatic fraction and the increase in polarity led to a structural conversion of humic acids in the composting process. Decomposition reduced the PAHs binding affinity and ameliorated the PAHs-degrading microbial accessibility [51]. Moreover, the density and diversity of microbes increases dramatically due to the introduction of exogenous microbes and nutrient availability. A wide variety of microorganisms from compost have the ability to enhance the passivation of metals and the degradation of organic pollutants [52]. As a conclusion, the decrease in heavy metals and organic pollutants during composting or compost treatment is either dependent on the adsorption by organic matter, or is reliant on the degradation by microbes and enzymes [43,53].

Composting process is suitable for barren land *in situ* remediation [47], since it can improve the soil quality (for organic matter and total organic carbon). Field composting with ideal organic amendment amounts (2/1) and C/N ratio (15/1) effectively reduced the concentration of total petroleum hydrocarbons (TPH: the mixture of hydrocarbons) in heavily contaminated soil. Also, the local dominant plant species with rhizosphere microbes further degraded the remaining petroleum hydrocarbons and their metabolites [54]. The interaction of compost (composting) and biochar also improved each other's efficiency on soil amendment and contamination remediation [55]. Biochar can enhance the microbial activity of composting and the composting process can improve the surface structure of biochar. This study confirmed that mixing compost and biochar reduced the mobility of Pb and Cu besides the improvement of soluble nitrogen, which resulted in higher seed germination and root elongation in mine soil [56]. Zeng et al. [57] systematically validated the mutual promotion effect on whether BCed (composted biochar) or BCing (biochar and biomass mixed before composting) had the greatest capacity for reducing the bioavailability and ecological risk of heavy metals in wetland soil. Another study found that biochar decreased the concentrations of free metals furthest and yet dissolved organic carbon (DOC) principally dominated the metal mobility after compost operation [58]. In terms of organic pollutants, the literature revealed the less effect of biochar integrated with compost than individual application owing to different mechanisms (biochar mainly exert the adsorption properties, while compost enhance the activity of microbes). The antagonistic interaction appeared to be between biochar and compost, owing to the fact that biochar reduced the available substrates for the microorganism [59]. However, research by Hua et al. [60] found that addition of biochar to composted sludge reduced the mobility and bioaccessibility of Zn, Cu and PAHs in co-contaminated soil.

Biochar

Biochar is a porous solid derived from the organic waste residues. It formed from the pyrolysis procedure without establishing meaningful charring and molecular structure changes to the biomass. The stack of the large sheet of polycyclic aromatic makes the biochar become polarizable, thus biochar could be served as an electron donor, acceptor or even show amphoteric characteristics to adsorbates (aromatic rings in the center of a given sheet as an π-acceptor, and carbon rings as π-donor closer to the edges) [9]. Furthermore, biochar reserves a considerable number of electron-withdrawing functional groups after pyrolysis [61]. It has high potential to sequester carbon, ameliorate soil fertility, reduce greenhouse gas emissions [62] and immobilize heavy metals and organic pollutants [63].

The possible mechanisms involved in biochar used for the remediation of multiple heavy metals are shown

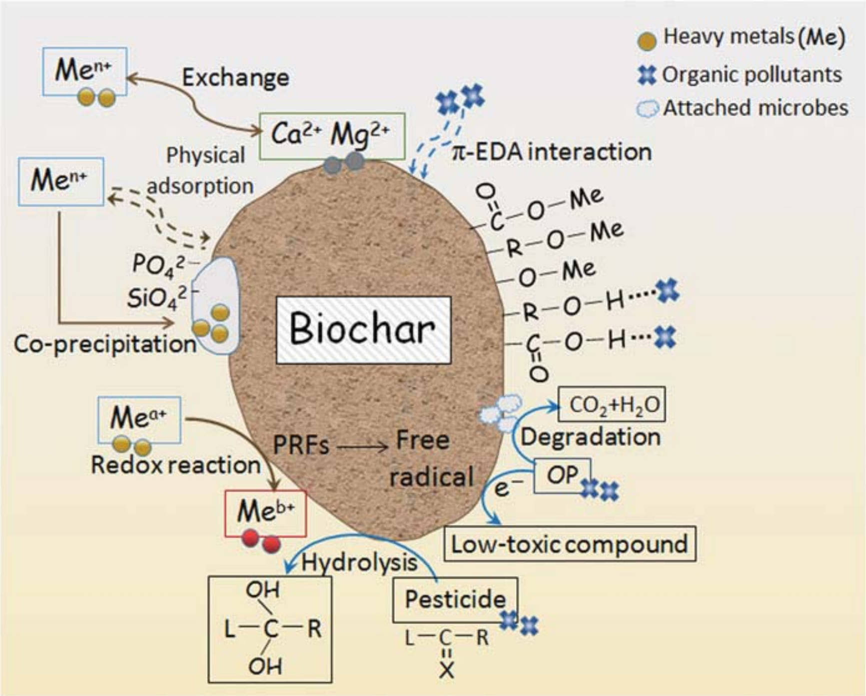

Figure 3. The mechanisms of biochar used for reducing available heavy metals and organic pollutants.

in Figure 3, as follows: (1) metal exchange with Ca^{2+}, Mg^{2+} and other cations correlated with biochar [64]; (2) metal binding with different functional groups on the surface of biochar [65,66]; (3) surface adsorption and precipitation by mineral components on the biochar, for instance Fe–Mn oxides, phosphates and carbonates [67,68]; and (4) redox reaction for changing the valence of metals to become low mobility and low toxicity [69]. Study served the DOC from biochar as an electron shuttle to simultaneously enhance the reduction of Cd (VI) and oxidation of As (III) [70]. Besides, most biochars are derived from alkaline substances and thereby have a high pH value, which is in favor of the formation of metal precipitates [71]. The dominant retentive mechanism of biochar probably depends on the soil properties, ambient conditions and types of biochar. According to Table 1, the effect of biochar often relies on the characteristics of biomass material, the pyrolysis temperatures, soil particle sizes and types of heavy metal [72–75].

Biochar has been reported to have adsorptive ability for organic pollutants [76]. The aromatic sheet of biochar show amphoteric characteristics to adsorbates, which declares the strong and nonlinear adsorption through π–π electron donor–acceptor (EDA) interactions. Besides, the mechanisms, contained micropore filling and hydrogen bonding, it depends on the surface polarity and the driving force of hydrophobic effects [9,77]. The study found that interactions of some organic sorption sites and inorganics in the initial biochar with high ash contents resulted in the obstruction of available sites [78]. However, other reports validate that minerals were conducive to the external distribution of polar groups on the biochar surface [9]. However, biochar may reduce the dissipation of organic pollutants due to its strong adsorption. Also, it is still unknown about the fate of the sequestered pollutants in the long term if the circumstances change. Research put forward a new insight, since the persistent free radicals (PFRs) in biochar are formed from the thermal decomposition of organic materials in the case of coexisting metal oxides [79]. The PFRs in biochar have been proven to be effective in transferring electrons to produce superoxide radicals and hydroxyl radicals. The research also verified that these free radicals with high reactivity are able to eliminate diethyl phthalate effectively [80]. In the presence of hydrogen sulfide, black carbon could act as the electron conductors and performed capacity to catalyze the transformation of mixing organic pollutants [81,82]. In addition, the study proposed that biochar derived from pig manure, which was pyrolyzed at 700 °C, has the ability to hydrolyze two pesticides (carbaryl and atrazine) [76]. A load of heavy metals and organic pollutants in the biomass involve in the formation of PFRs in biochar, which contributes to the reuse of hyperaccumulator biomass as a feedstock [83]. In addition, the study initially used the adsorption

Table 1. Consequence of biochar application on multiple heavy metals in soil.

Feedstock	Contaminants	Calcination temperature (°C)	Effect	References
Orchard prune	Cd, Pb, Tl, and Zn	500	Increase the cation-exchange capacity and the water-holding capacity; and the bioavailability of heavy metals in the mine tailings decreased.	[72]
Wheat straw	Cd and Pb	550	Increased the total organic carbon and soil pH; the extractable Cd and Pb and their content in plant tissue were decreased over 3 year period; bonding with the mineral phases and cation exchange are major mechanisms.	[64]
Sugarcane -straw	Cd and Zn	700	Increased the sorption of Cd and Zn in two heavy-metal-contaminated tropical soils, but the sorption or precipitation reactions are reversible under buffer acidic conditions.	[73]
Bamboo and rice straw	Cd, Cu, Pb and Zn	750 (bamboo); 500 (rice straw)	Rice straw biochar was more effective than bamboo in decreasing extractable heavy metals in soil, which were significantly correlated with soil pH, DOC and available P.	[75]
Broadleaf hardwood	Ni and Zn	600	Significant increase in the residue fractions of Ni (II) and Zn (II) led to the reduction of leachabilities of both metals.	[74]

capacity of biochar to bind specific degrading bacteria and constituted the biochar with immobilized microbial organisms (IMO). The organic pollutants were gathered around the IMO biochar and further were decomposed by the adsorbed microbes [84].

The advantages of biochar are exerted in heavy metals and organic pollutants co-contaminated soil [67,85]. Biochar produced from dairy manure biomass had been confirmed to immobilize Pb and atrazine in soil, and the efficiency was enhanced with the increasing treating time and biochar proportion. Up to 57% and 66% of available Pb and atrazine were reduced by biochar after 210 d, respectively [86]. A part of the metal ions, which bound on biochar, could not only act as the adsorption sites for organophosphorus pesticides, but also catalyze the hydrolysis and their other degradation ways [87]. However, the application of pesticides is necessary in agriculture and forestry fields, the utilization of biochar might offset the pesticide efficacy [88]. The soil organic matter which attached to biochar might reduce the available nutrients to earthworms, and the earthworms would weaken the immobilization capacity of biochar [89].

Phytoremediation technologies

Phytoremediation (phytoextraction, phytodegradation, phytostabilization and phytovolatilization) is a promising technology that exploits the inherent ability of plants to transform the pollutants through the conversion of usable sunlight energy into chemical energy. Details are shown in Figure 4. The plants, which are selected for the remediation of co-contaminated soil, possess the ability to tolerate high concentrations of heavy metals due to the mechanisms such as detoxication, compartmentalization, exclusion, chelation and sequestration [90]. Since the heavy metals cannot be broken down, they may be stabilized around roots or accumulated and translocated to the aboveground part of plants where it is insensitive to toxicity and/or easily removed by harvesting or volatilization [91]. The mechanisms for the root uptake of multiple metals from soil are related to the active transport that depends on membrane transport proteins and metals pumping ATPase. There are a variety of metal ligands in plants, including organic acid, phytochelatins (PCs) and plant metallothionein (MTs). The concentration of free metal ions might decrease, because the complexes between ligands and metal ions are transported into the cell wall and the vacuole [92]. Hyperaccumulators assisted with chelators, growth hormones or acidifiers are very popular in past decades due to the low maintenance and high esthetic value [93]. Nevertheless, they are likely to cause metal leaching into deeper soil layers even groundwater, especially in the case of added chelators. To address the problem, the incorporation of gravel sludge and red mud into the soil for metal immobilization, followed by sulfur treatment for metal remobilization, which enhanced the phytoextraction efficiency of Zn and Cd up to 50% by *Salix smithiana* [94]. The study combined phytoremediation with biochar to improve the growth, resistance and remediation efficiency (mainly phytostabilization purposes) of plants in mine tailings [95].

However, the phytoremediation is usually slow and incomplete owing to the limitations in plant catabolism capacities and root depths [96]. Rhizosphere microorganisms are able to increase the concentrations of hydrogen, organic acid and siderophores, which have been proven to be beneficial for the solubilization of nutrient ions and tolerance of abiotic factors [97,98]. Integrated employment of microorganisms with vegetation will recoup the weakness of individual treatment. Plant roots are an excellent location for microbial

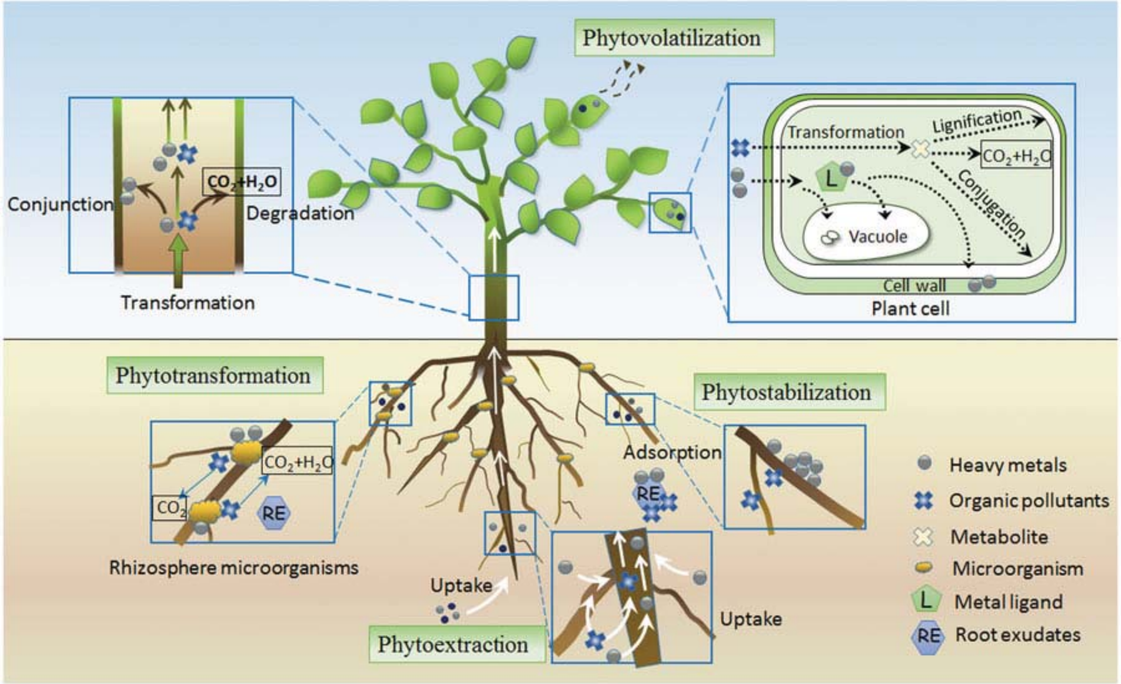

Figure 4. The mechanisms of phytoremediation used for co-contaminated soil with heavy metals and organic pollutants.

attachment, and the roots exudates provide nutrients for microbial growth. In turn, the metabolic activities of beneficial microbial consortia raise the mineral nutrition and plant hormone (e.g. indole-3-acetic acid (IAA), siderophores and 1-aminocyclopropane-1-carboxylate (ACC) deaminase) to improve the plant biomass in co-contaminated soil [31,99]. The mechanisms of bacteria, used to improve the plant stress resistance, can be summarized as follows: (1) raising plant growth by extracellular substances; (2) establishing an antioxidant system and mitigating oxidative stress; and (3) immobilizing pollutants or altering their available state by the functional groups on the cell surface and the extracellular polymers [100]. Reports showed that siderophore-producing bacteria (SPB) could enhance the bioavailable concentration of Cr and Pb via forming stable complexes which were diverted from the iron (essential elements) channel in their host plant [101].

The mechanisms of phytoremediation for highly recalcitrant organic pollutants are composed of: (1) uptake by plants and then pollutants are stored and/or participated in the metabolism [102,103]; (2) degradation by root exudates (e.g. enzymes, organic acids and biosurfactants); (3) transformation by rhizosphere microorganisms [104]; and (4) adsorption by the surface of the root system. Moreover, the root elongation allows the "trapped" pollutants, which are sequestrated in micropores to become accessible to degrading bacteria through the decomposition of soil aggregates by releasing organic acids [54]. Furthermore, plant cultivation of mixed species enhanced the removal efficiency of phenanthrene and pyrene, due to the interactions of roots in three probable aspect (roots' interaction improves the root exudation and enzymatic activity, interaction of roots modifies the root surface properties, and intertwined roots make it possible for water, nutrients and microbes penetrate into deeper soil) [105]. Reports showed that the extending mycorrhizal hyphae expanded the area of soil–roots contact. It indicated that the root colonization of bacteria increased the partitioning of organic pollutants between roots and aqueous soil pores, thereby enhancing the uptake of fluorene and phenanthrene by the root [106,107].

According to Table 2, plant–microbe interactions could achieve the goals of simultaneous remediation of co-contaminated soil with heavy metals and organic pollutants [108–110]. The microbial species for promoting phytoremediation efficiency include degrading bacteria, resistance-enhanced bacteria and plant growth-promoting bacteria[111]. Due to the specificity of bioremediation, the interplanting among different species coupled with regular inoculation of bacteria and fungi in multi-element contaminated soil, could receive better metals phytoextraction and recalcitrant compound mineralization [112,21]. The cooperation of rhizobia and legumes is essential in nitrogen fixation. They also have the ability to enhance the resistance of heavy metals and the elimination of organic pollutants [113].

Phytoremediation is often controlled by the behavior of pollutants, microbial interactions and climatic

Table 2. The effect of plant-microbe on remediation efficiency for compound contamination with heavy metals and organic pollutants.

Plant species	Bacterium	Pollutants	effect	References
C. odorata	*Chromolaena odorata* (L)	Cd, Ni, Zn and crude oil	The largest phytoremediation efficiency for Zn, Cd and Ni was 63%, 62% and 47%, respectively, and the removal efficiency of crude oil up to 80%	[108]
Sedum alfredii	*Pseudomonas* sp. DDT-1	Cd, DDT and its metabolites DDE	Increased *SA* root biomass, the concentration of Cd and DDs reduced by 31.1% and 53.6%, respectively	[21]
Sedum alfredii	*Burkholderia cepacia*	Cd, Zn, Cu, Pb, As and phenanthrene	Improved the soil N and P nutrition, raised the metal translocation factor, tolerance index and phytoextraction efficiency, and up to 96.3% of phenanthrene was eliminated	[14]
Sedum alfredii	*Bacillus subtilis, Flavobacterium and Pseudomonas sp.*	Cd and carbendazim	The microbial biomass, microbial diversities, and dehydrogenase activities were enhanced; increased the removal of Cd and carbendazim	[110]
Brassica napus	*Pantoea* sp. FC 1	Cd and phenol	Promoted the growth of plant and bacteria and increased the efficiency of phenol dissipation and Cd accumulation	[131]
Sedum alfredii and *Festuca arundinaceae*	BDE-degrader *(Bacillus cereus strain JP12)*	Cd, Pb, Zn and decabromodiphenyl ether (BDE-209	Improved plant growth and soil microbial activity, increased the BDE-209 dissipation and enhanced the metal phytoextraction	[109]

conditions [114]. In the actual application process, exogenous bacteria may be not able to survive in the co-contaminated field, due to the fact that they could not outcompete the indigenous microbes for nutrients [113]. Besides, their growth is suppressed by the toxicity of combined pollutants. Rapid reduction of exogenous microorganisms makes it necessary to regularly re-inoculate various species of microbes [111]. In addition, the approach about the accurate colonization of bacteria to the plant roots is an unresolved issue in the phytoremediation processes of co-contaminated soil.

Genetic engineering remediation technologies

Suitable biological genetic engineering can be used to enhance the detoxification process in soil remediation. It is conductive to increase the plant biomass and root exudates, thereby improving the efficiency of soil remediation [115]. Genes which involved in the transformation of combined pollutants should be extracted and cloned, and then, they are incorporated into a transgenic plant or constructed a new strain. A study found that transgenic plants reduced the ethylene levels via the expression of bacterial ACC deaminase genes. The genes were beneficial to roots extending thus strengthening the uptake of heavy metals and rhizospheric dissipation of xenobiotics [116]. Glutathione (GSH) in organisms could not only act as a master factor in keeping bacteria from different surrounding stresses [117], but also serve as the substrate for biological synthesis of the metal-binding phytochelatins to mitigate the reduction of biomass. Research introduced the bifunctional GSH synthase gene (*gcsgs*) into *Enterobacter* sp. CBSB1 to improve the phytoextraction efficiency of the host plant (*Brassica juncea*) on the remediation of co-contaminated soil with multiple metals (Cd, Pb and Zn) [118]. Overexpression of the mammalian genes encoding cytochrome P450s in transgenic rice by agrobacterium-mediated transformation led to promote the metabolic degradation of various classes of herbicides [119]. Another study used *Alfalfa* which coexpressed the glutathione S-transferase (GST) and human P450 2E1 (CYP2E1) by the genetic engineering technique, which showed a synergistic effect on enhancing the tolerance and remediation efficiency to Hg and trichloroethylene in soil [120]. Furthermore, *yellow lupine* that was inoculated with the engineered endophyte (held the pTOM-Bu61 plasmid about toluene/TCE degradation and Ni resistance and sequestration system) showed greater potential to enhance the phytoremediation of organic pollutants and toxic metals [121]. Unfortunately, it is still difficult to control the expression levels of the transferred genes in the cell receptors. The effect of certain individual genes may also be restricted within a narrow scope, thereby retrenching their application [113]. In addition, it is essential to assess the risk of biological engineering technology, in order to avoid the introduction of genetically engineered organisms damaging the balance of natural ecosystems.

Biochemical remediation technologies

Due to the complexity of compound contamination in soils, the application of individual remediation is difficult to achieve the desired remediation effect. In order to complement each other, many researches are dedicated to effectively implement physicochemical and

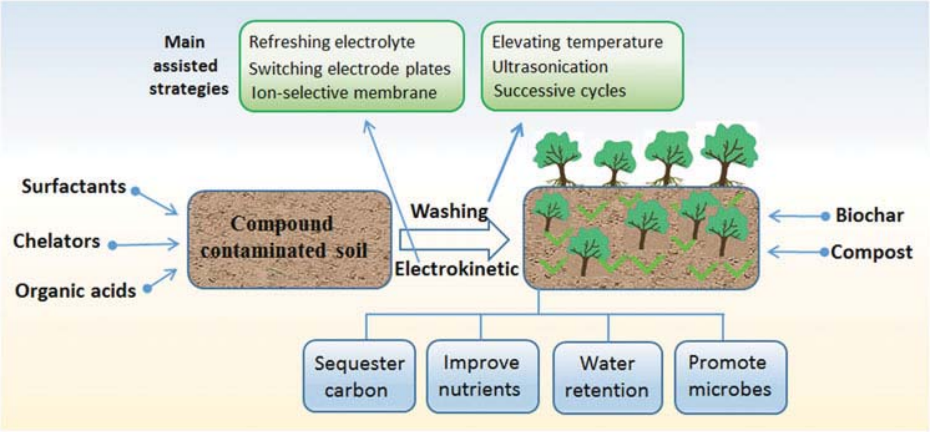

Figure 5. The main operations of combined biochemical remediation technologies.

biological technologies synchronously or successively for the remediation of co-contaminated soil. For the purpose to shorten the treatment cycle of biological remediation and mitigate the damage to soil ecosystem in the meanwhile, the comprehensive schemes have been proposed for the co-contaminated soil (Figure 5). Researches made use of chelators and surfactants to enhance the extraction of heavy metals and PAHs in soil-washing processes, following by degrading bacteria inoculation with nutrients supplement to remove the residual PAHs and restore biological function [122]. Sung et al. [123] used pure water to remove the dissolved metals, mitigating the adverse effect of metal toxicity on soil microbial degradation. Treating the washed soil with compost-assisted cultivating plants achieved rapid transformation into the late phase of phytoremediation process, which could shorten the experiment period [124]. The remediation efficiency of biotechnologies can be enhanced in combination with electrokinetic remediation (EK) for the co-contaminated soil with heavy metals and organic pollutants [124,125]. An experiment was conducted to confirm that the integration of electrokinetics and biostimulation (BioEK) appeared to be that synergistic effect on the remediation efficiency for heavy metals and petroleum [13]. This phenomenon is due to the fact that: (1) the EK process could change the composition of microbial community and enhance the microbial activity on account of yielding anodic oxygen via water electrolysis [126]; (2) the generation of an electric field might increase the bioavailability of pollutants [124]; (3) the duration of the electric field would enhance bacterial movement and receive a more homogeneous distribution of nutrients, thereby providing more opportunities for microbial contact with pollutants; (4) the microbial metabolism could produce a considerable amount of H_2O which help to improve the electro-osmotic flow; and (5) the organic acids generated by biodegradation process is conductive to dissolve metal ions and mobilize free metals by electromigration [13]. Lee et al. [127] applied the bioleaching process by addition of sulfur-oxidizing bacteria as the pretreatment procedure in order to the metal migration. Incorporation of the electrokinetic process could effectively remove the heavy metals from soil. Tourmaline as a novel adsorbent could spontaneously adsorb heavy metals via the water automatic polarization and surface ion exchange [128,129]. It also possesses the intricate chemical structure with ability for electrostatic and magnetic field generation, stimulating microbial growth and metabolic activity. Research initially applied the tourmaline united with *Phanerochaete chrysosporium*, and showed the accelerating effect to enhance the bioremediation process of the co-contaminated soil with PAHs and OCPs [130].

Conclusions and expectations

Co-contaminated soil has emerged increasingly in people's lives. These pollutants pose a risk to natural ecosystems, which even cause adverse health effects on humans through the food chain. Biological technologies are recognized to be environmentally friendly and promise methods for the remediation of contaminated soil. The use of these technologies can effectively minimize the ecological risks through the passivation of heavy metals and degradation of organic pollutants, even if the interactions of multiple pollutants tend to influence the remediation effects. As an ideal technology to deal with the increasing serious compound contamination, some aspects still need to be improved:

1. To date, most of the technologies remain as artificially controlled conditions such as laboratory, greenhouse and experimental plots. It is necessary

to apply the technologies in contaminated soil of actual sites in order to accept the inspection from natural environmental factors.

2. Some materials (e.g. hyperaccumulator) that had been used for the remediation of contaminated soil resulting from subsequent treatment. The pollutants accumulated in organisms will return into the soil with the death of organisms and/or the changes in the environment. It is important to discuss the appropriate process with subsequent research in order to avoid secondary pollution.
3. The remediation idea should be transformed from pollutant reduction to pollutant reclamation. Actually, garbage is a misplaced resource, and the high concentrations of pollutants may be another resource. Future research needs to be conducted for technology improvement to accomplish the transformation. For example, recyclable material could be developed for the sorption and immobilization of heavy metals, and the adsorbed metals can be recovered after extraction. Also, the biomass from hyper-accumulators could be served as the raw material for biochar.
4. The low bioavailability often restricts the degradation efficiency of organic compounds which is largely hydrophobic. It is critical to screen the special degrading bacteria that have the ability to produce surfactants. The biodegradable surfactant can not only emulsify lipid compounds and enhance the biodegradation rate but also avoid the introduction of additional chemical compounds to the environment.
5. The inadaptability of exogenous bacteria renders a bad situation in the competition with local bacteria, which reduces the efficiency of microbial inoculation. The assisted strategies regarding effective bacterial colonization in plant roots and bacteria compatibility combination matching researches will be beneficial to improve bioremediation effectiveness. These factors need deeper exploration.
6. Combined remediation technology has great advantages in co-contaminated soil. Considering the potential costs, it is worth further study about the feasibility of serving compost (composting) or biochar as the carriers of nanomaterials to decrease available combined pollutants in contaminated soil.
7. In arable land, a part of pesticide residues and essential nutrients elements in geobiochemical circulation are important for vegetable cultivation. It is necessary to assess the relationship among the applied technology, effectiveness of pesticides and soil organisms (e.g. earthworms). Further work is required to balance the effects of the employed technology in nutrient retention and the normal growth of earthworms on the achievement of sustainable agriculture goals and environmental purpose.
8. Little is realized about the complexity of compound contamination in the soil. The difficulties in remediation of co-contaminated soil, caused by the intricate relation amongst various co-existing pollutants, should be an in-depth study. Besides, the effect and mechanism of interaction with combined pollutants on the soil remediation efficiency also need intensive study.

Disclosure statement

The authors report no declarations of other interest. The authors alone are responsible for the content and writing of this article.

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