



Recent advances in conventional and contemporary methods for remediation of heavy metal-contaminated soils

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Abstract

Remediation of heavy metal-contaminated soils has been drawing our attention toward it for quite some time now and a need for developing new methods toward reclamation has come up as the need of the hour. Conventional methods of heavy metal-contaminated soil remediation have been in use for decades and have shown great results, but they have their own setbacks. The chemical and physical techniques when used singularly generally generate by-products (toxic sludge or pollutants) and are not cost-effective, while the biological process is very slow and time-consuming. Hence to overcome them, an amalgamation of two or more techniques is being used. In view of the facts, new methods of biosorption, nanoremediation as well as microbial fuel cell techniques have been developed, which utilize the metabolic activities of microorganisms for bioremediation purpose. These are cost-effective and efficient methods of remediation, which are now becoming an integral part of all environmental and bioresource technology. In this contribution, we have highlighted various augmentations in physical, chemical, and biological methods for the remediation of heavy metal-contaminated soils, weighing up their pros and cons. Further, we have discussed the amalgamation of the above techniques such as physiochemical and physiobiological methods with recent literature for the removal of heavy metals from the contaminated soils. These combinations have showed synergetic effects with a many fold increase in removal efficiency of heavy metals along with economic feasibility.

Keywords Heavy metals · Contaminated soils · Nanoremediation · Microbial fuel cells · Biosorption

Introduction

Since the beginning of the industrial modernization, anthropogenic factors are the main cause of the release of heavy metals and organic pollutants into the atmosphere. Soils, being the ultimate part of the ecological system, are profoundly polluted (Wu et al. 2010). Processes like pollution,

salinization, and erosion are weakening soil's physical, chemical, and biological properties. Due to pollution, many toxic materials have been released and accumulated in the soils. Contaminated soils have clear consequences on the social, economic, and environmental fronts.

Heavy metals are categorized as high density- and high atomic weight-based metallic elements which are toxic even at a very low concentration (< 1 ppb) (Olaniran et al. 2013). These metals are an indispensable part of all biological systems and must be present in optimal concentration ranges. At very low concentrations, they tend to decrease the metabolic functions of the body, while at higher concentrations they hinder the metabolic reactions of chemical functional groups and other metal ions present in our body. Sometimes, these heavy metals can alter the active sites of the biological molecules and can be toxic for both microorganisms and macro-organisms (Garbisu and Alkorta 2003). In the worst scenarios, some metals can even mount their way up the food chain and hoard in the human body causing bioaccumulation (Wu et al. 2010). Table 1 summarizes the problems caused by heavy metals in plants and humans with their origins and

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Table 1 Sources of various heavy metal contaminations and their lethal effect on the environment

Heavy metals	EPA regulatory limit (ppm)	Sources	Toxic effects on living beings
As	0.01	Geogenic processes Smelting Thermal power plants Burning of fuel	Affects ATP synthesis and oxidative phosphorylation in humans. Reduction in seed germination and fruit yield, stunted growth, wilting, and chlorosis in plants
Cd	5.0	Zinc smelting E-waste incineration Combustion of fuel Petroleum industries	Leads to cancer, mutations, endocrine disruption, lung damage, and disturbs Ca^{2+} regulations in humans Stunted root and shoot growth, decrease in nutrient content, and poor seed germination in plants
Cr	0.1	Mining Industrial coolants Leather tanning	Hair loss in humans Decrease in plant nutrient acquisition, inhibition of germination process, reduced shoot and root growth, and reduction of plant biomass
Cu	1.3	Mining Electroplating Smelting Petroleum industries	Cerebral and nephron damage, liver damage, chronic anemia, and stomach and intestine disorders in humans Reduction in seed germination, causes plant vigor, and iron intake in plants
Hg	2.0	Fluorescent lamps Thermal power plants Electrical appliances Hospital waste Chloralkali plants	Autoimmune diseases, depression, drowsiness, fatigue, hair loss, insomnia, memory loss, anxiety, blindness, mood swings, brain damage, and lung and kidney failure in humans Stunted growth, reduced tiller and panicle formation, yield reduction, bioaccumulation in shoot and root of seedlings, reduction in germination percentage, reduction in flowering and fruit weight, and chlorosis in plants
Ni	0.2	Smelting Thermal power plants Battery manufacturing industries	Skin allergies, lungs and nose cancer, long-term inhalation leads to sinuses and throat infection and infertility, and hair loss in humans Decrease in chlorophyll content and stomatal conductance, affects Calvin cycle and CO_2 fixation, reduced plant nutrient acquisition, decrease in shoot and root growth, and chlorosis in plants.
Pb	15	Smelting, bangle industry, ceramics, lead acid batteries, E-wastes Thermal power plants Petroleum industries	Memory loss, poor infant growth, cardiovascular disease, and learning and coordination problems in humans Suppressed seed germination and growth, poor CO_2 fixation, and decrease in plant protein growth.
Zn	0.5	Smelting Electroplating Petroleum industries	Dizziness and fatigue in humans Reduced germination and biomass yield, and decrease in chlorophyll, carotenoid, starch, and amino acid contents in plants

permissible limits in soils (Dixit et al. 2015; Chibuikwe and Obiora 2014).

The real problem of this decade is the presence of heavy metals in contaminated soils along with various other industrial pollutants termed as co-contamination. According to the EPA record, 40% of the hazardous waste-polluted areas, presented in national priority list, are co-contaminated with heavy metals and organic pollutants (Olaniran et al. 2013). Bioremediation of heavy metals is more difficult than that of organic contaminants, as the latter can be mineralized into carbon dioxide and water, but heavy metals cannot be mineralized and can only can be converted to less toxic form or immobilized to reduce their bioavailability. Besides, heavy metals impede the biodegradation of organic and inorganic contaminants making co-contaminated soils difficult to remediate.

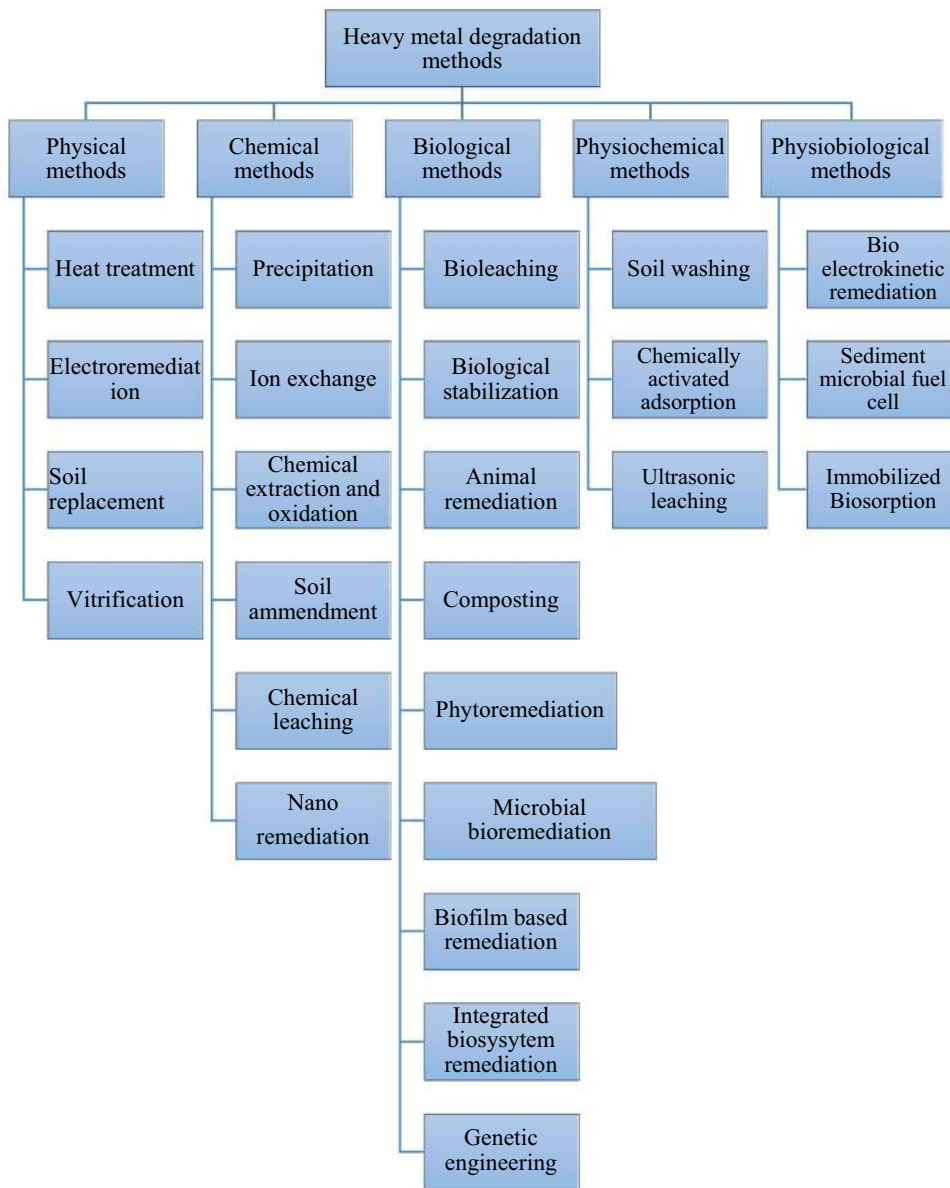
Pollution due to heavy metals has become the foremost issue because of its pervasive practices in industries and

untreated dispersal of wastes containing these metals. Also, their toxicity to human beings, plants, and animals is becoming a major medical/health concern. Major heavy metal contaminations arise from industrial effluents and agricultural activities. In this review, we will go through various conventional and advanced methods for the remediation of contaminated soils and weigh their pros and cons. Figure 1 describes different methods of heavy metal (co-contaminant) remediation, categorized as physical, chemical, biological, physiochemical, and physiobiological methods.

Physical methods

Physical methods of heavy metal remediation in contaminated soils have a wide range of spectrum for different waste products. Almost all of the pollutants can be removed through physical removal methods. However, there are

Fig. 1 Different methods for the remediation of co-contaminated soil



disadvantages too. Generally, the pollutants removed using the physical techniques require further processing and have a relatively high cost of application as compared to other techniques. Physical separation methods are mostly based on particle size distribution of pollutants. Few such physical treatments of heavy metal-contaminated soil are described below:

Heat treatment

In this method, the substrate (like soil or sludge) is heated to 300–400 °C. During this process, hydrocarbons and heavy metals, are exposed to very high temperature, making them evaporate and later are recovered by condensation. The advantages of this process are shorter treatment time and

complete degradation or removal of metals like Cd and Cu (94 and 97%, respectively) (Shi et al. 2013). Also, the heavy metals can be recovered from ash generated by thermochemical methods such as treatment with KCl and MgCl₂ at a high temperature of 900–1000 °C. However, the disadvantage of this technique is the need of very high temperature for operations. Such high temperatures lead to more leaching of the metals and also greater loss of humus (Shi et al. 2013).

Electroremediation

Electroremediation works on the principle of electrokinesis. This process involves application of low electric current to the contaminated substrate for the confinement of the pollutants near the vicinity of electrodes from where they can

be recovered later. During the process, contaminants are destroyed, mineralized, and mobilized (Elicker et al. 2014). The advantage of this process is lesser or shorter time interval. It is reported that pre-acidification of substrate improved the remediation results as it increased the dissolution of heavy metals (Wang et al. 2005a).

Electrokinetic remediation basically works on three principles:

1. Electromigration of charged pollutants: it includes metals getting ionized in the applied electric field, leading positively charged (cations) heavy metals to move toward the cathode.
2. Electro-osmosis: it includes movement of electrolytic ions due to viscous drag caused by charged ions' electromigration.
3. Electrophoresis: it includes migration of colloidal charged ion particles (Gao et al. 2013a, b).

During the process, the H^+ ions produced during hydrolysis at the anode are drifted toward the cathode by an electric field and exchange with cationic metals on the surface (Kim et al. 2009; Peng and Tian 2010). The remediation of heavy metals can be achieved by ion exchange, electrodeposition, or precipitation upon their migration to the electrodes.

Poor extraction of heavy metals from soil is the major setback of this technique. Recent reports revealed that the use of enhancing agent aided the solubility of cations and their migration toward the cathode. Pietro et al. investigated an enhanced EK (electrokinetic) treatment of marine sediments co-contaminated with Hg and PAHs (polyaromatic hydrocarbons). MGDA (methylglycinediacetic acid) and non-ionic surfactant were used as novel enhancing agents (EA). The results revealed a synergic action of EK and EA, which led to high Hg and PAH removals (> 60% mobilization of metals occurred). Hence, the use of enhancing agents facilitates more cost-effective and efficient removal of contaminants (Falciglia et al. 2017).

Soil replacement method

Soil replacement method is based on the dilution of pollutant's concentration in the soils via partially or completely replacing the contaminated soils. In this method, the entire biome of the contaminated soil is isolated with its surrounding to arrest it from affecting the natural and normal environment. Three major modus operandi techniques that sum up the soil replacement method are as follows:

1. The first is the replacement of soil by itself, briefly; the new soil replaces the contaminated soil by complete removal. The major challenge with this technique is the necessity to treat the removed soils feasibly to avoid

incurred secondary pollution, if any. Also, this technique is limited to applications at very small areas.

2. The second technique includes the deep burrowing of the soils or soils spading from the contaminated area. By this method, the pollutants get degraded due to lowering of their concentrations in the contaminated soils.
3. In the third technique, namely soil importing, the clean soils are brought from other areas and mixed with the contaminated soils. This decreases the concentration of the pollutants automatically at the contaminated site.

Though the aforementioned soil replacement methods are effective, but being costlier these methods are generally applied when a small area of soil is heavily contaminated (Yao et al. 2012).

Vitrification technology

Vitrification is the process of heating contaminated soils (substrate) to a very high temperature until they liquidize (melting) and then rapidly freeze, forming solids through glass transition. This glass-like solid formation, also called as vitrified product, entraps and immobilizes the contaminant, hence isolating them from the environment. It has low porosity and leaching activity. Vitrification is thus capable of treating co-contaminated soils.

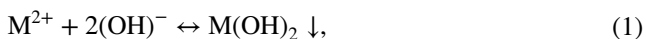
In this method, electric current is used on heat-contaminated soil to a very high temperature (1700–2000 °C), which melts the metals to the vitrified form (Navarro et al. 2013). In Japan, this method was used to reduce the radioactive wastes produced from its nuclear plants and also after the nuclear attack on Hiroshima and Nagasaki. Moreover, few new amendments in this technique outlined the increased immobilization/stabilization efficiency to almost 96% by treatment with fly ash, activated carbon, and nano-metallic additives at 1200 °C (Mallampati et al. 2015).

Chemical methods

By using the chemical methods for soil remediation, we aim at remediating the contaminants that have been hoarded in the soils or in making such kind of changes to their chemical characteristics that decrease their hazardous properties (Leštan et al. 2008). Although chemical treatments are highly effective at field scale, they have the drawback of by-product formations, which increases further downstream processing steps. Below are few such chemical treatment techniques for co-contaminated soils.

Precipitation

It is the most conventional method used for effective elimination of heavy metals from contaminated sources. The mechanism involved is as follows:



where M^{2+} stands for dissolved metal ions, OH^{-} stands for the precipitant, and $M(OH)_2$ stands for insoluble metal hydroxide.

Chemical precipitation occurs at basic pH in the range of 9–11 (Wang et al. 2005b). During this treatment, the associated organic contaminants also undergo alkaline hydrolysis (Emmrich 1999; Bhogle and Pandit 2017; Albers et al. 2017). The benefits of using precipitation comprise its simple, cost-effective, and nontoxic operations. Still, this process requires ample amount of chemical reagents to reduce cation charged metals to a permissible limit of discharge. Other drawbacks are the secondary waste generation, slow and poor settling of precipitate, the aggregation of different metal precipitates, and slow degradation rate of sludge (Aziz et al. 2008).

Ion exchange

The ion exchange process is used to exchange cations or anions from the contaminants and is used effectively in industrial sectors to decrease the concentration of heavy metals in the effluent stream. In this method, heavy metal (undesirable) ions are swapped by other cations which are usually non-polluting in nature (Dabrowski et al. 2004). Co-contaminated soil can also be remediated by using suitable substrate (soil) solution and cation exchange matrix. The heavy metal cations in the soil get exchanged with the cation present in the matrices, maintaining the balance of charge transfer (Kim et al. 2005). In various research studies, natural zeolite has been extensively exploited for the exchange of heavy metal cations such as Cu, Co, Zn, and Mn from co-contaminated soils (Li et al. 2018; Wen et al. 2018; Boros-Lajszner et al. 2018). Matrices generally used are synthetic organic ion exchange resins. However, membrane fouling, pH sensitivity, and non-selectivity of the membrane are few of the drawbacks of this technique.

Chemical extraction and oxidation

Chelating agents are organic compounds which have metal ions binding sites in their structure (Xue et al. 2009). Chelating agents such as EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid), and a chelating resin produced by Diaion named CR11 have been used to treat heavy metal-contaminated sludge. EDTA is an

effective reagent in removing metals and has the advantage of being recoverable post-reaction. It has high affinity for metals and forms metal–EDTA complexes. One such study was done using EDTA and hydrogen peroxide to extract organic and heavy metal pollutants. 3% hydrogen peroxide (H_2O_2) and 0.1 M EDTA removed approximately 70% of the petroleum and 60% of the Cu and Pb in the soils, respectively. Oxidation and extraction together, regardless of the sequence, were effective in bioremediation of TPH (total petroleum hydrocarbon) and heavy metals (Yoo et al. 2017). Nowadays, biodegradable chelants made via green chemistry are being used such as GLDA (diacetic glutamic acid). It is used for the removal of different metals such as Ni, Cd, and Cu-contaminated sludge at acidic pH of 4. When used in the ratio of 3:1 (chelator to sample) the removal efficiency was observed as 89% for Cd, 82% for Ni, and 84% for Cu (Wu et al. 2015). In a recent study, citric acid (167.6 mM) was used as a chelating agent for the effective removal of Zn from contaminated soils (about 92.8%) at acidic pH 4.43 within 30 min (Asadzadeh et al. 2018).

Chemical leaching

This process involves dissolving heavy metal ions into the leaching liquid and extracting them out. The leaching solution is generally acidic in nature to enhance the solubility of the metal ions. This acidification is generally achieved by using inorganic acid such as H_2SO_4 , HCl, or HNO_3 , maintained at a pH of 1.5–2.0 (Dermont et al. 2008). Chemical leaching is preferred when the concentration of heavy metals is significant and the area of action is huge (Alghanmi et al. 2015). The standpoint of this technique is the need of hefty amount of acid to maintain the pH for suitable solubilization, and later neutralization of such acidified sludge in the downstream requires large operational cost.

Soil amendments (chemical fixation)

In this technique, the solubility and mobility of heavy metal contaminants are decreased using chemical agents such as fly ash, cement, silica, and lime. This process of using chemical agents for immobilization of toxic metals is termed as chemical fixation and the chemicals used for this process are termed as amendments. Metals such as As, Pb, and Cr are the best suited for this process, while metals like Cd, Cu, and Zn can also be stabilized. In a study, calcined cockle shell (CCS) comprising lime showed effective immobilization of Cd, Pb, and Zn in mine tailing soils in 28 days of incubation period. Upon extraction using acid leaching, Cd, Pb, and Zn were reduced up to 85, 85, and 91%, respectively, suggesting CCS to be low-cost soil amendment (Islam et al. 2017).

Similarly, silica treatments were found to immobilize inorganics by the formation of hydroxides, metal silicates, or polymerized silicates. These silicates encapsulate metals or provide active sites for the adsorption of metals (Camenzuli et al. 2017). A study done by Wolfgang Friesl-Hanl showed the heavy metals' (Cd, Zn, and Pb) immobilizing effect of gravel sludge, red mud, and their combinations (in situ). The high immobilizing efficacies (91, 94, and 83% of Cd, Zn, and Pb, respectively) were attributed to red mud's high alkalinity and high contents of iron oxides, clay minerals, and calcium carbonate (Friesl et al. 2004).

Recently, an organic polymer chelator potassium dipropyl dithiophosphate (PDD) (5%) in combination with humic acid (7%), generated very stable chelating precipitate by reacting with the heavy metals present in contaminated soil sediment. The obtained stabilization efficiencies for heavy metal were reported as Cu 99.98%, Zn 90.66%, Pb 99.38%, and Cd 92.83% in the sediment (Xu 2017). Likewise, in a study, FeHP (iron hydroxyl phosphate) was used as a chemical fixation agent to simultaneously immobilize Pb, Cd, and As in the soil contaminated with a mixture of heavy metals from the wastewater irrigation area. The immobilization efficiency of Pb, Cd, and As was observed as 59, 44, and 69%, respectively, with only 10% usage of FeHP proving it can be used as a broad-range soil amendment (Yuan et al. 2017).

Nanoremediation

Nanoscale zero-valent iron particles (nZVI) have been most widely used in nanoremediation and are ideal candidates to remediate heavy metals from industrial waste. nZVI has a metallic iron core and iron oxide shell. Its metallic iron core possesses the well-characterized reducing or electron-donating power, while the surface iron hydroxides offer the coordinative and electrostatic functions to attract and adsorb charged ions of heavy metals. Hence, nZVI has two nanocomponents with distinct and complementary functions for the removal of oxyanions (e.g., As(V), Cr(VI)) and cations (e.g., Cu(II), Zn(II), Cd(II), Pd(II), Ni(II)). Nanomaterials are also explored as adsorbents. A recent study evaluated the adsorption of heavy metals (Cd (II), Pb(II), and As (II)) from soil and aqueous samples by zeolite-aided zero-valent iron nanoparticles. The mechanism involved the complex formation with modified nanoparticle, followed by co-precipitation, and finally removal (Li et al. 2018). The advantage of nanoremediation comprises eco-friendly end products, which are produced in very less quantity (Li et al. 2017a). In a study, nano-ZnO particles were investigated for bioremediation of Cd- and Pb-contaminated site. Heavy metal-contaminated sites cause low CAT (catalase coding gene) activity in plants growing in that region, leading to their poor defense mechanism. The presence of ZnO nanoparticles (ZnONPs) in the contaminated soil led to improved

CAT and POX (peroxidase coding gene) activity in plants and thereby protected the plants against oxidative stresses. Decreased heavy metal accumulation in plants showed the decrease in the presence of contaminants in the soils (Venkatachalam et al. 2017). Similarly, nanomagnetite coated by silica and MgO (MTM) showed excellent removal capacities toward heavy metals (Pb, Cd, Cu). The heavy metal removal mechanism involved was mainly substitution, followed by precipitation (Nagarajah et al. 2017).

Biological methods

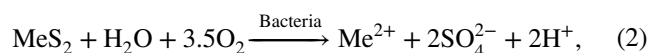
The use of microorganisms, plants, and animals for bioremediation has its own advantages over the conventional methods. These are economically feasible, practical, and moreover do not create any secondary pollution. The contaminant does not require any other treatment and also the natural flora and fauna of the contaminated land can be restored to the original form (Abbas et al. 2014). Below are few techniques being used for remediation using biological agents.

Bioleaching

In this technique, microbes such as iron-oxidizing bacteria (*Acidithiobacillus ferrooxidans*) or sulfur-oxidizing bacteria are used for leaching purpose instead of chemical reagents. There are two methods by which the microbe aids in metal leaching, as discussed below.

Direct surface attachment

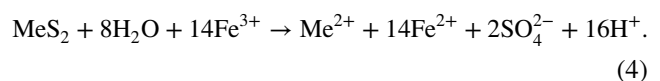
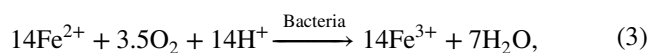
In this technique, bacteria directly interact with heavy metal-contaminated sites by attaching to the metal salts and cause dissolution of metals as explained by the following equation:



where MeS_2 is an insoluble metal sulfide and Me^{2+} is a free metal ion.

Indirect bacterial oxidation

Bacteria such as iron-oxidizing bacteria lead to the formation of Fe^{3+} . This Fe^{3+} then reacts with the metals and metal solubilization occurs.



According to a recent discovery of an active strain, Hyhel-1, identified as *Bacillus* sp., was utilized to bioleach copper from heavy metal-contaminated e-wastes. Interestingly, this strain does not need an acidic environment and works better at neutral pH and moderate temperature. Thus, Hyhel-1 strain offers a new cost-effective alternative to recover metals from e-waste without using solvents or acidification (Rozas et al. 2017).

Biological stabilization

In this technique, immobilized bacteria act as solubilizing agents. In a study, nutrient beads of immobilized sulfur-reducing bacteria (SRB) were used for effective transformation of heavy metals into the more stable bound phases. Polyvinyl alcohol (PVA) trapped SRB, provided a protection to bacteria from metal toxicity, and at the same time allowed increased surface area for transmission of matter between cells and sediments. The removal efficiencies of Cu, Zn, Pb, and Cd were obtained as 76.3, 95.6, 100, and 91.2%, respectively. The advantages of this process are that it is recyclable and has no secondary waste generation (Li et al. 2017b).

Animal remediation

When different kinds of wastes which are generally organic in nature are composted, many soil macrofauna and mesofauna help in the remediation process by using such organic wastes in their own metabolism. Moreover, they boost up the metabolic activity of soil microbes. Generally, abiotic conditions are difficult and unfriendly for soil decomposer animals to perform the bioremediation process. The physiochemical conditions of the soil may not always be acceptable by most of the species or animals, due to which they may not be able to colonize in the soil. Furthermore, animals do not generally possess significant metabolic capabilities to reduce the chemicals to completely nontoxic or less toxic states; one may debate that these decomposer animals are incapable of remediation processes.

Recently, a tunicate, *Styela plicata*, was studied for its bioconcentration capacity in Pb- (40%) and Cd- (13%) polluted environment, and hence its use for the bioremediation activities (Colozza et al. 2017). Vermicomposting has proved to be an efficient and faster method of decomposition of household-related wastes which utilizes earthworms than in the conventional composting process (Haimi 2000). Earthworms by their activities in soil generate $-COOH$ and $-CO$ groups that acidify the soil and in turn activate heavy metals, but because of its slow rate more studies are yet to be done to increase the performance (Wu et al. 2010). According to a study by Suthar et al., *Eisenia fetida* was fed on paper mill wastewater (PMS) sludge and bioaccumulation of metals was observed. A significant decrease in the level

of Cd (32–37%), Cr (47.3–80.9%), Cu (68.8–88.4%), and Pb (95.3–97.5%) was reported, which indicates vermistabilization as a suitable routine for bioremediation of heavy metals (Suthar et al. 2014).

Composting

In this technique, compost is mixed with contaminated soil samples and checked for heavy metal remediation. Compost consists of nutrients for the indigenous microbes present in the contaminated soil. These microbes utilize these nutrients for the remediation of contaminants present. Hence by this method, compost acts as both soil amendment agent and bioremediation technique. In the study of Taiwo et al., *Hibiscus cannabinus* seeds were used to co-remediate metals (Fe, Mn, Cu, Zn, and Cr). In this technique, compost along with plant technology remediated 72% Mn, 65% Fe, 60% Zn, and 42% Cu respectively (Taiwo et al. 2016). Compost acts as a stabilization agent in the heavy metal-contaminated sites by forming the complexes, or helps in absorption or (co) precipitation of heavy metals (Chen et al. 2015).

Phytoremediation

Phytoremediation involves the application of plants and different plant-associated microbes to partially or completely remove selected contaminants/pollutants from different contaminated sources (Dixit et al. 2015). This process is based on the plant's ability to take up, store, or degrade pollutants that are present in the vicinity of the plant, irrespective of the soil and water environments (Khan et al. 2004). The efficiency of phytoremediation is dependent on various biological processes such as the interaction between plant and microbes (a rhizospheric process), uptake capacity of plant, translocation and tolerance mechanisms, and plant chelation ability. Recent advancements in various forms of phytotechnology have made our understanding more wide and clear in the fields of plant and soil sciences (Mani and Kumar 2013). There are a number of factors that regulate the efficiency of the plant species to bioremediate heavy metal-contaminated sites, as follows:

1. Accumulation capacity of the candidate plant.
2. Different types of metal ions/contaminants.
3. Plant growth rate at the contaminated site.
4. Planting density.

Other factors that are important in selecting plants for phytoremediation are their fast growth rate, ease in harvesting, high tolerance limits, and efficiency to accumulate different types of metal contaminants. Phytoremediation can be subdivided based on the mode of the action of plants for removing or reducing the toxic contaminants from the soils as follows:

Phytoextraction

In this type of phytoremediation, accumulator plant species are used to extract metals or organic contaminants from soils by accumulating in various plant parts that can be harvested. Generally, plants prefer accumulating essential metals more than heavy metals, where the low accumulation of heavy metals can be explained by competition for binding sites. For instance, lower accumulation of Cd in cowpea plant is reduced in the presence of higher valence cations (Fe) (Akanang and Adamu 2017).

Phytotransformation

It involves the incorporation of partially or completely degraded organic molecules into plant tissues. In this technique, plant uptake soil pollutants which further undergo enzymatic breakdown into simpler forms that can be utilized by plants for metabolic growth processes. *Cannas* plant was found to detoxify various soil xenobiotics by undergoing phytotransformation (Kvesitadze et al. 2006).

Phytostimulation

It involves the stimulation of the microbial and fungal populations in soils due to secretion of plant exudates, enzymes, or by-products into the root zone which in turn degrades organic pollutants. This technique relies on the symbiotic effect of plant and plant growth-promoting microbes. In a recent study done on *Brassica campestris* L. (mustard), an endophytic fungi, isolated from heavy metal-contaminated site, *Mucor* sp. MHR-7, showed reduction in heavy metal toxicity by 94% along with increased phytostimulation (Zahoor et al. 2017).

Phytostabilization

This approach of phytoremediation exploits the ability of the plants to reduce the migration of various forms of contaminants by checking unwanted processes such as erosion, leaching, or runoff. In this way, they are able to reduce the bioavailability of pollutants in the environment, thus inhibiting their mobility to the food chain. Effective phytostabilization of heavy metals especially Ni and Cr was observed in the roots of *Nerium oleander* (Elloumi et al. 2017).

Studies have also explored *Festuca rubra* L., a grass also named as red fescue, for its role in phytostabilization of heavy metal-contaminated soils. Nowadays, research is progressing toward enhanced phytostabilization using various soil additives such as inherent mineral sorbents (Touceda-González et al. 2017; Radziemska et al. 2017). Radziemska studied the decrease in heavy metal (Pb, Zn, and Cd) concentrations in soils by the presence of minerals (dolomite,

halloysite, and chalcedonite) through phytostabilization in the roots of *Festuca rubra* L. (Radziemska 2018). Hence, aiding phytostabilization using soil additives has come up as a promising technique in remediation of multimetal-contaminated soils.

Phytovolatilization

In this process, plants absorb contaminants from the soil and metabolically transform them into volatile by-products and thereby release them into the atmosphere. Few studies have shown the application of this technique for remediation of Se and Hg from the contaminated soil samples (Henry 2000) (Bañuelos et al. 2000). This process is extensively studied for the production of Se gas from organic and inorganic Se compounds (Terry et al. 1992; Brooks 1998). Considerable attempts have also been made in inserting Hg reductase genes in the genome of plants to enable phytovolatilization (Brooks 1998; Bizily et al. 1999). Studies on As phytovolatilization have been carried out on *Pteris vittata*, where up to 90% phytovolatilization of As was observed at laboratory scale, suggesting the ability of the plant to release Se using secretory glands present on its frond's edges (Sakakibara et al. 2010). Researchers have also studied the suitability of this process for the remediation of soil contaminated by radioactive substances (Dushenkov 2003). Apart from the advantages, phytovolatilization is still a controversial technique as it releases toxic heavy metals back into the environment.

Rhizofiltration

This process mainly concerns the uptake of pollutants such as heavy metals and organic contaminants from wastewater and water streams contaminated with industrial wastes (Mathew 2005). The total amount of metals removed can be estimated by multiplying the amount of metal concentration in the harvested plant material and the harvested amount of biomass (Salt et al. 1998). In a recent study by Chen et al., plant growth-promoting bacteria (PGPB) were utilized, which helped in increasing the bioavailability of heavy metal Ni for the plant (Chen et al. 2017).

Plants that can accumulate high amount of various heavy metals from soils were termed as 'hyperaccumulator' and they translocate them from the roots to the aboveground plant organs such as shoots and leaves at a very high concentration without showing any phytotoxicity. Such hyperaccumulator plants overcome phytotoxicity due to the presence of a versatile property known as hypertolerance, making them as sensitive as non-hyperaccumulators. The amount of hyperaccumulation of different heavy metals can vary significantly in different species or also within the same species based on their ecotype and populations (Rascio and

Table 2 Different types of plant species used for removal of heavy metals

Plant species	Heavy metals	Concentration range of removal ($\mu\text{g g}^{-1}$)	References
<i>Phytolacca acinosa</i>	Mn	12,180–19,300	Xue et al. (2004)
<i>Sedum alfredii</i>	Cd	15,000	Tian et al. (2011)
<i>Cardaminopsis halleri</i>	Zn, Pb, Cu, Cd	138–21,500	Dahmani-Muller et al. (2000)
<i>Armeria maritima ssp. halleri</i>			
<i>Agrostis tenuis</i>			
<i>Pityrogramma calomelanos</i>	As	8350	Visoottiviset et al. (2002)
<i>Pteris vittata</i>	As	6030	Visoottiviset et al. (2002), Selvankumar et al. (2017)
		100–400	
<i>Salsola kali</i>	Cd	2016–2696	de la Rosa et al. (2004)
<i>Mentha arvensis</i>	Hg	1331–1816	Manikandan et al. (2015)
<i>Noccaea caerulea</i>	Cd, Zn	–	Rees et al. (2015)
<i>Miscanthus sp. Goedae-Uksae 1</i>	As, Cu, Pb, Ni, Cd, Zn	–	Bang et al. (2015)

Navari-Izzo 2011). In a study by Stein et al., *Arabidopsis halleri*, commonly known as Rockcress, were grown on contaminated brownfield sites and were found to be slurping up and bioaccumulating heavy metal ions from soils into leaves. Its bioaccumulation concentration was as high as Zn 5.4 and 0.3% Cd based on dry biomass (Bradley 2017). Table 2 presents a list of plant species being used for phytoremediation. Phytoremediation is a comparatively slower process than existing traditional physical and chemical techniques, because it requires several growing seasons with appropriate soil conditions that can support their growth for site cleanup (McIntyre 2003; Mathew 2005).

Microbial remediation

In such kind of bioremediation processes, microorganisms remediate organic contaminants along with heavy metals. Organic contaminants are converted to products such as CO_2 , water, or other metabolites which are further directly used by microbes in their metabolism and growth. Microorganisms perform bioremediation by two main methods: either they release contaminant-degradative enzymes or they develop resistance toward these contaminants. In case of heavy metal bioremediation, the uptake of heavy metals by microorganisms takes place either by bioaccumulation which is an active process and/or through adsorption which is a passive process. Microbial cell wall comprises various functional groups such as carboxylate, hydroxyl, amino, and phosphate. The metal ions can easily bind to such groups and be separated from the environment. Metal ions bind to the bacterial cell surface via different interactions such as covalent bonding, and electrostatic and van der Waals forces (Rajendran et al. 2003). Microorganisms which act as metal accumulators possess an inherent property of converting toxic form of metal contaminants to nontoxic or less toxic

form. There are various mechanisms by which organisms survive metal toxicity:

1. Extrusion system: metals are pushed out through the cells using mechanisms such as chromosomal or plasmid-mediated events.
2. Biotransformation: this is a process by which microorganisms convert the toxic metal to nontoxic forms.
3. Using enzymes like oxidases and reductases: microbes produce these enzymes to convert pollutants to metabolic products.
4. By producing exopolysaccharide (EPS): microorganisms get adapted to the contaminated surrounding by secreting EPS, which develops as an outer hydrophobic cell membrane comprising efflux pumps against the cell membrane disrupting contaminants (e.g., solvents) (Dixit et al. 2015; Garbisu and Alkorta 2003; Singh and Ward 2004; Wu et al. 2010).
5. Synthesizing metallothioneins: these are the metal-binding proteins to which metals form a complex.

Any organism possessing all of these mechanisms working together will be extremely metal-resistant bacteria, but generally microorganisms lack such complete machinery of resistance against metals. This brings forth the need of mutual interaction between microbes, where they complement each other and is named as the mixed culture.

Actinobacteria are excellent candidates for these mixed cultures because of their proven versatility and abundance in the environment. Recent works highlighted that actinobacteria strains are able to remove heavy metals and pesticides simultaneously (Alvarez et al. 2017).

Several works reported the ability of actinobacteria to bioremediate organic compounds or heavy metals. *Streptomyces*, *Rhodococcus*, and *Amycolatopsis* are among the most studied genera.

Few theories regarding such interactions between microbes in mixed culture works are as follows:

1. Conversion of metals into less toxic form, excreting them out, and then immobilization onto the exopolysaccharide of another organism.
2. Extracellular reduction or oxidation of metals by one bacteria, followed by their absorption and intracellular immobilization by metallothionein of another bacteria.
3. Biomineralization of metals by capable bacteria where the rest of the bacteria nutritionally help the bacteria in the process.

A study on marine living bacteria reported various other strategies (apart from above listed) to resist high concentrations of Pb/Hg. These strategies include extracellular sequestration, alteration in cell morphology, altered permeability, or intracellular accumulation, precipitation of heavy metals, biosorption of heavy metals, or their volatilization, demethylation (Naik and Dubey 2017). Table 3 lists different microorganisms that are used for bioaccumulation of heavy metals. Few sulfur-reducing bacteria utilize heavy metals as their electron acceptor for respiration and precipitate them as their metal sulfides and hence help in bioremediation of heavy metals. These bacteria produce hydrogen sulfide by

using sulfate as electron acceptor, which helps in oxidizing the organic matter.

Fungi are also being utilized as a contrivance for remediation of heavy metal-contaminated areas because of their ability to accumulate toxic metals. *Coprinopsis atramentaria* is studied for its bioaccumulation capacity of 76% of Cd²⁺, when the concentration of Cd²⁺ was 1 mg L⁻¹, and 94.7% of Pb²⁺, when the concentration of Pb²⁺ was 800 mg L⁻¹. Hence, it has been recognized as an able accumulator of heavy metal ions and a very important tool for mycoremediation (Lakkireddy and Kües 2017).

Antarctic-inhabiting psychrotolerant yeasts are also studied for their heavy metal tolerance and are found to remediate 1 mM of Cr(VI), Cd(II), and Cu(II) by 55, 68, and 80%, respectively (Fernández et al. 2017).

Algae also perform well in the field of bioremediation. The term 'phycoremediation' is used to denote the remediation which includes either removal, or degradation and assimilation, using various types of algae and cyanobacteria (Chabukdhara et al. 2017). Similar to bacteria, algae have various chemical moieties on their surface such as hydroxyl, carboxyl, phosphate, and amide, which act as metal-binding sites (Abbas et al. 2014; He and Chen 2014). *Phaeophyta macroalgae* (brown algae) act as a sink for heavy metals. It has a large amount of carboxylic groups on its cell wall

Table 3 Various microbial strains used and their maximum removal capacity for heavy metal remediation

Microbes	Heavy metals	Total uptake (mg g ⁻¹)	References
<i>Aspergillus niger</i>	Co, Cd, Cu, Zn	6.71	Tsekova et al. (2014)
<i>Aspergillus awamori</i>		7.18	
<i>Aspergillus ussami</i>		6.40	
<i>Rhizopus delemar</i>		30.28	
<i>Penicillium brevicompactum</i>		25.89	
<i>Saccharomycopsis lipolytica</i>		0.62	
<i>Candida blankii</i>		1.00	
<i>Saccharomyces cerevisiae</i>		1.94	
<i>Hansenula schneegii</i>		1.11	
<i>Debaromyces senii</i>		0.25	
<i>Bacillus circulans</i>	Cr	34.5	Srinath et al. (2002)
<i>Bacillus megaterium</i>	Cr	32.0	
<i>Yarrowia lipolytica</i>	Cd	650	Strouhal et al. (2003)
	Ni	1100	
	Co	180	
	Zn	180	
<i>Geobacillus toebii</i> subsp. <i>Decanicus</i>	Cd, Cu, Co, Mn	17.75, 18.60, 11.43, 21.75, respectively.	Özdemir et al. (2013)
<i>Geobacillus thermoleovorans</i> subsp. <i>Stromboliensis</i>	Cd	17.44	Özdemir et al. (2012)
<i>Bacillus cereus</i>	Mn, Ni, Co,	35, 28, 27, 30, 17, and 28, respectively	Banerjee et al. (2015)
<i>Bacillus subtilis</i>	Hg, Cu, Pb	34, 25, 29, 29, 13, and 30, respectively	
	Mn, Ni, Co,		
	Hg, Cu, Pb		
<i>Bacillus sphaericus</i>	Cr	29.28	Velasquez and Dussan (2009)
<i>E.coli</i> AS21	Ni	0.27	Chaudhary et al. (2017)
<i>Bacillus subtilis</i> 38 (B38)	Cd, Cr, Hg, Pb	3.04, 1.83, 4.09, 2.48, respectively	Wang et al. (2014)

leading to high level of heavy metal accumulation due to electrostatic attraction between metals and cell wall. In a study, different species of brown algae were examined for their metal uptake activity. Among them, *Padina sp.* and *Cystoseira sp.* were reported to have effective metal uptake capabilities (Ali et al. 2017).

Metal removal using biofilm

The biofilm acts as an efficient bioremediation tool and biological stabilization agent. Biofilms have very high tolerance against toxic compounds even when the concentration is lethal for planktonic cultures. In a study done on *Rhodotula mucilaginosa*, metal removal efficiency was in the range from 4.79 to 10.25% for planktonic cells and 91.71–95.39% for biofilm form (Grujić et al. 2017). Biofilms perform bioremediation in two ways:

1. They act as biosorbent and adsorb heavy metals onto surfaces.
2. Exopolymeric substances present in biofilms contain molecules with surfactant or emulsifier properties, which enhance the bioavailability of contaminants (El-Masry et al. 2004).

Integrated phytoremediation system (IPS)

This method involves the presence of plant and microorganism working hand in hand, in a symbiont relationship. In a recent study, IPS comprising plant, fungi, and bacteria was used for As, Cd, Pb, and Zn bioremediation. In the study *Acacia saligna* along with rhizosphere bacteria aided the phytostabilization of heavy metals in the roots of *Eucalyptus camaldulensis* (Guarino and Sciarriello 2017). Plant growth-promoting bacteria (PGPB) are those that constitute the rhizosphere which facilitates the growth of plants in severely heavy metal-contaminated soils. They have been used intensively as adjuncts in heavy metal phytoremediation (Glick 2010; Gamalero and Glick 2011; Kong et al. 2015). These bacteria decrease the bioavailability of heavy metals by binding them with their anionic functional groups and chelating them by secreting extracellular metabolites such as EPS, siderophores (chelator), and organic acids (Ledin et al. 1999; Chen and Cutright 2003; Ma et al. 2011; Park et al. 2011; Madhaiyan et al. 2007).

Another experiment demonstrated that *Magnaporthe oryzae* CBMB20 and *Burkholderia sp.* CBMB40 reduced Ni and Cd availability in soils and decreased their accumulation in tomato roots and shoots by immobilizing them (Kuffner et al. 2010; Ahmad et al. 2014; Dourado et al. 2013). In a study conducted on *Solanum nigrum* growing in Pb-contaminated soils inoculated with *Mucor circinelloides*, the efficiencies of removal was in the order of:

microbial + phytoremediation (58.6%) > phytoremediation (47.2%) > microbial remediation (40.2%) > control. Soil fertility was increased after bioremediation due to change in enzyme activities (Sun et al. 2017).

Genetic engineering

With the advanced genetic engineering tools, it is possible now to engineer microbes with desired characteristics like ability to tolerate metal stress, overexpression of metal-chelating proteins and peptides, and ability of metal accumulation. The design of smart strains can bind to specific metal ions, precipitate, and transform them to less harmful groups (Valls and De Lorenzo 2002).

Corynebacterium glutamicum, the workhorse of biotechnological research, has been used as an As biocontainer and genetically modified using overexpression of *ars* operons (*ars1* and *ars2*) to sanitize As-contaminated sites (Mateos et al. 2017). Likewise, overexpression of CrMTP4, coding metal tolerance protein (MTP) responsible for Cd tolerance and uptake, was reported. Engineered *Chlamydomonas reinhardtii* yielded a significant increase in tolerance to Cd toxicity and its accumulation (Ibuot et al. 2017).

Physiochemical methods

Physiochemical methods are developed as an amalgamation of both physical separation and the chemical extraction methods of soil remediation, as they work better together rather than being singularly used (Dermont et al. 2008). Various physiochemical methods for the remediation of contaminated soils are discussed below.

Soil washing

Soil washing involves removal of those soil particles, which host most of the pollutants, from the bulk soil fraction using aqueous chemical extraction on a solid substrate (Wuana and Okieimen 2011). It is an ex situ remediation technique in which violent mixing and scrubbing of soil particles with a washing liquid cause desorption of heavy metal pollutants from the contaminated soils. Recently, application of low-frequency ultrasonic waves aided desorption of pollutants due to microscale sonophysical effects and macroscale mixing (Park and Son 2017). The advantages of this process are working under low acidic conditions and less requirement of washing liquids. Soil washing becomes highly unsuitable due to various drawbacks such as highly bound metal ions on soil particles, surface morphology, and density of metal-contaminated soil particles, different chemical forms of metals, contamination of metal ions in all particle size

fractions of soils, and high amount of humic content at the contaminated site (Dermont et al. 2008).

Chemically activated adsorption

Adsorption is enhanced by chemically modifying the adsorbate to increase its adsorptive potential such as activated carbon. A microporous activated carbon, i.e., citric acid-treated sawdust impregnated with $ZnCl_2$, revealed the highest potential (0.23 mol/g and 0.33 mmol/g for Cd^{2+} and Ni^{2+} respectively) at a dose of 0.5 g/L within a contact time of 150 min (Nayak et al. 2017).

Ultrasonic leaching

This technique involves the extraction of heavy metal from soils in highly acidic solvent under ultrasonic treatment which enhances the rate of extraction. During sonication, fragmentation of soil particles leads to diffusion of heavy metals from soils to the acidic solvent, augmenting the overall extraction process. In a study, ultrasonication was performed after acidification of heavy metals Cu, Zn, and Pb at pH of 0.75 maintained using conc. HNO_3 . Solubilization of Cu by 95%, Zn by 82.2%, and Pb by 87.3% occurred (Deng, Feng et al. 2009).

Physiobiological methods

Physiobiological methods are developed as an amalgamation of both physical and biological methods of soils remediation. Various physiobiological approaches for the remediation of contaminated soils are discussed below.

Bio-electrokinetic approach

In a study, heavy metals in the phosphate-associated contaminated soils were detoxified using microbial pretreatment (BIO) and electrokinetic remediation (EKR) in combination. This study provided compelling evidence that the sequential usage of the bioleaching and electrokinetics is superior to the individual methods for the detoxification of heavy metals from the contaminated soils. The detoxification efficiencies of heavy metals in a sequential system were higher than those using the single BIO and EKR technique except for As, and the detoxification efficiency of Zn was found to be the highest. Bioleaching, generation of passivation, and migration direction of the ions are reported to be the attributed factors to the final results (Huang et al. 2017).

Sediment microbial fuel cells (SMFCs)

SMFCs are novel technology for the simultaneous production of renewable energy and bioremediation of heavy metals. SMFCs lack any membrane and are completely anoxic as compared to conventional microbial fuel cells. SMFC utilizes exoelectrogens, which have the ability to transfer electrons to the electrodes by using natural electron shuttles, and electro-trophs, which have ability to accept electrons from electrodes hence reducing the metal ions. These electro-trophs help in reducing metals present in the sediments. This powering by microbes is an emerging technique for the remediation of heavy metals from sediments, which are used as inoculum for these fuel cells (Abbas et al. 2017).

Immobilized biosorption

Biosorption is a fast method of passive metal removal from the contaminated samples using biological biomass/adsorbents. It has many advantages compared with the conventional techniques. When we encapsulate the biomass it improves the biosorption performance of the biomass as well as increases its physical and chemical stability and reusability. In our previous work, the *Agrobacterium* biomass was encapsulated in alginate with iron oxide nanoparticles and showed an adsorption capacity of 197.02 mg g^{-1} for Pb, and was seen to be effective for five consecutive cycles (Tiwari et al. 2017). Large-scale application in industries was made possible due to the reusability property of such adsorption techniques. The other offered advantages of immobilizing the microbial biomass in polymeric matrixes are the improvement in the biomass rigidity and heat resistivity with optimum porosity for practical applications. Hence, it became popular for implementing immobilization techniques for heavy metal treatment from industrial effluents with improved efficiencies (Aryal and Liakopoulou-Kyriakides 2015; Wang and Chen 2009).

Tables 4 and 5 list out various biosorbents used for the bioremediation of heavy metals. Several biosorbent materials have high affinity and selectivity toward heavy metals. Research studies have explored several biosorbents for their metal-binding efficiency by varying various experimental parameters. Biosorbents are alive or dead biomasses which have chemical groups on their surface for selective biosorption to occur. These biomasses are commonly bacteria, yeast, fungi, and algae obtained from activated sludge or fermented wastes. Various other fast-growing organisms, e.g., crustaceans (particularly their shells), moss, and seaweeds are also being used as biosorbents. Agricultural waste products such as tea waste, whey, exhausted coffee, straw, and defatted rice bran are also used for biosorption.

In general, biosorption efficiency of any biosorbent irrespective of its chemical nature depends upon a number of

Table 4 Effect of different experimental parameters such as pH, temperature, and contact time on heavy metal removal capacity of different microbial strains

Heavy metals	Microbes	pH	Temp (°C)	Time (h)	C_0 (mg L ⁻¹)	q_m (mg g ⁻¹)	References
Cr	<i>Bacillus sphaericus</i>	4	–	24	30	7.44	Velasquez and Dussan (2009)
	<i>Chlorella miniata</i>	4.5	–	24	100	42.8	Han et al. (2014)
	<i>Micrococcus species</i>	5	–	18	100	–	Congeevaram et al. (2007)
	<i>Bacillus thuringiensis</i> strain OSM29	7	32	0.5	25	71.94	Oves et al. (2013)
	<i>Bacillus laterosporus</i>	2.5	25	2	–	159.5	Zouboulis et al. (2004)
	<i>Bacillus licheniformis</i>	2.5	50	2	–	142.7	Zouboulis et al. (2004)
Cu	<i>Aspergillus flavus</i>	–	26	–	1400	963	Iram and Abrar (2015)
	<i>Enterobacter cloacae</i>	–	–	–	100	6.60	Iyer et al. (2005)
	<i>Bacillus thuringiensis</i> OSM29	6	32	0.5	25	39.84	Oves et al. (2013)
	<i>Micrococcus luteus</i> DE2008	6.5–7	27	12	80.24	408	Puyen et al. (2012)
Cd	<i>Enterobacter cloacae</i>	–	–	–	100	16	Iyer et al. (2005)
	<i>Bacillus thuringiensis</i> OSM29	6	32	0.5	25	59.17	Oves et al. (2013)
	<i>Bacillus laterosporus</i>	2.5	25	2	–	72.6	Zouboulis et al. (2004)
	<i>Bacillus licheniformis</i>	2.5	50	2	–	62	Zouboulis et al. (2004)
	<i>Pseudomonas sp.</i> LKS06	6	30	1	150	27.69	Huang and Liu (2013)
Pb	<i>Bacillus thuringiensis</i> strain OSM29	6	32	0.5	25	30.76	Oves et al. (2013)
	<i>Pseudomonas aeruginosa</i> ASU 6a	6	30	0.5	0–160	123	Gabr et al. (2008)
	<i>Bacillus cereus</i>	6	25	1.33	75	23.25	Çolak et al. (2011)
	<i>Bacillus pumilus</i>	6	25	1.33	75	29.57	Çolak et al. (2011)
	<i>Pseudomonas</i> LKS06	6	30	1	300	81.74	Huang and Liu (2013)
Co	<i>Enterobacter cloacae</i>	–	–	–	100	4.38	Iyer et al. (2005)
	<i>Cryptococcus humicola</i>	–	29	5	0.56	1.61	Kulakovskaya et al. (2018)
Ni	<i>Bacillus thuringiensis</i> OSM29	7	32	0.5	25	43.13	Oves et al. (2013)
	<i>Pseudomonas aeruginosa</i> ASU 6a	7	30	0.5	0–160	113.6	Gabr et al. (2008)
As	<i>Pseudomonas sp.</i> As-1	7	37	–	1.03	0.745	Patel et al. (2007)
	<i>Pseudomonas vancouverensis</i>		25	96	0.1	> 0.09	Valenzuela et al. (2009)
Hg	<i>Gracilaria corticata</i>	7	23	0.5	1.0	90%	Esmaili et al. (2015)
	<i>Sargassum glaucescens</i>	5	23	1.5	0.2	94.5%	Esmaili et al. (2015)
	<i>Yarrowia lipolytica</i> 70562	6.4	25	8	18	99.26%	Dil et al. (2017)

external factors such as the solution chemistry, i.e., its pH, metal ion concentration, and the concentration of the biomass as well as physiochemical parameters such as temperature, contact time, and the nature of the aqueous environment (Rani et al. 2010; Das et al. 2008; Abbas et al. 2014). Free or unbound microbial biomass for heavy metal adsorption was not found to be efficient enough and suffered from various cons such as low-density particle sizes, low mechanical stability, and difficulty in post-operation recovery.

Conclusions

In this review, we have reviewed most of the methods used for remediation of soils starting from conventional physical methods to recent advances in biosorption, microbial fuel cell techniques, and various other bioleaching modifications,

which are now being followed worldwide. Conventional methods being expensive and inefficient have slowly paved the way for new methods. Biosorption- and microbial fuel cells-based techniques have come up as strong contenders in recent years. Biosorption is a technique where the biomass exhibits a property like that of a chemical sorbent or ion exchanger, but of biological origin. This characteristic of adsorption and concentration of heavy metals is observed in most inactive dead biomass. Exploiting this property and enhancing it by adding with other popularly known adsorbents have made it even better over the years. The attractive features of biosorption, being its low cost, high efficiency and reusability, have made it an easy approach for remediating soils and also in helping us now to replace many conventional methods. Likewise, the new electro-troph and exoelectrogen studies have opened the gate to the use of contaminated samples for generating electricity. Many other

Table 5 Effect of different experimental parameters such as pH, temperature, and contact time on heavy metal removal capacity of different biosorbents

Heavy metals	Biosorbents	pH	Temp (°C)	Time (h)	C_0 (mg L ⁻¹)	q_m (mg g ⁻¹)	References
Cr	<i>Spirulina platensis</i> extract beads	2	24	24	100	41.2	Kwak et al. (2015)
Pb	SiO ₂ nanoparticles immobilized <i>Penicillium funiculosum</i>	5	25	0.33	20–100	262.2	Mahmoud et al. (2012)
	<i>Arthrospira platensis</i> cells immobilized in sodium alginate	4	27	1	500	424	Duda-Chodak et al. (2013)
	<i>Halomonas BVR 1</i> immobilized alginate	8–10	27	2	75	9.68	Manasi et al. (2014)
Cu	MNPs–Ca-alginate immobilized <i>P. chrysosporium</i>	5	35	8	200	176.33	Xu et al. (2012)
	Magnetic calcium alginate hydrogel beads (m-CAHBs)	2	27	6	259	159.24	Zhu et al. (2014)
As	Ca-alginate encapsulated <i>Pseudomonas alcaligenes</i>	4	37	–	1	0.465	Banerjee et al. (2016)
Hg	<i>Phoenix dactylifera</i> biomass alginate	7	35	3	100	46.73	Rajamohan et al. (2014)
Cd	<i>Chlorella</i> –biochar immobilized complex	6	26	48	100	217.41	Shen et al. (2017)
Ni	<i>E. coli</i> ATCC 29522-aided bentonite clay	5	37	24	100	58.82	Senoro et al. (2017)
Zn	Nano-Se immobilized <i>Phanerochaete chrysosporium</i>	6.5	30	96	40	13.9	Espinosa-Ortiz et al. (2016)

modifications in various aspects of conventional techniques have made heavy metal remediation a cost-effective, efficient, and recyclable technique with negligible secondary waste generation.

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest in the publication of this article.

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