REVIEW ARTICLE



Remediation techniques for removal of heavy metals from the soil contaminated through different sources: a review

Salwinder Singh Dhaliwal¹ · Jaswinder Singh² · Parminder Kaur Taneja³ · Agniva Mandal⁴

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Abstract

Heavy metal pollution is one of the serious problems and contaminates the environment by different means with the blow of industries in several countries. Different techniques like physical, chemical, and biological have been used for removal of heavy metal contaminants from the environment. Some of these have limitations such as cost, time consumption, logistical problems, and mechanical involvedness. Nowadays, in situ immobilization of metals, phytoremediation and biological techniques turned out to be best solution for elimination of metal(loid) s from the soil. Here, we reviewed the different remediation techniques for extraction of heavy metals from soil and especially highlighting in situ immobilization technique. The aim of remediation efforts at the contaminant site is to restrict the heavy metal to enter in the environment, food chain, and exposure to humans beings. The type of method used at a given site depends on the various factors like natural processes take place at the contaminated site, soil type, type of chemicals, and the depth of contaminated site.

Keywords Biological method · Contaminated soil · Heavy metals · Phytoremediation · Soil remediation technologies

Introduction

Soil is the essential environmental element which constitutes the ecosystem. Soil provides the basis for plant and animal productivity and also supports the survival and development of human being (Wang et al. 2011). One of the major environmental concerns is the contamination of soil and water by release of heavy metals through industrial and urban wastes.

Responsible editor: Elena Maestri					
	Salwinder Singh Dhaliwal dhaliwalss764@gmail.com				
	Jaswinder Singh singhjassi75@yahoo.co.in				
1	Department of Soil Science, Punjab Agricultural University, Ludhiana, Punjab, India				
2	Department of Zoology, Khalsa College Amritsar, Amritsar, Punjab, India				

- ³ Department of Soil and Water Conservation, Government of Punjab, Bathinda, Punjab, India
- ⁴ Department of Agricultural Chemistry and Soil Science, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, West Bengal, India

The word "heavy metals" mean an element having high density greater than 4–5 g/cm³ and toxic to human being even at very low concentration (Duruibe et al. 2007). Examples of heavy metals are the element present in platinum group, copper, iron, lead, arsenic, mercury, silver, chromium, zinc, and cadmium (Aziz et al. 2017; Sumiahadi and Acar 2018; Baker and Brooks 1989). The word metal(loid)s mean a chemical element that exhibit some properties of metals and some of non-metals. The introduction of metals and metal(loid)s into the environment by any method may spread to different components of the environment like soil, water bodies, plants, and animals. Even in the Arctic, heavy metals are found in water, soil sediments, and plants in varied amount (Szefer et al. 1997). The sources of heavy metal and its amount depend upon the parent rock, human activities, and physicochemical properties of soil. Understanding the origin of heavy metal and their accumulation and interaction in the soil are on priority in environmental monitoring. Among the physicochemical properties, pH and organic matter are the important parameters which play a key role in the accumulation and the availability of heavy metals in soil environment (Ramos-Miras et al. 2011).

Heavy metals are not permanently fixed by soil and sediment but they interact and distributed throughout soil and sediment components by various methods like ion exchange, adsorption, precipitation, and complexion. Due to their nondegradability, heavy metals are present in the soil for a long period of time. In the present review, the contamination of soil with heavy metals, their distribution in soil, and remedial measures are discussed.

Different sources of soil contamination with heavy metals

Heavy metals are naturally present in the parent rocks. They are also generated in the environment as byproducts by manmade activity. Soil environment becomes contaminated by heavy metals when (i) they are transfer from different mines to various environmental sites; (ii) their rates of production by man-made cycles are more faster than natural ones; (iii) the different forms of heavy metals found in the environmental system may turn into more bio-available; (iv) the concentrations of the metals and metal(loid)s in the waste products are high as compared with those in the receiving environment (Duruibe et al. 2007; Lianwen et al. 2018). Mining and manufacturing industries are the main sources of heavy metals that pollute the soil, ground water, and air. With the speeding up of urbanization and industrialization and release of different kind of exhausted gases, sewage irrigation, industrial waste, and sludge farm application are the source of heavy metal contamination (Chandrasekaran et al. 2015; Huang et al. 2016; Rezania et al. 2016; Wan et al. 2016; Karakagh et al. 2012). Expansion of industrialization leads to deterioration of the soil health by polluting river or releasing their effluents directly into the sewage system or at the periphery of the cities. The reason for heavy metal deposition in the environment is atmospheric deposition due to combustion of fuel, waste from industries like textile and dye industries, electroplating waste, cycles and spare parts, smelting and mining processes, metal coating, sewage sludge, and use of chemical fertilizers (Zeng et al. 2017). In agricultural soil, the composition of heavy metal is governed by the parent rock material, aerosol particles from fossils fuel combustion, land

Fig. 1 Flow diagram showing graphical representation of pollution caused by different sources

filling, organic material applications, and contaminants in fertilizers and other sources (Bolan et al. 2014). The following are some common causes responsible for heavy metals deposition in the environment (Fig. 1).

Pollution causes through anthropogenic sources

Both natural and anthropogenic sources cause the emission of heavy metals into the surroundings. They are naturally present in the soil by the weathering of parent rocks by pedogenic processes. Over the last few decades, the anthropogenic emissions of lead have been increased largely during mining, smelting activities, automobile exhausts, and lead paints than their natural release form parents rock (Miralles et al. 2006). Other heavy metals like cadmium is released as a waste product in lead and zinc refining; emission of mercury also occurs during degassing of the earth's crust (Sumiahadi and Acar 2018). Heavy metals come into the environment from a variety of sources in the form of atmospheric deposition from metal mines, landfills, application of fertilizer, animal manures, coal combustion, petrochemicals, and leaded gasoline.

Mining activities

The anthropogenic sources are the major causes of heavy metal emission specifically during mining operations and even the metals persist in the environment after the mining activities (Nriagu 1989). Water bodies are mostly polluted through mining activities (INECAR 2000). The emission of heavy metals occurred in the form of elemental, inorganic, and organic compounds. The potential for contamination of heavy metal is increased when mined ores are dumped in manual dressing processes (Huan et al. 2017).

Fertilizers

Firstly, human persuade on the soil through agriculture. Plants require micronutrients and macronutrients for growth and also to complete their life cycle. Metals which are necessary for



plant growth and scarce in the soil have been supplied with these elements either by foliar spray or in the soil application (Dhaliwal et al. 2009; Dhaliwal et al. 2013). A huge amount of fertilizers are added to soils during extensive and intensive farming to supply adequate amount of nitrogen, phosphorus, and potassium for crop growth (Huan et al. 2017; Dhaliwal et al. 2019). Use of certain fertilizers that contains phosphorus unconsciously adds toxic elements to the soil including F, Hg, and Pb (Duruibe et al. 2007).

Pesticides

Several pesticides used widely in horticulture and agriculture practices from the past contained extensive heavy metal concentration. Recently in the UK, 10% of the chemicals were legalized as fungicides and insecticides which contain lead, mercury, manganese, copper and zinc. Such pesticides are copper-containing fungicidal sprays such as copper oxychloride and copper sulfate (Bordeaux mixture) (Ghnaya et al. 2009; Goswami and Das 2015). For many years, lead arsenate was used to control some parasitic insects in fruit orchards. Different formulations of As, Cr, and Cu are now used to preserve timbers in many neglected sites. Such contamination in future causes problems if such sites will be used for agricultural purposes (Huang et al. 2016; Jinadasa et al. 2016).

Biosolids and manures

Biosolids are defined as organic solid produced from wastewater treatment processes that can be beneficially recycled. In most of the countries, application of bio-solid materials in agriculture land is a widespread practice that permits the reprocess of biosolids obtained from urban populations. The application of several biosolids like municipal sewage sludge, compost, and manures to land unwillingly leads to the addition of heavy metals in the soil environment (Ghnaya et al. 2009). Manure is considered to be an important fertilizer, but in pig poultry, Cu and Zn are added to the diets as growth promoters but cause health problem. (Lianwen et al. 2018).It is estimated that in the USA, more than half of 5.6 million tons of sewage sludge is applied annually to land for agricultural utilization (Goswami and Das 2015).

Pollution caused through atmospheric deposition

Industrial activities such as burning of coal and petroleum have intensive mark in soils regarding heavy metals. Over time, the release of heavy metals exceeds natural levels which include nickel, zinc, lead, and copper (Boyd 2004). Pollution due to atmospheric activities has been recognized as a potential threat to many lives in the industrial regions of the northern hemisphere (Shotyk et al. 2003). Lead and boron are another universal tracers of anthropogenic contaminant in the environment and health care (Mielke et al. 2005). The main source of lead emissions contains power-generating plants, smelting units, emissions from auto-mobiles and natural sources include volcanoes, hydrothermal vents etc. (Weiqing et al. 2016). Boron, is a quite variable trace constituent in the atmosphere (conc. between 0.2 and 300 ppb) and present in gaseous as well as particulate matter with the gaseous phase more than 90–95% of the total content (Rose et al. 2000; Rose-Kaga et al. 2006).

During high-temperature processing, metals such as arsenic, lead, and cadmium are released in the form of volatile particles. These elements were converted to fine particulates in the form of oxides (Duruibe et al. 2007). Stack emissions can be scattered over a wide area by wind until dry or wet precipitation procedure remove them from the gaseous stream. Fugitive emissions are generally scattered in smaller area because emissions are carried out near the ground level. Types of sources and site-specific conditions influence concentration of metals emitted. It has been noticed that plants and soils close to smelting works possess high concentration of Zn, Cd, and Pb. Combustion of petrol also leads to the aerial emission of Pb and responsible for the presence of Pb in soils of urban areas and adjoining sites. Tyre and lubricant oil industry also added Zn and Cd in the soil (Huang et al. 2016; Jinadasa et al. 2016).

Effects of polluted water on soil contamination

Wastewater irrigation has been established to decreases soil pH and increase organic carbon content and soil conductivity but causes heavy metals accumulation in the plowing layer of farmland (Aulakh and Singh 2008). Increased concentrations of toxic metals have been studied in soils with regular application of wastewater sewage sludge (Azad et al. 1986; Sharma and Dhaliwal 2019). Significantly higher concentrations of Pb, Cr, Cd, and Ni extractable with DTPA and total digestable that have been reported in land irrigated with wastewater were 1.8, 35.5, 3.6, and 14.3 respectively as compared with well-irrigated soils with pipes (Dheri et al. 2007). The toxic effects of heavy metals on living organisms are summarized in Table 1.

Remediation of contaminated soil with heavy metals

Heavy metals are converted into different forms and its availability in the soil decreases with time (Lund et al. 1980). The sequential extraction technique to remove metals from the soil/ground in different ways is useful to understand the process of movement and bioavailability of the metal. The interchangeable and water-soluble forms of metals are considered to be available for plants. These heavy metal forms must be Table 1Toxic effects of someheavy metals on human health(EPA: United StateEnvironmental ProtectionAgency)

Heavy metals	EPA (regulatory limits ppm)	Toxic effects
Ag	0.10	Exposure may cause skin and other body tissues to turn gray or blue-gray, breathing problems, lung and throat irritation, and stomach pain
As	0.10	Affects essential cellular processes such as oxidative phosphorylation and ATP synthesis
Ba	2.00	Cause cardiac arrhythmias, respiratory failure, gastrointestinal dysfunction, muscle twitching, and elevated blood pressure
Cd	5.00	Dysfunction, muscle twitching, and elevated blood pressure, carcinogenic, mutagenic, endocrine disruptor, lung damage, and fragile bones, affects calcium regulation in biological systems
Cr	0.10	Hair loss
Cu	1.30	Brain and kidney damage, elevated levels result in liver cirrhosis, and chronic anemia, stomach and intestine irritation
Hg	2.00	Autoimmune diseases, depression, drowsiness, fatigue, hair loss, insomnia, loss of memory, restlessness, disturbance of vision, tremors, temper outbursts, brain damage, lung and kidney failure
Ni	0.20	Allergic skin diseases such as itching, cancer of the lungs, nose, sinuses, throat through continuous inhalation, immunotoxic, neurotoxic, genotoxic, affects fertility, hair loss
Pb	15.00	Excess exposure in children causes impaired development, reduced intelligence, short-term memory loss, disabilities in learning and coordination problems, risk of cardiovas- cular disease
Se	50.00	Dietary exposure of around 300 µg day ⁻¹ affects endocrine function, impairment of natural killer cells activity, hepatotoxicity, and gastrointestinal disturbances
Zn	0.50	Dizziness, fatigue etc.

Source: Dixit et al. 2015

remediated from the soil due to their environment toxicity (Petruzzelli 1989). Some of the European countries are investing a lot to remediate contaminated land. There are some laws and regulations, such as the Resource Conservation and Recovery Act (RCRA) and the superfund amendments and the Reauthorization Act (SARA), that focused on standard and behavior of techniques related to remediation. The UK also approved the Environmental Protection Act in the 1990s which clearly established the polluter's responsibility principle (Kim et al. 2001).

Here, we discuss different methods of remediation of soil which include physical, chemical, and biological processes. The pros and cons of these remediation technologies are given in Table 2.

Physical remediation

The remediation methodologies via physical techniques include washing of soil, soil extraction, soil solidification, and soil stabilization of heavy metals. Physical method for migrating contaminated land and disposal in landfills is quite expensive. It also includes the method of replacement of soil and thermal desorption. Substitution of soil means to replace or partially replace the contaminated soil with clean soil to reduce the concentration of pollutants (Qian and Liu 2000; Zhang et al. 2004) of particular area.

Zhou et al. (2004) divided this method into three types: soil substitution, sweeping of soil, and the importation of land from uncontaminated sites; (1) the substitution of the soil involves removal of contaminated soil and putting it in another soil. The above-mentioned technique is very suitable for land in small area with contamination. In addition, the replaced soil must be treated in a feasible ways failing which the second contamination will occur; (2) the excavation of the soil is the deep excavation of contaminated soil, which causes the spread of the contaminant in the deep sites and reaches the goal of dilution and natural degradation; (3) the importation of new land consists of adding a large amount of pure soil in place of the contaminated soil. In some aspects, soil substitution reduces the effect of

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Table 2 Pros and cons of different remediation techniques and their proce	edure
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S. no.	Remediation		Procedure	Pros	Cons
1.	Physical remediation		Techniques include washing of soil, thermal desorption, and replace or partially replace the contaminated soil with clean soil to reduce the concentration	Complete amelioration of heavy metals through removal of contaminated layer of soil	It is a laborious, time consuming, and not economically viable method
2.	Chemical remediation	Vitrify technology	Temperature of the soil increases at a high range of 1400–2000 °C. Energy can be supplied by burning fossil fuels or by heating directly using microwave, electrodes, and plasma.	Removal of contaminants through weathering of organic matter by maintaining high temperature directly in the soil. Highly efficient method of amelioration of contaminated soil by eliminating heavy metals	This technology is very complicated, requires more energy of fusion, expensive, and limited application
		Chemical leaching	Washing of contaminated soil with water, chemical, reagents and other fluids or gases capable of eliminating the contaminant from the soil. Heavy metals in the soil were transferred to the liquid phase through precipitation, ion exchange, abalation and adoptition	Heavy metals are leached down from the upper layer facilitating plants to grow favorably	Not the permanent solution for deep rooted crops
		Chemical fixation	The addition of reagents or materials into the contaminated soil to form slightly insoluble materials.	Heavy metals fixed in the soil through adsorption, resulting least availability becomes for growing plants	Not permanent solution because the heavy metals get released into the soil under conducive conditions for weathering
		Electro kinetic method	High voltage is applied to create electric field gradient at the two sides. In this process, charged pollutants were moved to poles through electro-migration, electro-osmotic flow, and elec- trophorasis process.	Beneficial for low permeability soils with low cost and easy installation	Low efficiency, unable to control pH, unable to use ion exchange membrane to improve migration
3.	Biological remediation	Using microorganism	Microorganisms transform heavy metals via changing their physical and chemical properties. It includes extracellular complexation, intracellular accumulation, and precipitation or oxidation-reduction process.	Microbial leaching is simple and effective for extracting metals from low-grade minerals.	Provide suitable condition for their growth some time laborious
		Phytoremediation	It involves the treatment of contaminated area with specific plants to eliminate pollutants by the breaking of contaminant by roots of plants to lesser toxic element or absorption of contaminant, storing it in the stems and leaves of the plant.	Plants tolerate high concentrations of metals in root, stem, and leaves.	Difficulty in the selection of plants for particular type of metals for remediation process.

contaminants on the environment. However, this technology needs a lot of work, costs a lot, and is suitable in small areas which are severely contaminated. The thermal desorption is carried out on the basis of volatility of pollutant particles which includes heating of the contaminated soil using steam, microwave, infrared radiation to convert the pollutant into volatile form. To achieve the aim of removing the heavy metals, the volatile heavy metals are collected by using the vacuum-negative pressure or carrier gas. Based on different temperatures, the thermal desorption occurs at high-temperature desorption (320-560 °C) and low-temperature desorption (90-320 °C). The USA used this technology for mercury collection on-site repair and developed commercial services. However, limited factors like high-cost devices and prolonged desorption time limit the application of these device in remediation of soil (Huan et al. 2017; Lianwen et al. 2018).

Remediation by chemical methods

The amount of heavy metal available to the plants can be reduced by the chemical methods. This can be achieved by one of method, i.e., changing the pH of the soil, which caused either precipitation of metal or formation of insoluble complexes with metals. The chemical remediation involves:

Using vitrify technology

The vitrification technology involves increase in temperature of the soil at a high-temperature range of 1400–2000 °C, which results into the decomposition or volatilization of organic matter. In this method, steam is produced and the pyrolysis product has been collected from an exhaust gas produced by the treatment system. For ex situ reclamation, energy can be supplied by burning fossil fuels or by heating directly using microwave, electrodes, and plasma. Electrodes can be inserted directly in contaminated soil during in situ remediation for direct application of heat. This technology has high efficiency and can eliminate heavy metals. However, this technology is very complicated and requires more energy for fusion, which makes it very expensive with limited application (Duruibe et al. 2007; Ghnaya et al. 2009; Goswami and Das 2015).

Remediation by chemical leaching

Chemical leaching is the technique used for washing of contaminated soil with water, chemical reagents, and other fluids or gases capable of eliminating the contaminant from the soil (Yang et al. 2010). Heavy metals in the soil were transferred to the liquid phase through precipitation, ion exchange, chelation, and adsorption and later estimated from the infiltrate. The infiltrate includes predominantly surfactant, inorganic fluent, and chelating agents. Tokunaga and Hakuta (2002) extracted metals from the artificially contaminated soil at different concentrations of nitric acid, hydrofluoric acid, sulfuric acid, phosphoric acid, and hydrochloric acid were evaluated as extractant for removing contaminants from the soil.

Through chemical fixation

Chemical fixation includes the addition of reagents or materials into the contaminated soil to form slightly insoluble materials, which reduces the movement of heavy metals into water bodies, plants, and other environmental media causing soil remediation (Huang et al. 2016; Jinadasa et al. 2016; Huan et al. 2017). Therefore, chemical fixation results in stabilization than decontamination, which includes transference of metal into an inactive form. Hodson et al. (2000) and Bilgin and Tulun (2016) evaluated the capacity of finely grounded, slightly crystalline apatite bone meal (Ca₁₀(PO₄).6H₂O) to immobilize metals in the form of metal phosphates and reduce the metal bioavailability in polluted soil.

By electrokinetic remediation

Electrokinetic remediation technology is one in which very high voltage is applied to create electric field gradient at the two sides (Luo et al. 2004). In this process, charged pollutants were moved to poles through electro-migration, electroosmotic flow, and electrophoresis process (Swartzbaugh et al. 1990). This method is beneficial for soil having low permeability, has advantages of low cost, and easily installation and operation (Virkutyte et al. 2002; Xu et al. 2006) while retaining original composition of soil (Zhang et al. 2004) and protect the ecotype (Luo et al. 2004). However, the treatment efficiency was low because this technology unable to control the soil pH (Fasani et al. 2017). The recent methods include addition of buffer solution to control soil pH or use of ion exchange membrane which controls the soil pH to improve migration.

Biological remediation

Bioremediation using microorganism (bacteria and Fungi) and phytoremediation (plant species) are major biological remedial techniques that includes former or later or combination of both the processes. These processes include method used by microorganisms or plants (Chang et al. 2008). Bioremediation using microorganism and plants is discussed under the following heads:

Biological remediation using bacteria

Microorganisms do not degrade the heavy metals but transform these metals via changing their physical and chemical properties (Table 3). Remediation mechanism includes extracellular complexation, intracellular accumulation, and precipitation or oxidation-reduction process. Galal et al. (2017) studied that microbial leaching is simple and effective for

Table 3 List of microorganisms used in biological remediation of soil contaminated with heavy metals

Heavy metals	Microorganisms	References	
	Bacteria	Fungi	
РЬ	Micrococcus luteus, Bacillus subtilis, B. firmus, B. megaterium, Aspergillus niger, and Penicillium species, Brevibacterium iodinium, Pseudomonas spp., Staphylococcus spp., Streptomyces spp.,	Candida sphaerica	Kumaran et al. 2011; De et al. 2008; Kumar et al. 2011; Puyen et al. 2012; Abioye et al. 2018; Luna et al. 2016
Cd	Pseudomonas aeruginosa, Alcaligenes faecalis, Bacillus subtilis, B. megaterium	Coprinosis atramentaria	De et al. 2008; Puyen et al. 2012; Lakkireddy and Kues 2017
Cu	Bacteria: Staphylococcus sp., Streptomyces sp., Enterobacter cloacae, Desulfovibrio desulfuricans (immobilize on zeolite), Flavobacterium spp., Methylobacterium organophilum, Arthrobacter strain, Enterobacter cloaceae, Micrococcus sp., Gemella spp., Micrococcus spp., Pseudomonas sp., Flavobacterium spp., A. faecalis (GP06), Pseudomonas aeruginosa (CH07)	Aspergillus versicolor, Aspergillu sniger (pre-treated with Na ₂ CO ₃ (0.2N)), Sphaerotilus natans, Aspergillus niger, Candida spp.	Abioye et al. 2018; Jafari et al. 2015; Kim et al. 2015; Kim et al. 1996; Roane and Pepper 2000; Marzan et al. 2017; Kumaran et al. 2011; De et al. 2008; Tastan et al. 2010; Javaid et al. 2011; Ashokkumar et al. 2017; Donmez and Aksu 2001
Ni	Micrococcus sp., Pseudomonas spp., Acinetobacter sp. Desulfovibrio desulfuricans (immobilize on zeolite)	Aspergillus versicolor, Aspergillus spp., Aspergillus niger (pre-treated with Na ₂ CO ₃ (0.2N), Aspergillus niger, Candida spp.	Congeevaram et al. 2007; Kumaran et al. 2011; Tastan et al. 2010; Javaid et al. 2011; Kim et al. 2015; Donmez and Aksu 2001
Hg	Klebsiella pneumoniae, Pseudomonas aeruginosa, Vibrio parahaemolyticus (PG02), Bacillus licheniformis, Vibrio fluvialis	Candida parapsilosis	Al-Garni et al. 2010; Jafari et al. 2015; Muneer et al. 2013, Saranya et al. 2017
Cr	Bacillus cereus, Acinetobacter spp. and Arthrobacter sp.	Aspergillus niger, Rhizopus oryzae, Saccharomyces cerevisiae, Penicillium chrysogenum, Aspergillus versicolor, Sphaerotilus natans, Saccharomyces cerevisiae, Phanerochaete chrysosporium, Hansenula polymorpha, S. cerevisiae, Yarrowiali polytica, Rhodotorula pilimanae, Pichiaguillier mondii, and Rhodotorula mucilage	Singh et al. 2013; De et al. 2008; Tastan et al. 2010; Achal et al. 2011; Ashokkumar et al. 2017; Parvathi et al. 2007; Chatterjee et al. 2012; Ksheminska et al. 2008
Zn	Bacillus firmus, Pseudomonas spp.	-	Salehizadeh and Shojaosadati 2003; Kumaran et al. 2011
Со	Enterobacter cloacae		Jafari et al. 2015

extracting metals from low-grade minerals. Microorganism also has the potential for the detoxification of sewage sludge, industrial waste, and the remediation of sediments and soils contaminated with heavy metals (Bosecker 2001).

Microbial biomass has different bio-sorptive abilities and varies significantly among microbes. However, the biosorption ability of each microbial cell depends on its pretreatment and the experimental conditions. Bacteria are important biosorbents due to their ubiquity, size, and ability to grow under controlled conditions and resilience to environmental conditions (Srivastava et al. 2015; Wang and Chen 2009). De et al. (2008) used mercury resistant bacteria such as *Alcaligenes faecalis, Bacillus pumilus, Pseudomonas aeruginosa*, and *Brevibacterium iodinium* for the removal of cadmium (Cd) and lead (Pb). In this study, *P. aeruginosa* and *A. faecalis* removed 70% and 75% Cd with reduction of 1000 mg/L to 17.4 mg/L of Cd by *P. aeruginosa* and to 19.2 mg/ L by *A. faecalis* in about 72 h. *Brevibacterium iodinium* and *Bacillus pumilus* remove greater than 87% and 88% of Pb with a reduction of 1000 to 1.8 mg/L in 96 h.

The use of indigenous facultative anaerobic bacteria *Bacillus cereus* to detoxify hexavalent chromium (Cr) was studied by (Singh et al. 2013). *Bacillus cereus* has an excellent capacity of 72% Cr (VI) removal at 1000 g/mL chromate concentration. The bacteria were capable of reducing Cr (VI) under a wide range of temperatures (25 to 40 °C) and pH (6 to 10) but optimum at 37 °C and initial pH 8.0. Several heavy metals have been tested using bacteria species like *Flavobacterium, Pseudomonas, Enterobacter, Bacillus*, and *Micrococcus* spp. Their great bio-sorption ability is due to

high surface-to-volume ratios and the potential active chemosorption sites (teichoic acid) on the cell wall (Mosa et al. 2016). Bacteria are more stable and survive better when they are in mixed culture. Therefore, consortia of cultures are metabolically superior for bio-sorption of metals and are more appropriate for field application (Kader et al. 2007). De et al. (2008) reported 78% reduction of Cr using bacteria consortium of Acinetobacter spp. and Arthrobacter spp. of 16 mg/L metal ion concentration. Micrococcus luteus was used to remove a huge quantity of Pb from a synthetic medium. Under ideal environments, the elimination ability was 1965 mg/g (Puyen et al. 2012). Abiove et al. (2018) investigated the bio-sorption of Pb, Cr, and Cd in tannery effluent using Bacillus subtilis, B. megaterium, Aspergillus niger, and Penicillium spp. B. megaterium recorded the highest Pb reduction (2.13 to 0.03 mg/L), followed by B. subtilis (2.13-0.04 mg/L). A. niger show the highest ability to reduce the concentration of Cr (1.38-0.08 mg/L) followed by Penicillium sp. (1.38-0.13 mg/L) while B. subtilis exhibited the highest ability to reduce the concentration of cadmium (Cd) (0.4-0.03 mg/L) followed by B. megaterium (0.04-0.06 mg/L) after 20 days. Kim et al. (2015) designed a batch system using zeolite-immobilized Desulfovibrio desulfuricans for the removal of Cr (VI), Cu, and Ni with removal efficiency of 99.8%, 98.2%, and 90.1%, respectively. Ashruta et al. (2014) reported efficient removal of Cr, Zn, Cd, Pb, Cu, and Co by bacterial consortia at approximately 75 to 85% in less than 2 h of contact duration.

Biological remediation using fungi

Fungi are widely used as biosorbents for the removal of toxic metals with excellent capacities for metal uptake and recovery (Fu et al. 2012; Akar et al. 2005; Dursun et al. 2003). Most studies showed that active and lifeless fungal cells play a significant role in the adhesion of inorganic chemicals (Tiwari et al. 2013). Srivastava and Thakur (2006) also reported the efficiency of Aspergillus sp. used for the removal of Cr in tannery waste water. A total of 85% of Cr was removed at pH 6 in a bioreactor system from the synthetic medium, compared with a 65% removal from the tannery effluent. This could be due to the presence of organic pollutants that hinder the growth of the organism. Coprinopsis atramentaria was studied for its ability to bio-accumulate 76% of Cd^{2+} , at a concentration of 1 mg/L of Cd^{2+} , and 94.7% of Pb^{2+} at a concentration of 800 mg/L of Pb²⁺. Therefore, it has been documented as an effective accumulator of heavy metal ions for myco-remediation (Lakkireddy and Kues 2017). Park et al. (2005) reported that dead fungal biomass of Aspergillus niger, Rhizopus oryzae, Saccharomyces cerevisiae, and Penicillium chrysogenum could be used to convert toxic Cr (VI) to less toxic or non-toxic Cr (III). Luna et al. (2016) also observed that Candida sphaerica produces bio-surfactants with a removal efficiency of 95, 90, and 79% for Zn and Pb, respectively. These surfactants could form complexes with metal ions and interact directly with heavy metals before detachment from the soil. *Candida* spp. accumulate substantial quantity of Ni and Cu, but the process was affected by initial metal ion concentration and pH (optimum 3–5) (Donmez and Aksu 2001). Several strains of yeast such as *Hansenula polymorpha*, *S. cerevisiae*, *Yarrowia lipolytica*, *Rhodotorula pilimanae*, *Pichia guilliermondii*, and *Rhodotorulamucilage* have been used to bio-convert Cr (VI) to Cr (III) (Chatterjee et al. 2012; Ksheminska et al. 2006, 2008).

Phytoremediation of soils contaminated with heavy metals using plant species

Phytoremediation involves a group of techniques to immobilize, degrade, and reduce the environmental toxins caused by anthropogenic sources using different plant species to cleanup contaminated areas (Mukhopadhyay and Maiti 2010). It involves different types of phytoremediation processes by use of typical plants to remove metal from contaminated sites (Table 4). Various studies reported that metals' bioavailability and their uptake by plants could be accomplished by addition of chelating agents, fertilizer, organic amendment, and ameliorating pH. Nowadays, the phytoremediation has received great attention for the remediation of contaminated soil (Huang et al. 2016). Phytoremediation involves the process for treating contaminated area with plants to eliminate pollutants. The basic principle of phytoremediation involves the breaking of contaminant by roots of plants to lesser toxic element or absorption of contaminant, storing it in the stems and leaves of the plant (Kaur et al. 2018). Therefore, it is supposed to be an alternative process to eliminate or, more precisely, reduce the amount of toxic pollutants in the environment (Yadav and Srivastava 2014). Several plant species showed the ability to accumulate high levels of heavy metals and are called hyper-accumulators (Memon et al. 2001; McGrath et al. 2001; Memon and Schroder 2009). These plants tolerate high concentrations of metals and had a spectacular ability to absorb metal of great importance for the phyto-extraction. For phyto-extraction, a plant must be a hyper-accumulator, with high growth rate and a potential to produce more biomass that can produce more than 20 t of biomass/ha/year (Huang et al. 1997; Yadav and Srivastava 2014). The ability of plants to absorb heavy metals (50–500 times) more than normal plants led to the revolutionary progress of phyto-extraction technology (Baker and Brooks 1989) and it may be possible through the genetic engineering to transfer of hyper-accumulator genes from plants having low biomass to plants with high biomass such as Brassica species (Cunningham and Ow 1996). About 400 hyper-accumulator plants were known (less than 0.2% of all angiosperms) and mainly belong to Asteraceae, Euphorbiaceae, Fabaceae,

Table 4List of several plantsreported for heavy metalsremediation

Plants	Contaminated area	Heavy metals
Allium schoenoprasum L. (Chive)	Soil	Ni, Co, Cd
Brassica juncea (L.) Coss (Indian mustard)	Soil and water	Cd, Cu, Zn, Pb
Brassica napus L. (Canola)	Soil	Cd, Cu, Zn, Pb
Cajanus cajan (L.) Millsp. (Pigeon pea)	Soil	As, Cd
Cicer arietinum L. (Chickpea)	Soil	Cd, Pb, Cr, Cu
Cucumis sativus L. (Cucumber)	Water	Pb
Eichhornia crassipes (Mart.) Solms (Water hyacinth)	Water	As, Cr, Zn, Cs, Co
Jatropha curcas L. (Purging nut)	Soil	Fe, Al, Cu, Mn, Cr, As
Lantana camara L. (Lantana)	Soil	Zn, Hg, Pb
Lens culinaris Medik. (Lentil)	Soil	Pb
Lepidium sativum L. (Cress)	Soil	As, Cd, Fe, Pb, Hg
Lactuca sativa L. (Lettuce)	Soil	Cu, Fe, Mn, Zn, Ni, Cd,
Medicago sativa L. (Alfalfa)	Soil	Pb, Co, As, Cd
Oryza sativa L. (Rice)	Soil	Cu, Cd
Pistia stratiotes L. (Water lettuce)	Water	Cr, Cd, As
Pisum sativum L. (Pea)	Soil	Pb, Cu, Zn, Fe, Cd, Ni,
Raphanus sativus L. (Radish)	Soil	Cr.As, Cd, Fe, Pb, Cu
Spinacia oleracea L. (Spinach)	Soil	Cd, Cu, Fe, Ni, Pb, Zn,
Solanum nigrum L. (Black nightshade)	Soil	Cr, Cd
Sorghum bicolor (L.) Moench (Sorghum)	Soil	Cd, Cu, Zn, Fe
Zea mays L. (Corn)	Soil	Cd, Pb, Zn, Cu

Source: Sumiahadi and Acar (2018)

Flacourtaceae, Brassicaceae, Caryophyllaceae, Lamiaceae, Poaceae, and Violaceae. The selection of the plant is also based on the availability of seeds, their ability to set up and grow in the contaminated soil, and to extract metal from the soil to the root biomass of the plant. Several studies have described the potential of plant as a heavy metal bioaccumulation from soil and water. Studies have shown that the use of plants through phytoremediation technology is an alternative to treating the areas which are contaminated by heavy metals and can also be used for environmental remediation solution (Bolan et al. 2014; Prasad 2003).

Even different plants have different responses to different exposures to heavy metals. Some plants are sensitive, while others have a high tolerance towards heavy metals. As a consequence of the plant-metal interaction, different plants accumulate heavy metals from the soil which reduce their growth and development. However, some plants have a high tolerance and can support growth and development under stress of heavy metals (Huan et al. 2017; Lianwen et al. 2018).

In a study, Garbisu and Alkorta (2003) reported that although most of the metals are important for biological systems and must be present within certain range but in high concentrations, these act in a harmful way by blocking or displacing the essential functional groups and molecules (Collins and Stotzky 1989). Various studies have reported that many plants, including the Brassicaseae family, e.g., *Brassica napus*, have different tolerable limit for heavy metal toxicity and show accumulation with various magnitudes (Marchiol et al. 2004; Simnova et al. 2007; Tickoo et al. 2007; Angelova et al. 2008; Bauddh and Singh 2009).

Here, we discuss some research conducted in phytoremedial technology which is effectively used for the heavy metals removal from contaminated soils.

A recent study was carried out to determine the potential of Brassica rapa plant species under the influence of electric field that can germinate and grow in mixed contaminated soil with PAH and various metals viz. Cd, Cr, and Pb (Cameselle and Gouveia 2019). It was observed that alternating current was the most suitable for commercial applications. The application of 1 Volt/cm potential gradient around B. rapa resulted in the effective elimination of compounds like phenanthrene andanthracene. The results of study revealed that different configurations of electrodes around the growing plants can be used to concentrate the contaminants or transport them from deep soil layers to the rhizosphere. Another experiment was conducted by Bello et al. (2018) to investigate the phytoremediation ability of Phragmites australis to remove nickel (Ni), cadmium (Cd), and lead (Pb) from contaminated water over a period of 6 weeks. The results showed that P. australis had a residual of 7% of Cd (93% removal), 5% of Pb (95% removal), and 16% of Ni (84% removal). While in the controlled experiment, there was a residual of 96% for

both Cd and Pb (4% removal) and 89% for Ni (11% removal). In another study, Lemna minor has higher potential for accumulation of Fe, Mn, Zn, and Co (Amare et al. 2017). On the other hand, Azolla filiculoides have high accumulation potential for Fe, Mn, Zn, and Cu, but moderate for Co, Cr, and Ni and even lower for Cd. Another study conducted by Goswami and Das (2015) revealed the phytoremediation ability of Brassica juncea (Indian mustard) treated with different concentrations of 25, 50, 100, 200, and 400 mg kg⁻¹ of CdCl₂ in the laboratory for 21 days. The results showed that plant has high tolerance to Cd up to 400 mg/kg, but there was decrease in tissue biomass, leaf chlorophyll, root and shoot length, and carotenoid content. The enrichment coefficient and the bud root translocation factor indicated the suitability of Indian mustard to remove the Cd from the contaminated soil. Yadav and Srivastava (2014) explained the mechanism of hyperaccumulation of members of the Brassicaseae family, in particular Brassica spp. A higher tolerance to cadmium ions has been identified on the basis of the absorption and efficient assimilation of sulfate. However, Bhadkariya et al. (2014) conducted a study on Brassica juncea plant and observed a strong a tolerance and build-up capacity for cadmium in Brassica juncea. The distribution of Cd in Brassica juncea was in the order of root > stem > leaves. The highest accumulative of Cd was 89.90 mg kg⁻¹in the whole plant during 60 days of development period. Therefore, Brassica juncea has proven to be an efficient accumulator for cadmium for phyto-extraction from cadmium-contaminated soil. Another study by Priva et al. (2014) reported the treatment of wastewater using two common plants Brassica juncea (mustard) and Allium cepa (onion plant). The standard cadmium content ranged from 0.017 to 0.009 and 0.0088 μ g L⁻¹ for *Brassica* juncea and from 0.023 to 0.012 and 0.009 µg/L for Allium cepa. A relative analysis of the wastewater treatment collected at two different locations in Jaipur has been explained on this result, using two different plants from the phytoremediation mechanism. The conclusion obtained that waste water discharge from industrial area of Sanganer and Jaipur must be used efficiently for the farming of mustard plant. Taamalli et al. (2014) evaluated he phyto-extraction potential of Cakile maritime (halophyte) and compared with Brassica juncea (glycophyte) which was recommended for phytoextraction of Cd. The results showed that translocation factor was higher in the case of Cakile maritime as compared with Brassica juncea at all external Cd doses. Two oil yielding plants namely Brassica juncea and Ricinus communis were also experimented for their tolerance and phyto-remedial potential of cadmium in contaminated soil by Bauddh and Singh (2012). In this study, the plants were exposed to different concentrations of Cd in soil and observed that Ricinus communis accumulated about two times higher Cd in shoots and four times higher in roots than Brassica juncea. The total elimination of metal from soil was greater in the case of Ricinus communis due to the more underground and aboveground biomass and suggesting that Ricinus communis has a better tolerance and phyto-reclamation potential to remove metal from contaminated soil. Moosavi et al. (2012) selected two oil crops and one cereal crop Safflower, Brassica napus, and wheat respectively to test its phyto-corrective potential. Result showed that percentage of seed germination, root and shoot length decreased with increasing concentration in the solution. Germination at 1000 mg/kg of cadmium level was not observed. The vigor of roots and seedlings is increased with the application of 200 mg kg^{-1} of BiNO₃. Park et al. (2012) examined the viability of the oil extracted from the seeds of Brassica napus plants in the contaminated areas. The results of the oil analysis of seed showed that almost 50% of the heavy metal remains in the waste. The phytorepair potential of halophytes like Atriplex halimus and Sesuvium portulacastrum will be a better alternative to saltsensitive plants for the remediation of contaminated soils (Moustakes et al. 2011)

The capacity of Brassica juncea (L.) and several other plant species was evaluated by Ishikawa et al. (2006). The results indicated that Brassica juncea was less able to accumulate Cd in sprouts than the hydroponic grown rice and sugar beet, and was also less effective when grown in soil cultivation. Rice and beet showed increased accumulation of not only Cd but also other heavy metals (Cu, Fe, Mn, and Zn) in their Brassica juncea buds when grown in two soils contaminated with Cd. Sequential ground extraction of Cd revealed that the rice was more effective than Brassica juncea in phyto-extraction of Cd. It has been suggested that Brassica juncea is less effective for Cd phyto-extraction from soil than rice at very low concentration of metal in the contaminated soil. Cadmium application also inhibited various growth and biochemical parameters in seedlings of five cultivars of Brassica juncea L. (Bauddh and Singh 2009).

The growth of plants, pigment concentration, biochemicals, and absorption of heavy metals in Brassica juncea L. in response to lead and cadmium stress were studied by John et al. (2009). The plant showed a decrease in growth, chlorophyll content, and carotenoids with Cd and Pb, but Cd showed more harmful effect than Pb. Protein content was decreased during the flowering phase to 95% and 44% during the treatment of Cd and Pb respectively. Proline content increased at low concentrations of Cd and Pb, but decreases at higher concentrations. It was found that the Cd accumulated more than Pb, but the absorption of Cd hindered at higher concentrations of Pb. Watanabe et al. (2009) selected three Caryophyllales species and cultivated under Cd treatment. Amaranthus tricolor proved to have high Cd storage capacity both in water and soil culture as compared with Brassica juncea. The result suggested that A. tricolor has better accumulating ability for Cd in the rhizosphere in lieu to high growth and biomass. Therefore, A. tricolor could be useful for phytoextraction of the cadmium-contaminated fields. In an experiment, Tickoo et al. (2007) evaluated the ability of Indian mustard for accumulation of cadmium and nickel with controlled conditions. For this, soils were falsely contaminated with different concentrations of cadmium acetate and nickel sulfate with control. Results reported higher accumulation of higher amount of heavy metals in shoot as compared with roots and was also observed that Brassica juncea accumulate cadmium better when compared with Nickel. Marchiol et al. (2004) evaluated phyto-extraction potential of Brassica napus (canola) and Raphanus sativa (radish) grown on contaminated soils with different metals. Radish has low phyto-remedial potential for multi-metal soils. Several Brassica species found to exhibit moderate accumulation of zinc and cadmium. Selected B. juncea, B. napus L., and B. rapa were grown in pots with contaminated soil to compare their phyto-extraction potential with Thlaspi caerulescens.

Remediation of heavy metals from contaminated soil using chelates and plant species

Phyto-extraction (phyto accumulation, phyto absorption, or phyto sequestration) is extracting soil or water contaminants from plant roots. However, the chelating agents helped in increasing the metal storage properties of plants and used to decontaminate the soil contaminated with metals. By formation of aqueous soluble metal complexes with the chelating agent, the solubility of the heavy metals increases. Therefore, metal can be extracted or desorbed from the different soil components or their surfaces which determines the degree of solubility of heavy metal with organic agents in the order of their constant metal stability (Garbisu and Alkorta 2003; Halim et al. 2003; McIntyre 2003; Ghosh and Singh 2005; Yang et al. 2005; Kotrba et al. 2009). Chelating agents such as synthetic ethylene diammine tetra acetic acid (EDTA) are studied for extracting metals from soils and sediments. It is believed that extraction with EDTA is effective in removing organic metals from soils. Furthermore, it is unlikely that the metals which are not released by washing with EDTA will be mobilized by natural processes and, therefore, may have little environmental significance. This phenomenon has been expanding due to its cost effectiveness as compared with other methods and also revealed a great prospective (Lianwen et al. 2018; Sumiahadi and Acar 2018).

Farid et al. (2015) observed a environment friendly technique in combination with a chelator EDTA during his laboratory experiment for soil cleaning that are contaminated by heavy metals under three concentration of Cd, i.e., 0, 10, and 50 μ M along with two concentrations 0 and 2.5 mM of EDTA. The presence of cadmium caused lowering in biomass and chlorophyll concentrations along with plant

growth while the application of EDTA improved the growth of plant by lowering the effects of cadmium. Further, the results proved that the chelating techniques can be used for the removal of heavy metal from contaminated soil in agricultural and industry. In another experiment conducted by Suthar et al. (2013) to explore natural and chemically induced phyto-extraction caused by Pb and Cd in spinach and mustards after applying EDTA. The addition of EDTA significantly increased the phyto-extraction rate of Pb and Cd concentrations in the plant shoots. Mustard showed better than spinach when extracting Pb and Cd from both contaminated soils. Results of study showed the effect of different concentrations of Cd, Cr, and Pb and EDTA application in two Brassica species, i.e., Brassica carinata and Brassica juncea. The application of EDTA had a significant effect on the fresh and dry weight of the plant bud, length of the root, fresh and dry root weight, and the accumulation of heavy metals on the ground (Iqbal et al. 2012). Heavy metals and EDTA exposure to Brassica species result in newly and abundantly synthesized polypeptides, which may play role in phytoremediation.

Turan and Esringu (2007) investigated the capacity of *Brassica napus* (canola) and *Brassica juncea* (Indian mustard) to uptake cadmium in a growth chambers. Results showed that application of EDTA increased cadmium availability and uptake by fourfolds in canola and 3.5-folds in Indian mustard when compared with control. Wu et al. (2004) also reported that EDTA has amplified shoot concentration of Cu and Pb in Indian mustard (*Brassica juncea*). The results further reported that addition of oxalic acid, malic acid, or citric acid to soil in similar amount had virtually given no results.

Singh et al. (1998) characterized the surface soils near some disposal sites in Belgium for total metal contents and various fractions. Residual fractions were low compared with total contents and various fractions. Residual fractions were low compared with total content (2–4% for Cd, 25–35% for Co, 7–18% for Mn, 4–22% for Zn, 11–42% for Pb). High metal concentration in the acid extractable and reducible fractions indicates pollution hazards. Singh et al. (1995) extracted the heavy metals with DPTA and NH₄NO₃ at different pH values in a clay loam and loam soil. They found that the DPTA extractable and NH₄NO₃ extractable Cd had decreased with increasing soil pH and the effect was more pronounced with NH₄NO₃ extractable Cd. Both extractants were found equally effective in relation to Cd concentration in plants.

A green house experiment with two *Brassica* species (*Brassica juncea* and *Brassica carinata*) were grown on artificially contaminated soil (20 and 40 mg Cd kg⁻¹) with EDTA added at rate of 1 g kg⁻¹ soil. The increasing Cd (0, 20, and 40 mg Cd kg⁻¹ soil) contaminated the biomass of both the *Brassica* species decreased (Ahmed et al. 2001). The results showed that EDTA made the cadmium more available to the plants and lowered the Cd content of the soil.

Chelating agents employed for decontaminating metal polluted soils. When chelating agents are applied into the soil, the solubility of heavy metals increased due to formation of watersoluble metal complex with the chelating agent. Metals are extracted or desorbed from different soil components or from the surfaces of these components. The extent of heavy metal solubilization by chelation with organic complexing agents follows the order of their stability constants, which were determined in aqueous solutions using the ratio of metal to chelating agent as protoned forms of 1:1. Synthetic chelating agents like EDTA are perhaps the most widely studied extractants for soils and sediments. It is generally believed that EDTA extraction is also effective in displacing organically bound metals present in soils. Furthermore, it is often a preferred reagent because it typically does not release metals firmly bound in crystal lattices. Moreover, metals not released by EDTA washing are unlikely to be mobilized by natural processes and thus may have little environmental relevance. The use of plants to remove heavy metals from soil is expanding due to its cost effectiveness as compared with conventional methods and it has revealed a great potential.

Conclusions

Soils are considered to be sole part of the Earth's ecosystem and play an important role in plant growth, degradation and recycling of dead biomass. But at present soils are contaminated due to accumulation of metals and metalloids through the emission of various resources which is very crucial concern for environmentalist. Frequently, several techniques have been developed for remediation of soil, among the best available technologies till date has been discussed above for the rehabilitation of sites contaminated by heavy metals. The objective of a remediation effort is to limit the extent of contamination in soils near hazardous waste site to prevent exposure of hazardous chemicals to people and other life forms. The remedial methodologies at a given site vary depending on the properties of the chemicals, type of soil, depth of contamination and natural processes occur at the site. The criteria for technologies selection and remediation treatments are: (1) long-term and short-term effective repair to achieve targets, (2) reduction of contaminant volume more effectively, (3) reduction of pollutant toxicity and most important is (4) profitability: as phytoremediation is less cost effective and the cheapest method to detoxify soil. Situation specific technologies are available for removal of heavy meals from the soil. Among different technologies used to ameliorate decontaminated soils, phytoremediation is the cheapest and fast technique to decontaminate soil from heavy metals. The objective of this review is to familiarize researchers with the remediation technologies available for the heavy metals removal from contaminated soils. But still it is necessary to develop environmentally friendly technologies and strategies that have a major impact on contaminated land.

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