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REVIEW ARTICLE

Phytoremediation: role of terrestrial plants and aquatic macrophytes in the remediation of radionuclides and heavy metal contaminated soil and water

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Abstract Nuclear power reactors are operating in 31 countries around the world. Along with reactor operations, activities like mining, fuel fabrication, fuel reprocessing and military operations are the major contributors to the nuclear waste. The presence of a large number of fission products along with multiple oxidation state long-lived radionuclides such as neptunium (^{237}Np), plutonium (^{239}Pu), americium ($^{241/243}$Am) and curium (^{245}Cm) make the waste streams a potential radiological threat to the environment. Commonly high concentrations of cesium (^{137}Cs) and strontium (^{90}Sr) are found in a nuclear waste. These radionuclides are capable enough to produce potential health threat due to their long half-lives and effortless translocation into the human body. Besides the radionuclides, heavy metal contamination is also a serious issue. Heavy metals occur naturally in the earth crust and in low concentration, are also essential for the metabolism of living beings. Bioaccumulation of these heavy metals causes hazardous effects. These pollutants enter the human body directly via contaminated drinking water or through the food chain. This issue has drawn the attention of scientists throughout the world to device eco-friendly treatments to remediate the soil and water resources. Various physical and chemical treatments are being applied to clean the waste, but these techniques are quite expensive, complicated and comprise various side effects. One of the promising techniques, which has been pursued vigorously to overcome these demerits, is phytoremediation. The process is very effective, eco-friendly, easy and affordable. This technique utilizes the plants and its associated microbes to decontaminate the low and moderately contaminated sites efficiently. Many plant species are successfully used for remediation of contaminated soil and water systems. Remediation of these systems turns into a serious problem due to various anthropogenic activities that have significantly raised the amount of heavy metals and radionuclides in it. Also, these activities are continuously increasing the area of the contaminated sites. In this context, an attempt has been made to review different modes of the phytoremediation and various terrestrial and aquatic plants which are being used to remediate the heavy metals and radionuclide-contaminated soil and aquatic systems. Natural and synthetic enhancers, those hasten the process of metal adsorption/absorption by plants, are also discussed. The article includes 216 references.

Keywords Radionuclides · Heavy metals · Terrestrial plants · Macrophytes · Chelating agents

Introduction

Phytoremediation is a promising phenomenon where green plants are used to decontaminate the polluted sites. Many plants are efficiently used in this process. Plants show different potential for the remediation of contaminants. Growth of plants and their survival in the contaminated sites are the main factors responsible for their efficiency in phytoremediation. The soil microbe interactions (Muratova et al. 2003; Wenzel 2009), addition of chelators (Liu et al. 2008; Doumett et al. 2008) and agronomic practices (Olson et al. 2008) are also

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applied to enhance the plant efficiency and the rate of phytoremediation. Thus, phytoremediation in an elaborated form can be defined as the use of green plants and their associated microbes, soil amendments and agronomic practices to remove, contain and render the environment harmless from contaminants.

This technique offers a green chemistry-based route to remediate contaminated sites containing radionuclides (Eapen et al. 2006; Kanter et al. 2010), heavy metals (Dahmani-Muller et al. 2000), polycyclic aromatic hydrocarbons (PAH) (Huang et al. 2004), petroleum (Sun et al. 2004; Euliss et al. 2008) and diesel (Lin and Mendelssohn 2009) efficiently. It could be potentially applied for the organic as well as inorganic contaminants (Efroymson et al. 2001; Susarla et al. 2002; Shaw and Burns 2003; Reichenauer and Germida 2008). Some plants have high potential for the metabolism and degradation of recalcitrant xenobiotics and can be considered as 'green livers' which act as an important sink for the chemicals that destroy the environment (Sandermann 1992). Some woody plant species are also used for the remediation of heavy metal-contaminated biosolids (Mok et al. 2012).

The plant used for the phytoremediation should have some specific features. It should (a) be fast growing, (b) have high metal tolerance, (c) be resistant to diseases, pest, etc., (d) be having dense root and shoot system (Couselo et al. 2012) and (e) be unattractive to animals so that there should be minimum transfer of metals to higher tropic levels of terrestrial food chain (Bruce et al. 2003). The plant should not be metal specific so that maximum pollutants can be remediated simultaneously (Miretzky et al. 2004).

Plants are beneficial for the remediation of contaminated aquatic as well as terrestrial systems. The aquatic and terrestrial systems are principally contaminated due to heavy metals and the radionuclides. The radionuclides are continuously added on to the environment by bombardment of a stable nucleus, natural cosmic radiation and through the anthropogenic activities such as nuclear testing, military operations, mill tailings, disposal of radioactive waste and radiological events such as Chernobyl accident and Fukushima natural disaster. Similarly, human activities such as mining, smelting, atmospheric dispersion and metal extraction from ore, etc. raise the heavy metal concentration to the contamination level. Human beings are getting exposure to these pollutants present in soil and waste streams directly or indirectly by different pathways such as through the consumption of contaminated food crops (Muchuweti et al. 2006; Arora et al. 2008), through the food chain (Fowler et al. 1987) or by contaminated water (Ruttenber et al. 1984). Therefore, there is a strong need to develop such green technique like phytoremediation that would provide an easy, affordable and eco-friendly route for the cleansing of soil and water resources. In this direction, literature study has been conducted to compile the contamination of soil and water caused due to the addition of heavy metals and radionuclides. Modes of phytoremediation and flora involved in the removal of heavy metal and radionuclide contamination are also compiled in the review along with the synthetic and natural chelators that has been proved to be effective to hasten the process of phytoremediation. This compilation might be helpful in dealing with phytoremediation of the heavy metal- and redionuclide-contaminated water and soil resources.

Radionuclide and heavy metal contamination

Radionuclide contamination

Radionuclide pollution is of great concern. Most of the radioactive wastes are generated during the operation of nuclear reactors, fuel fabrication units, fuel reprocessing plants, research laboratories working with radionuclide production and applications of radioisotopes in medicine and industry, accidents and disasters. Even coal-fired power plants generate huge amounts of fly ash containing radionuclides.

During mining and milling operations of uranium (U), radium (Ra) and their fission products are mainly produced. Ra is a highly radioactive metal which has four most commonly occurring isotopes in nature (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) of which ^{226}Ra has longest half-life period i.e. 1,601 years. This radioactive metal has been reported for causing leukemia in human beings. According to a survey of groundwater samples collected from different countries, cases of the mentioned disease were higher in the countries having high concentration of Ra in groundwater (Lyman et al. 1985).

Even low-level radioactive waste contains high concentration of Cs and Sr along with the other radionuclides as shown in Fig. 1 (Balarama Krishna et al. 2004).

^{137}Cs and ^{90}Sr having $t_{1/2}$ of 30.17 and 28.8 years, respectively, are amongst the most abundant radionuclides in the nuclear fission products and considered as hazardous radiotoxic elements for the environment due to their long lives. Their environmental hazardous nature is partially due to the mobility in aquatic system. Due to solubility in water, they can easily enter the food chain and ultimately in the human beings. The metabolic resemblance of Cs and Sr with potassium (K) and calcium (Ca), respectively, helps them to get allocated easily in the whole human body (Volkle et al. 1989). Preferentially, Cs is deposited in the muscles, and Sr finds its place in the bones and teeth.

Apart from the anthropogenic activities, natural disasters such as earthquakes and tsunamis also promote the leakage of a considerable amount of radioactivity in the environment (Yoshida and Kanda 2012). For instance, various Cs isotopes (^{134}Cs, ^{136}Cs and ^{137}Cs) along with the others (tellurium

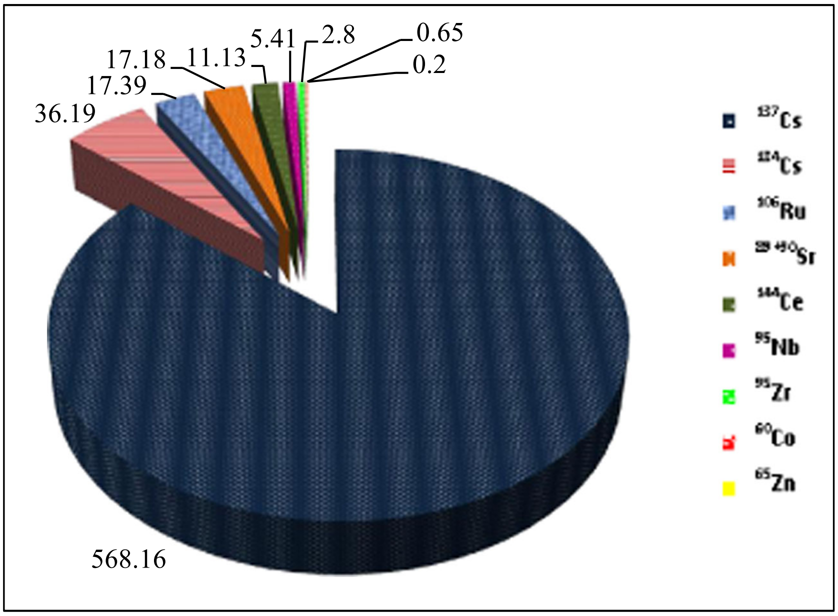

Fig. 1 Composition of low level radioactive waste solution

(^{129m}Te, ^{129}Te, ^{132}Te), iodine (^{131}I, ^{132}I), barium (^{140}Ba) and lanthanum (^{140}La)) were released during the Fukushima Daiichi nuclear power plant accident at Japan (Endo et al. 2012). No acute radiation injuries have been reported in the accident. However, possibilities of tumoregenesis due to the low dose exposure will be increased in the coming future.

Besides these radionuclides, alpha emitters such as ^{239}Pu, ^{237}Np, $^{241/243}$Am and ^{245}Cm and beta emitters such as technetium (^{99}Tc) and ^{129}I are particularly hazardous due to their long half-lives in the range of hundreds of year to millions of year.

Heavy metal contamination

Heavy metal pollution could arise naturally as well as by human activities. Volcanic explosion, forest fire and rock seepage are the natural sources of the heavy metal contamination. Human activities such as mining, smelting operations and many other industries such as thermal power plants and battery industries contribute majorly towards the heavy metal contamination. Disposal of the coal combustion residues in terrestrial systems also pollutes the land with heavy metals (Dellantonio et al. 2010). Atmospheric deposition, municipal wastes, use of sewage water as fertilizers and phosphate fertilizers used in agriculture play an important role in the heavy metal contamination in soil as well as in crop plants (Dong et al. 2001).

Human beings require some heavy metals such as copper (Cu), manganese (Mn) and zinc (Zn) in definite amounts for their body growth and metabolism. But, some heavy metals like mercury (Hg) and lead (Pb) prove to cause very dangerous effects due to bioaccumulation and biomagnifications. Heavy metals get introduced in the human body mainly through the water and food. A mild heavy metal contamination in drinking water may lead to potential health risks in the long-run (Pandey et al. 2010). Sometimes, inhalation of heavy metal-contaminated air can also increase its concentration in the body. Vegetables grown in the vicinity of metal smelters have potential health risk due to high cadmium (Cd), Pb and Zn contents (Kachenko and Singh 2006). There is no obvious contamination in crops growing in a low heavy metal contaminated soil but in long-term accumulation of heavy metals in soil may lead to increase in nickel (Ni), arsenic (As), Hg and Pb contents in the eatables (Jia et al. 2010). The heavy metal accumulation in the crops is greatly influenced by total metal concentration in soil and pH of the soil (Jung and Thornton 1996). Extraction potential of metal accumulator plants increases up to a certain level, and after that, the increase in metal concentration decreases the bioaccumulation coefficient (phytoextraction rate of metal) (Hamadouche et al. 2012).

Types of phytoremediation

Phytoremediation can be classified broadly in two categories: direct phytoremediation and explanta phytoremediation (Alkorta and Garbisu 2001). Direct phytoremediation involves the uptake/absorption of the pollutants through roots and translocation to the upper part of the plant. In explanta phytoremediation, pollutants are confined to the rhizosphere only. The explanta remediation is also called as rhizoremediation as the pollutants are retained or degraded in the rhizosphere only (Kuiper et al. 2004;

Wu et al. 2006; Gerhardt et al. 2009). In this type of remediation, plants release the various enzymes (Wang et al. 2004; Reboreda and Cacador 2008) and enhance the microbe growth (Chekol et al. 2004) in the rhizosphere for accumulation or coprecipitation of the pollutants.

In higher plants, about 20 % of total carbon content assimilated by photosynthesis is released as root exudates. Root exudates contain sugars, polysaccharides, organic, amino acids, peptides and proteins. The carboxylates exuded in the rhizosphere have their implications in the complexation of metals in the rhizosphere (Hinsinger et al. 2006). The heavy metal-contaminated soil may be better remediated by using higher plant density, a managed practice that would narrow the distance between individual plant rhizosphere (Gonzaga et al. 2006). The plants change the redox conditions, pH and organic content of soil which affect the mobility of the pollutants (Jacob and Otte 2003) in soil.

In direct phytoremediation, the endophytes (organisms that inhabit the plant organs) facilitate the rate of the phytoremediation. Some endophytic bacteria and endophytic fungi are known for increasing the rate of phytoremediation. These microbes enter in the plants via root and get disperse in the whole system (Li et al. 2012). These are resistant to the pollutants and decrease the toxicity of pollutants to plant and increase their degradation (Newman and Reynolds 2005). Microbes help the plant to grow in a contaminated soil (Jankong and Visoottiviseth 2008; Venkatesan et al. 2011) and facilitate the remediation of pollutants via their precipitation (Essa et al. 2012; Yadav et al. 2011) and stabilization in the rhizosphere as well as in the plants (Javaid 2011; Khandare et al. 2012). The microbes enhance both direct as well as explanta phytoremediation.

Modes of phytoremediation applied for the removal of heavy metals and radionuclides

Different modes of phytoremediation are employed for the remediation of soil and water contaminated with the metal and radionuclides. Plants respond to high metal toxicity either by stabilization in root zone that prevents metal translocation to the above ground parts of the plant or by extracting a high amount of metals and store them in stems and leaves (Jagatheeswari et al. 2013). The plant (hyperaccumulator or excluder) used for the phytoremediation also decides the route/type of remediation. Hyperaccumulator plant species accumulate metal mostly in the shoot as compared to the root, and in the case of excluder plants, the contaminants are confined to the root as compared to the shoot system (Singh et al. 2010; Coinchelin et al. 2012; Mohebbi et al. 2012). Hyperaccumulators have capacity to accumulate excessive amount of metals from the contaminations. Heavy metal tolerance in hyperaccumulators is so high that could cause toxicity in normal plants. The leaves of such plants may tolerate concentrations >100 mg/kg of Cd, >1,000 mg/kg of Ni and Cu, or >10,000 mg/kg of Zn and Mn (dry weight) when grown in a metal-rich medium (Ucer et al. 2013).

The different modes of phytoremediation provide an economically feasible and environmentally viable route for the cleaning of contaminated soil and water sources. Types of phytoremediation used for the remediation of heavy metal and radionuclide contaminations are discussed below.

Phytostabilization/phytosequestration

Phytostabilization/phytosequestration refers to the transformation of pollutants to a static complex. Due to the complex formation, there is precipitation within the root system zone. Microbes immobilize the pollutants by releasing chelating substances such as organic acids which form complex with the metals and prevent their entry in the plant. In the root, absorption, adsorption and accumulation take place by vacuole sequestration or cell wall binding that prevents the pollutants especially metal ions leaching into the groundwater, and there is no further translocation of pollutants to the shoot system. Arbuscular mycorrhizal symbiosis contributes positively in heavy metal immobilization (Gohre and Paszkowski 2006). The fungus works like the plant itself for the stabilization of metals in the soil. The processes involved are precipitation of metals in the polyphosphate granules, adsorption of pollutants on the fungus cell wall, chelation of the pollutants by the secretion of ligand molecules inside the fungus, etc. Some plants like signal grass (*Brachiaria decumbens*), when grown in heavy metal-contaminated soil, showed considerable growth and high metal accumulation in roots that are very important characteristics for a plant being used in phytostabilization (Andreazza et al. 2013). Further, plant should be a poor translocator of metals to the aerial parts to prevent its entry in living beings and must have dense root system that quickly grows to cover the contaminated site to accelerate the remediation (Yang et al. 2014). The process of phytostabilization can be hastened by organic as well as synthetic modifications. The effects were more accentuated in organically amended soil than in synthetically amended soils (Epelde et al. 2009). However, attention should be paid to metal leaching when organic additions are considered for the phytostabilization (Ruttens et al. 2006).

Phytoaccumulation/phytoextraction

The phytoaccumulation involves the extraction of the pollutants from soil via roots and translocates them to the upper part of the plant (Boonyapookana et al. 2005). The plant is further harvested and disposed off safely. Plants having high metal tolerance and can accumulate high concentration of pollutants (hyperaccumulator plant species) are used in this technique. The plants that produce high biomass can accumulate the high concentrations of the pollutants than other plants (Zhuang et al. 2007). Due to the dilution factor of the plant parts, trees accumulate higher amount of heavy metals as compared to the bushes and grasses (Irshad et al. 2014). To assess the capability of terrestrial plants for metal extraction, soil-specific screening should be performed. According to Ramaswami et al. (2001), terrestrial plants showed greater extraction capacity for U in sandy soil as compared to the organic soil. In organic soil, organic matter appears to seize the metal and reduces its availability to the plant. Addition of synthetic chelating agents to soil increases the bioavailability of metals to the plant and sometimes induces hyperaccumulation in normal plants (Mcgrath and Zhao 2003). For instance, EDTA amendment in soil increases ^{134}Cs availability twice for the root uptake in Indian mustard (Tjahaja et al. 2013). Even sewage sludge when amended with contaminated soil produces fertilizing effects and accelerates the biomass production accompanied by increased phytoaccumulation (Zaier et al. 2010). Type of soil amendment with respect to the metal to be remediated considerably affects the phytoextraction capacity of the plant (Brunetti et al. 2011). Rhizosphere microbes also enhance the process by increasing the roots surface area and also increase the availability of toxic metals in the rhizosphere (Souza et al. 1999a, b).

Phytovolatilization

Phytovolatilization, mainly concerned with the remediation of organic acids, is also helpful for the volatilization of heavy metals from the contaminated sites. Plants uptake pollutants from the soil and release them into the atmosphere by evaporation. The plant roots take up the metals by phytoextraction, and xylem helps in translocation to the shoot system. There is a biological conversion of metals into gaseous forms. The different parts of the shoot, especially leaves, release the metals into the atmosphere in gaseous forms. Plants such as Chinese brake (*Pteris vittata*) extract As from soil in the elemental form. Further, absorbed metal get converted into gaseous form by the biological processes within these plants and finally released in the atmosphere (Sakakibara et al. 2007).

In soil, As exists in four oxidative forms i.e. −3, 0, +3 and +5, but commonly found species are As^{+3} and As^{+5} (arsenite and arsenate, respectively). According to the earlier reports, microorganisms and enzymes help in the reduction and methylation of these forms within the plants. Trimethylated and dimethylated As species get readily evaporated from the foliages surface (Zhao et al. 2010). But recently, it has been proved that the plants do not involve in the methylation of neither inorganic As nor the mono and dimethylated As species to volatile trimethylated As species instead of which these volatile species are taken up by root from the soil itself (Jia et al. 2012).

Similarly, selenium (^{79}Se) which is of concern because of its long half-life (327,000 years) can be removed from radioactive waste by phytovolatilization. Se exists in five oxidation states (−2, 0, +2, +4 and +6) of which selenate species (+6) is majorly found in terrestrial sources and taken up from the soil by sulphate transporters of the plant. Plant enzymes convert the inorganic Se to the volatile form, dimethyl selenide (DMSe) through the various biochemical processes. Other volatile forms of Se that are released by the plants are dimethyl diselenide (DMDSe), dimethyl selenone, dimethyl selenylsulfide and methaneselenol (Terry et al. 2000).

Hg, known to cause various neurodegenerative diseases, is also remediated by phytovolatilization. Among all forms of Hg, methylated form (MeHg) of Hg is of main concern due to its biomagnification in the food chain (Kumar et al. 2014). Plants uptake the metal through roots and translocate them via vascular system to the upper plant parts and finally get transpirated. Enzymes within the plant transform the metal to the volatile form (Hg^0). Reports are also available for the volatilization of Hg through the root system of transgenic plants (Ke et al. 2001).

Phytofiltration

Phytofiltration may be defined as the use of plant roots to absorb, concentrate and/or precipitate harmful pollutants or metals from aqueous streams. The contaminants either get adsorbed onto the root surface or absorbed in the roots. This phenomenon is associated to the wastewater treatment. The plants having dense root system are used in phytofiltration which helps the plant to concentrate the maximum amount of pollutants. In phytofiltration, plants are grown hydroponically, and after the development of a dense root system, they are relocated to polluted aqueous stream. Various plants have shown their potentiality for phytofiltration. Some aquatic plants (floating and rootless macrophytes) have high capacity for the phytofiltration of heavy metals from the aqueous streams (Zhang et al. 2011; Xie et al. 2013). Besides the macrophytes, terrestrial plants are also used to remediate the aqueous streams. The roots of many hydroponically grown terrestrial plants are proved to be effective for the removal of toxic heavy metals from aqueous solution (Dushenkov et al. 1995) and also for radionuclide removal from groundwater (Lee and Yang 2010). As water moves to the roots, metals dissolved in it are also carried to the root surface and get adsorbed there. The entry of pollutants into root cells is prohibited by the barriers of cell membranes which immobilized the pollutants to root cell surfaces (Yadav et al. 2011). Biotic and abiotic factors of aqueous system such as pH and temperature ionic populations greatly influence the metal bioaccumulation (Xing et al. 2013). Some ornamental plants such as pearl grass (*Micranthemum umbrosum*) proved to be very effective in accumulation of heavy metals from the polluted water stream. The mentioned plant bio-concentration factors for As and Cd are found to be very high as compared to the other As and Cd phytoremediator plant species (Islam et al. 2013).

Hydraulic barriers

Hydraulic barriers involve the use of hydrophilic plants which uptake a large volume of water. The underground water resources may get contamination by soil leaching or through the surface water. To prevent such type of pollution, generally tall trees are allowed to grow on contaminated land. These plants control the migration of contaminants by rapid uptake of large volume of the contaminated surface water. Such plants have deep root system which helps the plant to prevent the underground water pollution. Vegetative caps and riparian buffer strips are such hydraulic barriers which control the migration of pollutants.

Vegetative caps are the long-term, self supporting cover of plants growing in and over materials that pose environmental risk. These caps help in preventing leaching of contaminants, soil erosion and migration of contaminants to the underground water. Riparian buffer strips are the linear band of vegetation along the bank of water resources. These bands involve grasses as well as trees. These buffer strips are helpful in increasing the water quality by removing pollutants. Rehabilitation of polluted streams is only possible if riparian zones start from headwaters and continuous with the catchment (Parkyn et al. 2003).

Terrestrial plants and aquatic macrophytes used for the phytoremediation of radionuclides and heavy metals

Plants have potential to accumulate essential and non-essential metals in their tissues. They are not capable of distinguishing the metals with the same physiochemical properties or between the two isotopes of the same metal. Along with the essential metals, they also accumulate their radioisotopes and toxic metals (Dushenkov et al. 1997). Due to this characteristic, various plants are extensively used for the remediation purpose. This approach is gaining more and more attention over the other conventional techniques of cleansing such as leaching (Mason et al. 1997; Lu et al. 1998; Santos and Ladeira 2011), reverse osmosis (Huikuri et al. 1998), use of ion exchange resins (Brings 2010) and many other physical and chemical treatments as it is eco-friendly and cheap and can be efficiently applied for the removal of contaminants from terrestrial as well as from aquatic systems (Zhu and Shaw 2000; Balarama Krishna et al. 2004; Lewandowski et al. 2006; Fulekar et al. 2010; Luksiene et al. 2013).

A number of plant species are successfully applied for the remediation of terrestrial and aquatic systems contaminated with radionuclides. Some plants such as grass (*Polygonum* sp.), reeds (*Phragmites australis*) and bulrush (*Typha latifolia*) are proved to be very effective in reducing the radioactivity of U polluted water. Wetlands with these plants species have been used to improve the water quality of streams receiving discharge from the U mines (Carvalho et al. 2011). Like aquatic system, soil contaminated with radionuclides could also be remediated by the use of plants (Rauret et al. 1995). A comparatively greater number of remediation cases have been studied for ^{137}Cs and ^{90}Sr in different plants relative to the other radionuclides (Entry et al. 1997; Zhu and Shaw 2000; Fuhrmann et al. 2002; Eapen et al. 2006). These radioisotopes are abundantly found in nuclear waste and are of main concern. Various plant species involved in the remediation of Cs and Sr are given in Tables 1 and 2. Few reports on remediation of cobalt (^{60}Co) are also available (Malik et al. 2000).

Terrestrial plants play a vital role in the phytoremediation of heavy metals and radionuclides in contaminated soil and aqueous resources. Some higher plants have developed such strategies which facilitate their survival and reproduction in the highly heavy metal contaminated soil (Dahmani-Muller et al. 2000). For example, willow (*Salix*) species proved to be very promising for the heavy metal phytoremediation of soil and water (Mleczek et al. 2010). These plants accumulate considerable amount of toxic metals in different parts. High metal tolerance in plants is due to the metal detoxification which is promoted by various antioxidant enzymes and other cellular antioxidants such as cysteine and thiols. These antioxidants are considered to be an important defence system against metal toxicity. Hyperactivity of enzymes overcomes the heavy metal toxicity by detoxification and helps the plants in hyperaccumulation (Ali et al. 2003).

A range of flowering plant families are being used for the phytoremediation purpose. The plants of Asteraceae family could accumulate comparatively a higher concentration of radionuclides and heavy metals than the other flowering species (Turnau and Mesjasz-Przybylowicz 2003; Tang and Willey 2003). The higher accumulation capacity for heavy metals and radionuclides in this family is due to the high transfer factor (ratio of contaminant concentration in plant and in the soil on a dry weight basis) and the occurrence of arbuscular mycorrhiza (AM) colonies with the abundant arbuscules which catalyze the process. When two or more heavy metals are present together, there is a competition for the binding sites in root zone, and bioaccumulation coefficients for each metal get reduced as compared to the single metal contamination (Keeling et al. 2003). In the case of some plants such as dahlia (*Georgina wild*), increase in the heavy metal concentration adversely affects the plant i.e. it decreases the growth of the plants (Shivhare and Sharma 2012).

Table 1 Plants effective in phytoremediation of ^{137}Cs contaminated sites

Scientific name	Common name	References
Lycopersicon esculentum Mill.	Tomato	(Brambilla et al. 2002)
Beta vulgaris var. *cicla* L.	Swiss chard	(Schuller et al. 2004)
Catharanthus roseus L.	Madagascar periwinkle	(Fulekar et al. 2010)
Amaranthus chlorostachys Willd.	Ringelblume	(Moogouei et al. 2011)
Calendula Alata L.	lamb's quarters	(Moogouei et al. 2011)
Chenopodium album L.	Cabbage	(Moogouei et al. 2011)
Brassica campestris L. perkinensis	Moss	(Chiang et al. 2005)
Funaria hygrometrica Hedw.	Barley	(Balarama krishna et al. 2004)
Hordeum vulgare L.	Redroot pigweed	(Bange and Overstreet 1960)
Amaranthus retroflexus L.	Indian mustard	(Fuhrmann et al. 2002)
Brassica juncea L. Czern.	Tepary bean	(Fuhrmann et al. 2002)
Phaseolus acutifolius A. Gray	Giant milky weed	(Fuhrmann et al. 2002)
Calotropis gigantea R.Br.	Christmas Bush	(Eapen et al. 2006)
Chromolaena odorata L.	Hemp	(Singh et al. 2009)
Cannabis sativa L.	Blue bunch wheatgrass	(Hoseini et al. 2012)
Agropyron spicatum (Pursh) Scribn & Smith	Great Basin wild rye	(Cook et al. 2009)
Leymus cinereus Scribn & Merr.	Cheat grass	(Cook et al. 2009)
Bromus tectorum L.	Crested wheatgrass	(Cook et al. 2009)
Agropyron cristatum L. Gaertn.	Khus	(Cook et al. 2009)
Vetiveria zizanioides L. Roberty.		(Singh et al. 2008)

Many crops also have efficiency to remove metals from the contaminated land. Field pumpkin (*Cucurbita*), maize (*Zea mays*), red beet (*Beta vulgaris*), cabbage (*Brassica oleracea* var. *capitata*), barley (*Hordeum vulgare*), white lupine (*Lupinus albus*), lentil (*Lens culinaris*), chickpea (*Cicer arietinum*) and many other crops that produce high biomass are efficiently used for phytoremediation (Rodriguez et al. 2007; Poniedzialek et al. 2010). The plants of Brassicaceae family proved their remediation potential against the heavy metals as well as the radionuclides. A well-known heavy metal hyperaccumulator plant species belong to this family that accumulates a high level of heavy metals is alpine pennygrass (*Thlaspi caerulescens*). The enhanced metal tolerance and phytoremediation potential of plant is possibly due to the presence of metal-binding peptides (Papoyan and Kochian 2004). The hyperaccumulator plants may have higher density of these metal transporters on the plasma membrane of root cells as compared to the non-hyperaccumulator species which enhance their accumulation capacity (Zhao et al. 2003). In this family, genus *Brassica* is more efficiently used for the

Table 2 Plants effective in phytoremediation of ^{90}Sr contaminated sites

Scientific name	Common name	References
Calotropis gigantea R.Br.	Giant milky weed	(Eapen et al. 2006)
Broussonetia papyrifera L. Vent.	Paper mulberry	(Li et al. 2011)
Parthenocissus quinquefolia L. Planch.	Virginia creeper	(Li et al. 2011)
Cannabis sativa L.	Hemp	(Hoseini et al. 2012)
Euphorbia macroclada Bioss.	Spurge	(Sasmaz and Sasmaz 2009)
Verbascum cheiranthifolium Bioss.	Mullein	(Sasmaz and Sasmaz 2009)
Astragalus gummifer L.	Tragant	(Sasmaz and Sasmaz 2009)
Vetiveria zizanioides L. Roberty.	Khus	(Singh et al. 2008)
Funaria hygrometrica Hedw.	Moss	(Balarama krishna et al. 2004)
Calotropis gigantea R.Br.	Giant milky weed	(Eapen et al. 2006)
Amaranthus retroflexus L.	Redroot pigweed	(Fuhrmann et al. 2002)
Brassica juncea L. Czern.	Indian mustard	(Fuhrmann et al. 2002)
Phaseolus acutifolius A. Gray	Tepary bean	(Fuhrmann et al. 2002)

remediation purpose than the other genus of the family. Various *Brassica* species produce a high amount of biomass and are adaptable to a range of environmental conditions which help them to accumulate pollutants rapidly (Palmer et al. 2001). *Brassica* species (Indian mustard (*Brassica juncea*), spinach mustard (*Brassica narinosa*) and Chinese cabbage (*Brassica chinensis*)) are very effectual for phytoextraction of U. The acid amendment, citric acid in particular, enhances the hyperaccumulation of U in shoots, whereas reverse effect is observed in the case of sunflower (*Helianthus annuus*) (Huang et al. 1998; Huhle et al. 2008). Another *Brassica* species, field mustard (*Brassica campestris*), is reported for its phytostabilizing capacity against the varied concentration of cadmium (Cd) (Anjum et al. 2014). On an agricultural land, accumulation of toxic metals in crop plants could be prohibited by using co-cropping method. When crop is co-cropped with the known hyperaccumulator species, metal accumulation reduced in that crop without affecting its growth (Xiaomei et al. 2005).

Members of Fabaceae or Leguminosae family have immense power for the extraction of heavy metals and radionuclides from polluted site. Leguminous woody species of this family have high potential and phytoremediation capability of removing the heavy metals. In these plants, maximum concentration of pollutants is confined to root only, whereas under stressed conditions, toxicity is also observed in the form of reduced chlorophyll and carotenoid contents. An increase in heavy metal concentration in the soil decreases the nodule formation which affects the nitrogenase activity (Ribeiro de Souza et al. 2012). Phytotoxicity observed depends upon the plant used for phytoremediation and the heavy metals to be remediated. For instance, in castor bean (*Ricinus communis*), adverse effects are observed due to Cd (De Souza Costa et al. 2012), whereas in Brazilian leguminous tree species, Pb is responsible for imparting toxicity (Ribeiro de Souza et al. 2012).

Among pteridophytes, some ferns of Pteridaceae family are documented for their potential of removing heavy metals and radionuclides (Chen et al. 2006; Shoji et al. 2008). Ferns preferentially accumulate higher metal concentration in aboveground biomass as compared to the roots (Baldwin and Butcher 2007). To evaluate the phytoremediation potential of ferns, it is recommended that metal uptake by fronds should be taken into consideration (Niazi et al. 2012). *Pteris vittata* (Chinese brake) is well known for arsenic hyperaccumulation. This plant species has enough tolerance for high concentration of As because of the presence of high density of specific As transporters. Reports revealed that due to the structural similarity of arsenic with phosphate, it is easily extracted and transported by the plant from contaminated site via phosphate transport system (Lee et al. 2003).

Along with the soil remediation, terrestrial plants are also applicable for the remediation of polluted aqueous streams. Sunflower (*Helianthus annuus*), purple guinea grass (*Panicum maximum*) and orange jewelweed (*Impatiens capensis*) are very effective in removing the heavy metals and radionuclides from contaminated water (Dushenkov et al. 1997; Roongtanakiat et al. 2010). The terrestrial plants accumulate higher metal concentration in their root when applied to an aqueous system (Caldwell et al. 2012). The phytofiltration of radionuclides by the roots of terrestrial plants is very effective and of vital interest for pilot scale experiments (Prasad 2007).

Besides the terrestrial plants, various aquatic macrophytes are also reported for remediation of contaminated aquatic ecosystems. Macrophytes are those plants which grow in or near water and are categorized as merged, submerged and free-floating plants. Duckweed (*Lemna minor*), water hyacinth (*Eichhornia crassipes*), hydrilla (*Hydrilla verticillata*) and water lettuce (*Pistia stratiotes*) are some of the aquatic macrophytes which are frequently used for the heavy metal remediation in aquatic system (Singh et al. 2012; Hua et al. 2012). Some adverse effects of toxic metals have also seen in macrophytes during remediation. Toxic metal exposure inhibits the chlorophyll synthesis in these plants. The sugar and protein contents of the macrophytes also get affected. Reduction in sugar level may be due to the increased sugar consumption by plant in stressed condition, and complexation of plant peptides with heavy metal reduces the total protein content of plant (Mishra and Tripathi 2008). Some aquatic plants such as duckweed (*Lemna gibba*) behave as bio-indicator for heavy metals that transfer heavy metals from contaminated site to the plant and could be used to monitor the transfer of metal from lower to higher trophic levels (Mkandawire and Dudel 2005).

Some aquatic and terrestrial plants used for the phytoremediation of soil and water contaminated with heavy metals and radionuclides are listed in Tables 1, 2 and 3.

Role of chelating agents in phytoremediation

Various chelating molecules contribute positively towards the phytoremediation. Various chelating agents synthesized by plants and artificial chelating amendments play a vital role in enhancing the metal phytoremediation. When plants are grown in toxic environment, chelating molecules are automatically synthesized by the plant in response to minimize toxicity and released by the plants in root exudates. These molecules help the plant in phytoremediation by accumulating, stabilizing and degrading the pollutants. Both natural and synthetic chelating molecules help the plant to survive and maintain its growth in contaminated environment.

Natural chelating molecules

Natural chelating molecules are those molecules which are synthesized by the plant itself in response to any type of

Table 3 Terrestrial and aquatic plants showing appreciable uptake of heavy metals

Plant	Heavy metal	References
Alyssum bertolonii L.	Ni	(Robinson et al. 1997a, b)
Jatropha curcas L.	Pb and Cd	(Mangkoedihardjo and Surahmaida 2008)
Azolla pinnata R.BR	Cr, Hg and Cd	(Rai 2008, 2010)
Brassica juncea L.	Cd, Cr, Cu and Pb	(Seth et al. 2012)
Salix viminalis L.	Cu, Pb and Zn	(Pitre et al. 2010)
Salix miyabeana Seemen.	Cu, Pb and Zn	(Pitre et al. 2010)
Cannabis sativa L.	Cd, Cr and Ni	(Citterio et al. 2003)
Cardaminopsis halleri L.	Zn, Cu, Sn, Fe and Al	(Neumann and Nieden 2001)
Ceratophyllum demersum L.	Pb and Cr	(Abdallah 2012)
Lemna gibba L.	Pb, Cr, Cd, Co and Zn	(Abdallah 2012; Megateli et al. 2009)
Eucalyptus globules	Cr and Zn	(Sarin and Pant 2006; Arriagada et al. 2010)
Eichhornia crassipes (Mart.) Solms	Zn, Cr, Cu, Cd, Pb, Ag and Ni	(Odjegba and Fasidi 2007)
Helianthus annuus L.	Cu, Zn, Pb, Hg, As, Cd and Ni	(Jadia and Fulekar 2008)
Hydrocotyle umbellata L.	Cr, Zn, Na and Cu	(Khilji and Bareen 2008)
Lemna minor L.	As, Hg, Pb, Cr, Co and Zn	(Parra et al. 2012)
Pteris vittata L.	As, Cu and Cr	(Kumari et al. 2011)
Cynodon dactylon (L.) Pers.	Pb, Co and Ni	(Rathi et al. 2011)
Vigna radiata (L.) R. Wilczek	Pb, Co and Ni	(Rathi et al. 2011)
Commelina benghalensis L.	Pb, Cd and Zn	(Sekabira et al. 2011)
Pluchea indica (L.) Less.	Cr	(Sampanpanish et al. 2006)
Cynodon dactylon (L.) Pers.	Cr	(Sampanpanish et al. 2006)
Vetiveria zizanioides (L.) Roberty	As, Cd, Cr, Cu, Hg, Ni, Pb, Se and Zn	(Danh et al. 2009)
Amaranthus spinosus L.	Cu, Pb, Cd, Zn and Cr	(Chinmayee et al. 2012)
Phyla nodiflora (L.) Greene	Cu and Zn	(Yoon et al. 2006)
Gentiana pennelliana L.	Pb, Cu and Zn	(Yoon et al. 2006)
Typha latifolia L.	Cu, Ni, Zn, Fe, Mn and Ca	(Taylor and Crowder 1983)
Lupinus species	Mn, Cd, Pb, Cr and Hg	(Ximenez-Embun et al. 2001)
Lolium italicum A. Braun	Zn and Pb	(Rizzi et al. 2004)
Festuca arundinaceae Schreb.	Zn and Pb	(Rizzi et al. 2004)
Anthyllis vulneraria L.	Zn, Cd and Pb	(Mahieu et al. 2011)
Festuca arvernensis	Zn, Cd, Pb	(Frerot et al. 2006)
Koeleria vallesiana	Zn, Cd, Pb	(Frerot et al. 2006)
Armeria arenaria Willd.	Zn, Cd, Pb	(Frerot et al. 2006)
Stackhousia tryonii Sm.	Ni	(Bhatia et al. 2005)
Sebertia acuminata Pierre ex baill.	Ni	(Jaffre et al. 1976)
Berkheya coddii L.	Ni and Co	(Robinson et al. 1997a, b; 1999)
Pistia stratiotes L.	Ag, Cd, Cr, Cu, Hg, Ni, Pb and Zn	(Odjegba and Fasidi 2004)
Sesbania drummondii (Rydb.) Cory	Pb	(Sahi et al. 2002)
Solanum nigrum L.	Cd and Pb	(Gao et al. 2012)
Arabis gemmifera Adans.	Cd and Zn	(Kubota and Takenaka 2003)
Sedum alfredii Hance	Cd and Zn	(Yang et al. 2004)
Zygophyllum fabago L.	Zn	(Conesa et al. 2006)
Helichrysum decumbens Cambess.	Pb	(Conesa et al. 2006)
Tamarix species L.	Co	(Conesa et al. 2006)
Poa pratensis L.	Pb and Cd	(Liu et al. 2006)
Genaphalium affine D. Don	Pb	(Liu et al. 2006)
Conyza canadensis (L.) Cronq.	Cd	(Liu et al. 2006)
Phytolacca acinosa Roxb.	Mn	(Liu et al. 2006)
Elsholtzia splendens Nakai F. Maek.	Cu, Zn, Pb and Cd	(Wang et al. 2005)
Trifolium repens L.	Cd, Zn and Pb	(Bidar et al. 2007)
Lolium perenne L.	Cd, Zn and Pb	(Bidar et al. 2007)
Raphanus sativus L.	Cd, Cr, Cu, Ni and Zn	(Pandey 2006)
Spinacia oleracea L.	Cd, Cr, Cu, Ni and Zn	(Pandey 2006)
Lepidum sativum L.	Pb and As	(Gunduz et al. 2012)
Lactuca sativa L.	Pb and As	(Gunduz et al. 2012)
Pisum sativum L.	Pb, Zn and Cu	(Kala and Khan 2009)
Amaranthus Hybridus L.	Cd, Ni, Pb and Hg	(Chunilall et al. 2005)
Amaranthus dubius Mart. Ex Thell.	Cd, Ni, Pb and Hg	(Chunilall et al. 2005)
Mimosa caesalpiniaefolia Benth.	Pb	(Ribeiro de Souza et al. 2012)
Erythrina speciosa Andrews	Pb	(Ribeiro de Souza et al. 2012)
Schizolobium parahyba (Vell.) S.F.Blake	Pb	(Ribeiro de Souza et al. 2012)
Sesbania drummondii	Pb	(Barlow et al. 2000)
Ricinus communis cv. Guarany	Cd and Pb	(De Souza Costa et al. 2012)

deficiency in plant or toxicity in root zone environment. Some plants release phytosidophores (PS) mainly under Fe and Zn deficiencies which mobilize heavy metals such as Cd along with the Fe and Zn in the rhizosphere and hence uptake of which is also enhanced (Awad and Romheld 2000).

Organic acid anions such as citrate, oxalate, malate, succinate, tartrate, phthalate, salicylate and acetate are produced by the plant in response to the metal ion toxicity. These anions released form complex with the suitable metal ions and prevent the plant root toxicity. Citric acid is a well-known chelator which enhances the heavy metal and radionuclide uptake capacity of the plants. Comparing to its bound form like potassium citrate, free acidic form, i.e. citric acid, is more effective in triggering metal hyperaccumulation (Huang et al. 1998). But at elevated level, citric acid may adversely affect the plant growth and result in reduced accumulation (Sinhal et al. 2010).

Various membrane-bounded transport proteins are present on plasma membrane which transports a specific anion out of the root cells to detoxify specific metal ion (Ma et al. 2001). Organic acids released by the plants are also involved in the processes like sequestration of metals in cell vacuole to increase the tolerance of plant in excess of heavy metals toxic environment. Different plant species depending on their genotypes acquire different mechanism like release of phytosidophores, precipitation and sequestration to reduce/remove the toxicity of metals (Khan et al. 2000). Peptide ligands, phytochelatins (PCs, enzymatically synthesized cysteine-rich peptides) and metallothioneins (MTs, small gene-encoded, cysteine-rich polypeptides) are also specifically synthesized by the plant in response to the heavy metal toxicity (Cobbett 2000).

Earlier, it was hypothesized that aminal and fungi respond to heavy metal stress by induction of MTs and plants by induction of PCs (Grill et al. 1987; Gekeler et al. 1988). Further, two MT genes and functional homologs of fungi MTs have been isolated from plant *Arabidopsis* and were involved in copper tolerance of the plant (Zhou and Goldsbrough 1994). The detoxification mechanism of plant MTs involves the reduction of reactive oxygen species in heavy metal-treated plant cells instead of sequestration of toxic metals into vacuoles or other organelles (Lee et al. 2004) and protect the plants from oxidative damage (Lv et al. 2012).

Report shows that organic compounds in root exudates significantly affect the growth of rhizosphere microflora, and these interactions play a vital role in successful application of plants in phytoremediation (Kozdroj and Elsas 2000). Among the rhizosphere micro-organisms, role of bacteria and fungi in phytoremediation is well-established. Arbuscular mycorrhizal fungi contribute to phytoremediation, particularly by stabilization/immobilization of the metal (Simon et al. 2006). Fungi improve the resistance of plant by enhancing the plant-soil interaction and by synthesizing various phytochelators which detoxify the metals in the rhizosphere (Barea et al. 2005). Inoculation with arbuscular mycorrhizal fungi could also promote the growth of plant by decreasing the metal uptake (Shivakumar et al. 2011). Similarly, bacteria could also serve as an effective inoculation for plants which help them in metal immobilization and their growth in a contaminated site (Aboudrar et al. 2013). Some bacteria such as *Bacillus licheniformis* BLMB1 strain when amended with contaminated soil enhance the metal uptake especially Cr extraction in plants (Brunetti et al. 2011).

Synthetic chelating molecules

Synthetic chelating molecules used in phytoremediation are the different amendments that are artificially primed for the excessive uptake of the metals by plants. These complexing agents immobilize the metal ions in the rhizosphere and increase their availability to the plant and hence contribute to higher metal uptake.

Organic acid molecules such as ethylenediaminetetraacetic acid (EDTA), *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), ethylenediamine-*N*,*N′*-bis(2-hydroxyphenyl)acetic acid (EDDHA), diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA) and trans-1,2-cyclohexylenedinitrilotetraacetic acid (CDTA) are frequently used to improve the phytoremediation potential of the plants. Application of EDTA to the contaminated soil enhances the translocation of the heavy metal from roots to shoots and then finally to the leaves. This chelating agent keeps the bioaccumulation factors higher in stems and leaves (Barren 2012). EDTA is a better chelating agent than the other organic acids as it changes the adsorded metal to loosely bound fraction which is easily bio-available (Chen et al. 2012). The uptake rate and selectivity of plants for metals depend largely on cultivar and chelator used in the process (Turgut et al. 2004). Chelating amendments help in maintaining the soil environment suitable for phytoremediation and increase the extractability of plants by transforming the metal to the extractable form. These two factors, metal speciation and the soil environment, greatly affect the extraction potential of the plant used in phytoremediation (Chiang et al. 2006). For instance, Cd and Zn speciation is greatly responsible for their uptake. Presence of the ligands in both the cases considerably enhances their uptake in the plant as compared to the free metals (McLaughlin et al. 1997).

Traditional organic materials for instance, rice straw, are reported as soil amendment used in phytoremediation of contaminated soil. These materials proved to be more effective and environment-friendly than the organic acids used in the study (Wu et al. 2012). Biosludge and biofertilizers enhance microbial activities that in return reclaim the heavy metal-contaminated soil and wastelands (Nanda and Abraham

2011). Municipal solid waste composts increase the metal accumulation in plants and also increase plant resistance to survive in highly toxic environment.

Although chelating agents are very proficient in metal phytoremediation, they also include some negative aspects that cannot be ignored. Excessive accumulation of metals accomplished by the use of these molecules may cause metal toxicity in plants, and the natural tactics of plant for metal remediation may alter. Chelating molecules are also known to affect the root to shoot metal translocation within the plants and considerable decrease in growth of the plant. In the case of some chelators, the considerable root and shoot weight drop was observed along with the excessive micronutrients uptake that adversely affect the plant metabolism (Farid et al. 2013). Therefore, some parameters like plant growth, interaction of chelator with the plant and environments and quantity of chelators to be used should be taken in consideration while using an artificial chelator in phytoremediation.

Disposal of phyto-biomass

There are some techniques reported in the literature for the safe disposal of contaminated phyto-biomass produced after the remediation of metals and radionuclides. Techniques such as composting, compaction and pyrolysis are being used as pretreatments to reduce the biomass and incineration, and ashing, liquid extraction and direct disposal of phyto-biomass are among the methods of final disposal (Sas-Nowosielskaa et al. 2004). Among the pretreatments, pyrolysis is found to be more effective and beneficial as it ends to the reduction of considerable volume of phytobiomass and leads to the production of useful end product i.e. pyrolytic gas. However, it costs almost double the amount used in the rest of two. For the final disposition of contaminated phyto-biomass, incineration or smelting is found to be promising. These methods of final disposal end to the recovery of metals from plant material and significant reduction in the waste volume. Disadvantage includes the production of dioxins in the treatment which promote the probability of cancer (Shibamoto et al. 2007). Another mode of fate of contaminated phyto-biomass is gasification. In this technique, valorization of contaminated biomass is carried out to produce electricity and heat (Vervaeke et al. 2006).

Conclusion

Phytoremediation is a green approach to decontaminate the polluted sites. Available literature reveals that this technique is an effective, economic, versatile and eco-friendly way of cleaning the environment. Plants play significant role in decontaminating aquatic and terrestrial sites polluted with heavy metals and radionuclides. Terrestrial plants like trees, grasses, flowering families and crops are used for the remediation of contaminated soil and water resources. Besides the terrestrial plants, macrophytes (merged, submerged and floating) have immense remediation potential to purify the water resources. Within the plant, metal complexing agents (PCs, MTs, organic acids) are synthesized in response to the toxicity. Along with the natural chelating molecules, various synthetic chelators are also supplemented in the contaminated site to speed up the process of phytoremediation.

The process of phytoremediation is more advantageous over the conventional methods due to various reasons. It is a cost-effective technique and needs not to have costly equipments. Further, special care is not required in growing the plants on the contaminated sites. It is a natural way to decontaminate the environment. This technique of remediation also has some weak aspects that includes a long time for the removal of contaminants from the sites as compared to the chemical methods of removal, and the scope is confined to the low level nuclear waste only. It also produces a large amount of contaminated phytomass, disposal of which is still a problem. With this, it also increases the possibility of toxin entry to the food chain. But still, it is a better option of remediation because of its eco-friendliness and cost effectiveness.

At present, phytoremediation is still considered as an emerging technology (Prasad and Freitas 2003) with respect to the metabolic pathways and growth behaviour of plants. Significant experimental/laboratory work has been carried out in this field, but commercialization of this technique is still lacking. Hence, more experimental work is needed to understand the phytoremediation process and its application at commercial scale.

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