# Chapter 17
# Biotechnological Aspects of Soil Decontamination

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**Abstract** Soils have been subjected to several contaminants that vary in concentration and composition. Soil pollution causes significant damage to the environment and human health as a result of their mobility and solubility. Significant progress has been made in regulating soil pollution, with a parallel development of methodologies for soil assessment and remediation. The selection of most appropriate soil and sediment remediation method depends on the site characteristics, concentration, type of pollutants to be removed, and the end use of the contaminated medium. This chapter provides the developing biotechnological aspects of soil decontamination. The study also reviews other available remediation options, which includes physical, chemical, and thermal technologies. All these technologies may be used in conjunction with one another to reduce the contamination to an acceptable level, and may offer potential technical solution to most soil pollution.

## 17.1 Introduction

Globally, the increasing human population, industrial revolution, and the number of anthropogenic inefficiencies with unplanned growth of urban system have been putting an intense pressure on the consumption of natural resources, thus threatening human health and the environment. Over time, the quantities of these

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nonrecyclable toxic by-products are at the levels that present an unacceptable risk to the sensitive biosphere (Sheoran et al. 2008; Sikdar et al. 1998)

Historically, soil pollution has been of very little concern, and its contamination is a relatively recent issue when, actually, it began a long time ago, particularly after the industrial revolution, even though only recently has mankind become aware of its dimension, persistence, and harmful effects (Castelo-Grande et al. 2010). Pollutants can be built up in the soil directly or indirectly from several sources, such as industrial emissions, mining and smelting of metalliferous ore, electroplating energy and fuel production, and sludge dumping. A wide range of inorganic and organic compounds cause contamination, and these include heavy metals, combustible and putrescible substances, hazardous wastes, explosives, and petroleum products. There has been increasing concern over the last few decades regarding organic pollutants, which includes PCBs such as dioxin, polycyclic aromatic hydrocarbons (PAHs) such as benzoapyrene, nitroaromatics such as trinitrotoluene (TNT), and linear halogenated hydrocarbons such as trichloroethylene (TCE). Major components of inorganic contaminants are heavy metals (Ghosh and Singh 2005). Heavy metals cannot be destroyed biologically and are present in soils as free metal ions, soluble metal complexes (sequestered to ligands), exchangeable metal ions, organically bound metals, precipitated or insoluble compounds such as oxides, carbonates, and hydroxides, or they may form part of the structure of silicate materials (indigenous soil content) (Davies et al. 2001).

Contaminated soils are the target of several thousands of pollutants that vary in their compositions and concentration. Elevated concentration of these pollutants impair the functioning of human population and pose significant risk to the development of flora and fauna (Scullion 2006). Contaminated soil fails to support crop growth and negatively affects its development because of interference of phytotoxic contaminants with metabolic processes and sometimes also leading to plant death (Hoffmann 1983). Besides this, soil toxicity disrupts biological cycling of nutrients and also affects the hydrosphere compromising with the quality of drinking water resources, and threatening the aquatic ecosystem (Bilek 2004). Human beings are also at risk from polluted soils, thus the magnitude of pollution in our soils calls for immediate action (Friberg et al. 1986; Knasmuller et al. 1998; Nathanail and Earl 2001). When contaminant concentrations in soil are too high for natural biodegradation to occur, cleanup action is warranted (Sikdar et al. 1998). Thus, in response to a growing need to address this environmental contamination, many remediation technologies have been developed to treat soil contaminated by various pollutants, including in situ (treating relatively undisturbed soils) and ex situ (treating excavated soils) methods either onsite or in designated soil treatment facilities. In situ has the advantage of minimal disruption to activities on site or on adjacent land. Ex situ approaches generally offer greater scope for managing conditions to optimize treatment efficiency and for controlling potential spread of pollutants. In situ methods are favored over the ex situ techniques due to their low cost and reduced impact on the ecosystem (Reed et al. 1992).

Biological, physical, chemical, and other technologies can be used in conjunction with one another to reduce the contamination to a safe and acceptable level (RAAG 2000). Physical methods employs soil washing, encapsulation, and solidification; precipitation and ion exchange are chemical treatments, and for the biological treatment plants are used. Even though many technologies are available for the decontamination of polluted sites, the selection depends on contaminant and site-by-site basis, regulatory requirements, costs, and time constraints. Since most remediation techniques are site-specific, the selection of appropriate technology is often a difficult, but extremely important step in the successful remediation of a contaminated site. Therefore, the successful decontamination of a contaminated site depends on proper selection of the methodology, its design, and adjustment of the remediation technology's operations based on properties of the contaminants and soils, and on the performance of the whole system (USEPA 1998; Khan et al. 2004 and Pazos et al. 2010).

This chapter provides the developing biotechnological aspects of soil decontamination, and also reviews various other physical, chemical, electro-remediation or electro-reclamation techniques. It also outlines the types of waste and media in which the technology could be successfully applied so that wide-scale implementation and commercialization of the technique may be recommended on a global basis.

## 17.2 Physical Techniques

Decontamination of soil relies on an understanding of the physical behavior of the pollutants in the site specific environment. Physical remediation methods are most effective in coarser textured soils, although fracturing of finer textured soils may extend their applicability, and for pollutants that are more soluble or volatile. This treatment can enhance the effectiveness of biological degradation of contaminates or indirectly cause their destruction (Scullion 2006).

### *17.2.1 Off-Site Management*

The most common traditional remediation technique is off-site management. The contaminated soil is taken for burial at land fill sites. This method of remediation merely shifts the contamination problem else where. Additionally, there are hazards associated with the transport of contaminated soil and migration of contaminant from landfill into adjacent environment (Williams 1988).

### 17.2.2 Isolation and Containment

Contaminants can be isolated and contained, to prevent further movement, to reduce the permeability of the waste to less than $1 \times 10^{-7}$m/s (as required by the USEPA), and to increase the strength or bearing capacity of the waste (USEPA 1994). This technique consists of the use of barriers that inhibit the migration of contaminants to the neighboring uncontaminated site. Physical barriers made of steel, cement, bentonite, and grout walls can be used for capping, vertical, and horizontal containment. Capping is a site specific proven technology, which uses synthetic membranes to reduce water infiltration. Horizontal barriers restrict the downward movement of metal contaminant within the soil, whereas vertical barrier reduces the migration from one site to another. These barriers are made of slurry walls, grout, or geomembrane curtains, and sheet pile walls. It is the least expensive approach, but leaves the contaminant in place without treatment. The selection of each technology is site-specific. They are beneficial where the area of contaminant is shallow but large. More research is required to match reactive media with contaminants, model life time performance, optimize retention times, and develop methods for regeneration of reactive media.

In terms of risk management, these above mentioned approaches aimed to control the pathway linking hazard and receptor without treating the source of the hazard. Remediation practices emphasized containment rather than treatment.

### 17.2.3 Solidification/Stabilization

Solidification process is a nondestructive physical method to immobilize the contaminants by encapsulating them in a solid of high structural integrity, while stabilization includes chemical reactions to reduce contaminant mobility. It is also known as waste fixation through both physical and chemical means. Some variants like liquid monomers that polymerize, pozzolans, bitumen, fly-ash, asphalt, and cement are injected to encapsulate the soils. Capping or jacketing or complete coating of the contaminated sediment with sandy material, such as clean sediment, sand, or gravel, which decreases the direct contact area between the water and the contaminated sediment, is what is done under encapsulation (Peng et al. 2009). Two ways of encapsulation are (i) microencapsulation (ii) macroencapsulation. Port land cement, pozzolans, or lime/hydrated lime, and organic polymers may be used for microencapsulation, whereas concrete, organic materials (polythene, polyesters, etc.), sulfur cement, etc. can be used for macroencapsulation.

Some researchers have reported that a good cap thickness was approximately 50 cm; and through capping the sediment by sands materials, the heavy metal concentration in water could reduce to 80 %. The cost of implementing this technology is dependent on the lithology of the site and the depth of the contaminant. As the depth of contamination increases, so does the cost (Khan et al. 2004). The stabilization converts the contaminants into less soluble immobilized and less toxic form by mixing soil or waste with chemical binders, such as cement, sulfide, and phosphate binders, polyester resins, or polysiloxane compounds to create a slurry, paste or other semi-liquid state, and is allowed time to cure into solid form (Wang et al. 2012). Additives through which solidification is achieved are either cement-based, pozzolon-based, the thermoplastic methods, the organic polymerization methods, the encapsulation method, and organophillic clay-based (Wang et al. 2012). Among these methods, cement-based solidification/stabilization is of increasing importance as option for remediating contaminated sites because of its low material and equipment cost.

This technique is suitable for contaminant in shallow depths and of large volume, and is not suitable for metals, which are not highly soluble, and do not form hydroxides, such as arsenic, chromium, and mercury. In situ solidification/stabilization techniques are preferred since labor and energy costs are lower, but site conditions, such as bedrock, large boulders, clay, and oily patches may cause mixing problems (Mulligan et al. 2001).

### *17.2.4 Vapor Extraction and Air Sparging*

Vapor extraction and air sparging techniques are based on the manipulation of pollutant distribution between liquid and vapor phases. These treatments promote the volatilization of pollutants (e.g., benzene, toluene, ethyl benzene, xylene, and chlorobenzenes) in unsaturated and saturated zones. Extracted gases or vapors may be adsorbed onto activated carbon or treated (e.g., by oxidation). The effectiveness of vapor extraction systems may be extended to semi-volatile pollutants by injection of heated air or heating by microwave/radiowave, and rates of extraction may be improved by increasing air flow rates to a point when mass transfer limits volatilization (George et al. 1992; Park et al. 2005). Air sparging also known as in situ air stripping or in situ volatilization induces partitioning of dissolved and free-phase contaminants into the vapor phase, and increases in dissolved oxygen can stimulate aerobic degradation. Benzene removal by air sparging has been shown by Adams and Reddy (2003). Both these approaches are less well suited to fine textured soils because of restricted rates of movement in the mobile phases and increased distances over which volatile organic contaminants have to diffuse through an aqueous phase. Also treatment rates are slower in soils with higher organic contents (Gomez-Lahoz et al. 1995).

### *17.2.5 Vitrification*

Vitrification of molten glass is another method of solidification/stabilization process requiring thermal energy. It uses heat of up to > 1,000 > 1,600 °C - > 2,000 °C to destroy organic pollutants by pyrolysis and immobilize most of the pollutants in organic (Gavrilesseu et al. 2009). It is a two stage process in which pollutants are desorbed at lower (<600 °C) temperature and then combusted. Vitrification is mainly used to remediate soils contaminated with heavy metals mixed with radioactive elements (Wang et al. 2012). It involves insertion of electrodes into the soil, which must be able to carry a current, and then to solidify, as it cools. Full scale applications exist for arsenic, lead, and chromium contaminated soils. Vitrification is expensive and suitable for shallow contamination and also toxic gases can be produced during the process, but is applicable to mixed wastes where few technologies are available (Mulligan et al. 2001).

The in situ or ex situ (where the soil is excavated and treated) vitrification consists in the insertion of graphite electrodes into the soil creating a high electric current, such that the released heat provokes the fusion of the soil matrix (Castelo-Grande et al. 2005). This leads to the formation of vitrified end product into which the contaminants are incorporated and subsequently immobilized. During this process, the majority of contaminants initially present in the soil are volatilized reducing their concentration in the soil and the waste, while the remainder are converted into a chemically inert, stable glass, and crystalline product. The vitrification can be performed by three different processes namely electrical process, thermal process, and plasma process. Precisely, electrical process makes use of application of electrical energy through graphite electrodes inserted into ground, whereas thermal process requires an external heat source and a typical reactor (Dermatas and Meng 2003); and moreover in plasma process, electrical discharges are used to achieve temperatures up to 5,000 °C .The advantage of this method is that the volume of waste can be reduced with long-term stability but it is a costly method (Suthersan 1997).

### 17.2.6 Mechanical Separation

This involves the size selection process to remove larger, cleaner particles from the smaller, and more polluted ones. Characterization in terms of particle size and contaminant level in each fraction is the most important parameter in determining the suitability of this process. They include hydrocyclones, which separate the larger particles greater than 10–20 μm by centrifugal force from the smaller particles, fluidized separation removes smaller particles at the top (Less than 50 μm) in countercurrent overflow in a vertical column, by gravimetric settling and flotation, which is based on different surface characteristics of contaminated particles, magnetic separation, used to separate these from ferrous metals. These methods have been used in mineral ore processing.

### 17.2.7 Pyrometallurgical Separation

Pyrometallurgical processes use high temperature furnace to volatilize metals in contaminated soil. Temperatures of 200–700 °C are used to evaporate the contaminant. After volatilization, metals are then recovered or immobilized. These methods are most applicable to mercury since it is easily converted to its metallic form at high temperature. Other valuable metals such as gold and platinum can also be recovered from low soil concentration. This type of treatment is usually performed off-site due to lack of mobile units, and is applicable to highly contaminated soils (5–20 %) where metal recovery is profitable. Prior to pyrometallurgical separation the soil must be concentrated by physical or soil washing.

### 17.2.8 Soil Washing

Soil decontamination can also be carried out by in situ washing of soil. It is a physical separation technique, which consists of extraction of contaminants by suspending them in watery solutions, i.e., by dissolution. The main principle of soil washing is a selective classification of highly contaminated pollutants followed by the solid or liquid phase separation of the remaining suspension (Bradl and Xenidis 2005). It may consist of excavation, fragmentation, separation in different grain sizes, washing of the different fraction, and their disposal (Castelo-Grande et al. 2010). This technique is often considered as a pretreatment for the reduction of the toxic contents of the contaminated soil, and to be treated by another technology. The physical process of soil washing involves two principal steps:

*Mechanical/Physical sorting* Physical separation may include screening followed by density or gravity separation. Mechanical screens and hydrocyclones are often used to separate the soils into various size fractions. The bulk oversize material consists of clean or slightly contaminated cobbles and stones, and may undergo a water rinse before being returned to the site as fill. The slit and clay fraction generally contains the highest concentration of the contaminants, and is usually treated by the solidification/stabilization techniques to immobilize the contaminants prior to land filling. The remaining fine and coarse sands can be further treated using density/gravity separation process to separate high density aggregates and metal fragments. Magnetic contents are removed manually with the help of magnets.

*Wash water treatment* Fresh water and cleaned process water are added to the soil. From the suspension, cleaned soils fractions are separated and contaminants are further proceeded for further treatment.

For the process of soil washing the knowledge of particle size dependent pollutant distribution is of vital significance. It is one of the few permanent treatment alternatives to remove metal contaminants from the soils. This technology is particularly cost-effective and well established in mineral industry.

## 17.3 Chemical Techniques

A range of chemical processes have been applied to soil to destroy or convert pollutants into less toxic forms, to extract them, or to immobilize them. Wood (2001) suggested that chemical treatments can be highly specific for some pollutants, e.g., PCBs and halogenated alkanes.

### *17.3.1 Oxidation-Reduction Reaction*

Chemical treatment by reductive as well as oxidative mechanisms may be used to detoxify or decrease the mobility of metal contaminants (Evanko and Dzombak 1997). This is commonly used for waste water treatment. Oxidation reactions detoxify, precipitate, or solubilize metals and involve addition of potassium permanganate, hydrogen peroxide, and hypochlorite, or chlorine gas. Neutralization reactions are performed to adjust the pH of acidic or basic soils (lime). Reduction reactions are induced through the addition of alkali metals, such as sodium, sulfur dioxide, sulfite salts, and ferrous sulfate. Sometimes chemical treatment is used to pretreat the soil for solidification or other treatments. These reactions are, however, not specific and, therefore, there is a risk of converting other metals into more toxic or mobile forms. Arsenic is most applicable for chemical oxidation since As (V) is less toxic than As (III). Hg, Pb, Se, and Ag are also applicable for reduction. These chemical treatments can be performed in situ by injection into ground water, but have the potential to introduce further contamination.

Over the last two decades, Fenton treatment has emerged as a viable remediation technology for PAH-contaminated soils. Several reviews on various Fenton-based treatments for contaminated soils have been published (Cravotto et al. 2005). In these works, PAHs have been grouped as hydrophobic or semi-volatile contaminants. PAHs are known to be toxic, mutagenic, carcinogenic, and teratrogenic, most commonly found at sites contaminated with coal tar and creosote, especially as the heritage from the manufactured gas plants (MGP) and wood treatment facilities of the last few centuries. Effective decontamination of the soil can be achieved by using advanced oxidation process (AOPs), which is based on Fenton’s reaction (hydrogen peroxide catalysed by iron), involving solely one or a combination of physical, chemical, biological, and thermal processes .Faster and more efficient degradation of recalcitrant compounds such as PAHs can be achieved using AOPs (Cravotto et al. 2007).

### *17.3.2 Immobilization*

Immobilization approaches are favored where pollution covers an extensive area, and where the main targets to be protected are water resources and plants. Immobilization can be achieved by complexing the contaminants or through increasing the soil pH by various amendments including addition of liming materials, phosphate compounds, and biosoilds (Alloway and Jackson 1991). Increased pH decreases the solubility of heavy metals like Cd, Cu, Ni, and Zn in soil. Although the risk of potential exposure to plants is reduced, their concentration remains unchanged. Mechanisms include increasing metal adsorption through higher surface charge, formation of insoluble metal complexes, precipitation, and redox reactions leading to immobile valency form. Basta et al. (2001) found that a range of soil amendments, especially alkaline biosolids, reduced the extractability and phytotoxicity of smelter waste polluted with Cd, Pb, or Zn.

### *17.3.3 Soil Washing (with Solvents)*

Soil contaminated with metal pollutants can be decontaminated by two treatment methodologies:

- That leaves the metal in the soil such as solidification/stabilization and vitrification, which immobilizes the contaminants, thus limiting their movement.
- That removes the heavy metals from the soils. Technology such as soil washing, in situ soil flushing transfer the contaminants to liquid phase by desorption and solubilization.

Soil washing for metals after physical treatment processes is then washed with solvents on the basis of their ability to solubilize specific contaminants and to transform them into nonhazardous material and also on their environmental impacts (Feng et al. 2001; Chu and Chan 2003; Khan et al. 2004). Soil washing usually employs wash solutions, such as acids, bases, chelating agents, reducing agents, or other additives as the extracting agents. Thus, heavy metals can be removed from soils using various agents added to the soil. This can be done in reactors or as heap leaching. These agents are inorganic acids such as sulfuric and hydrochloric acids (pH less than 2), organic acids including acetic and citric acids (pH not less than 4), chelating agents such as ethylenediaminetetracetic acid (EDTA) and nitrilotriacetic acid (NTA), and the various combinations of the abovementioned .The cleaned soil can then be returned to the original site. Both organics and metals are removed. The effectiveness of this treatment approach can be high for hydrophilic pollutants such as aniline and phenols (Rajput et al. 1994). Metal removing efficiencies during soil washing depends on the soil particle size, metal characteristics, extractant chemistry, and processing conditions. pH plays a very important role in metal extraction from soils (Peters 1999). Limited

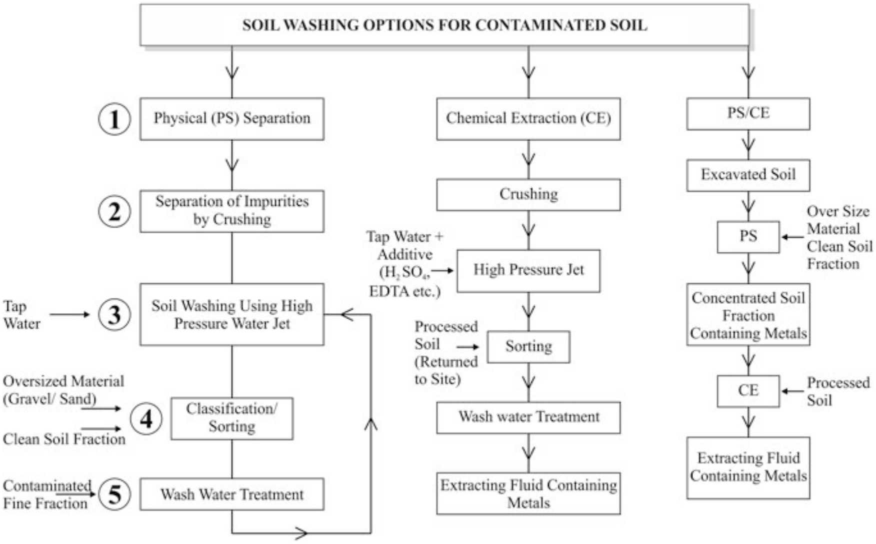


**Fig. 17.1** Schematic diagram of soil washing

experience with such technique has demonstrated that they create new problems, e.g., increase in mobility (and bioavailable) of the remaining metals in the decontaminated substratum, redistribution of pollution to other remaining fractions of the process (resins, sludges, etc.) (Woelders 1998; Dermont et al. 2008) (Fig. 17.1).

### *17.3.4 Soil Flushing*

This is in situ innovative remediation technology in which water is used with or without additives as flushing solutions to solubilize contaminants in soil to an area where they can be removed, with various methods of infiltration, such as infiltration basins, injection wells, and an infiltration trench. Various additives include organic or inorganic acids, sodium hydroxide, which can dissolve organic soil matter, water soluble solvents such as methanol, displacement of toxic cations with nontoxic cations, complexing agents such as EDTA, acids in combination with complexing agents or oxidizing/reducing agents. Once the water is pumped from soil, it must be extracted and then treated to remove the metals in wastewater treatment facilities or reused in the flushing process (Fig.17.2). Significant removal of chromium was achieved. Levels of chromium were reduced to 18 from 2,000 mg/l (USEPA 1996). Urlings (1990) decrease the Cd content 90 % of the soil from 10 to less than 1 mg/kg with dilute hydrochloric acid (pH 3). Since

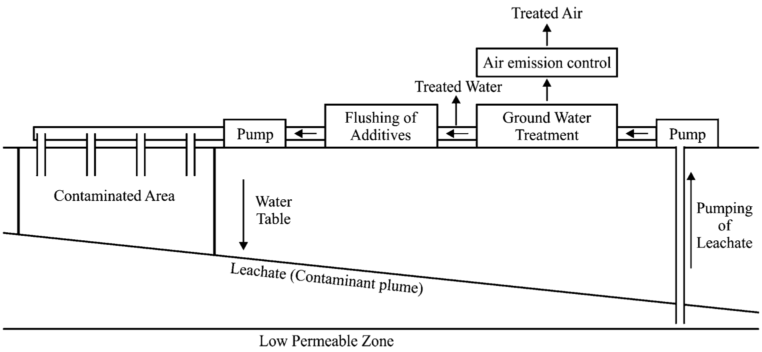


**Fig. 17.2** Schematic representation of soil flushing

flushing is conducted in situ, it reduces the need for excavation, handling or transportation of hazardous substances (Khan et al. 2004). More demonstrations are needed in this methodology, in addition to developing more understanding into the mechanisms for solution, metal recovery, and use of nontoxic additives.

### *17.3.5 Dechlorination*

Sometimes, reduction reaction can contribute to the decontamination of polluted soils. Chemical-reductive dechlorination is one such technique. Dechlorination, also known as dehalogenation, is a chemical technique based on the loss of halogen atoms (i.e., atoms of chlorine, fluorine, bromine, and iodine) from the halogenated organic molecules. Thus, converting toxic compounds into less toxic substances. These substances are frequently soluble in water, thus enhancing their separation from the soil. This technique applicable to polychlorinated biphenyls (PCBs), halogenated semivolatile volatile organic compounds, and pesticides (Castelo-Grande et al. 2010).

## 17.4 Biological Techniques

These techniques use living organisms in order to transform or degrade contaminants into less toxic form or remove the toxic contaminants of the soil (Kavamura and Esposito 2010). Microorganisms, soil invertebrates, and plants have all been exploited as potential agents of soil bioremediation, although most treatments have been based on microbial activity. The strategies can be applied in both in situ or ex situ ways depending on the contaminant and soil characteristics. Although biological solutions to inorganic pollution exist, the main emphasis has been on the treatment of organic compounds.

### 17.4.1 Biodegradation of Soil Pollutants

Degradation of soil pollutants mostly involves consortia of microorganisms, and may be achieved using in situ, on-site, or bioreactor approaches. On-site processes or bioreactors are likely to involve solid phase approaches such as landfarming (spreading of excavated contaminated soils in a thin layer usually combined with cultivation and/or nutrient inputs) or more "engineered" solutions compositing or the use of bio-piles (piles of polluted soils constructed to facilitate aeration and addition of nutrients). It can be applied to soils contaminated by crude oil, and also efficient in degradation of polycyclic hydrocarbons (PAHs). The management of the treatment environment is easiest with on site process bioreactors and difficult with in situ approaches, with bio-piles and compost techniques intermediate in this respect. Biodegradation technique is effective on a range of organic constituents. Bioaugmentation (addition of cultured microorganisms with the capacity to degrade target contaminants) or biostimulation (addition of nutrients to increase indigenous biomass or of substrates to promote cometabolism) of soil microbial populations may provide a means of accelerating pollutant degradation (Singer et al. 2005). There are many environmental factors that limit microbial biodegradation of soil pollutants including low temperature, restricted activity under anaerobic conditions, low levels of available nutrients or co-substrates, and limited bioavailability of pollutants. Although soil animals are not thought to have a significant direct role in the biological degradation of contaminants, their activities may stimulate microorganisms and improve the soil environment for microbial degradation (Haimi 2000).

Soils on many polluted sites are physically degraded and macro-fauna such as earthworms can improve these conditions (Scullion and Malik 2000). Recently, interest in the role of earthworm as "bioreactors" for degradation of contaminant such as trinitrotoluene have been reported. Biodegradation rate is controlled by microbial catabolic capacity, (Renoux et al. 2000). The presence of high concentration of heavy metals may inhibit the microbial growth and also the volatile components tend to evaporate rather than biodegrade. Thus, in most of these treatments, there will be some loss to atmosphere through volatilization and some physical or chemical stabilization of pollutants. Bioreactor treatments are increasingly favored as the microbes may also lead to formation of biofilm, which might accumulate organic pollutants for subsequent degradation of high molecular weight PAHs and heavy metals (Sheoran et al. 2010).

### 17.4.2 Bioleaching

It is a process of recovery of metals by some microorganisms capable of dissolving them from the environment. It is an effective alternative to chemical extraction processes. Microorganisms like *Thiobacillus ferrooxidans* and *T. thiooxidans* bacteria under aerobic and acidic conditions (pH 4) at temperature between 15 and 55 °C, depending on strain promote the microbiological leaching of metals such as copper, silver, uranium, and zinc by the oxidation followed by electron transfer to oxygen inducing the metal solubilization (Gadd 2004; Kavamura and Esposito 2010). Leaching can be performed directly by oxidation of metal sulfides to produce sulfuric acid, which then can desorb the metals on the soil by substitution of protons. Indirect leaching involves conversion of $Fe^{2+}$ to $Fe^{3+}$, which in turn oxidizes sulfur minerals to $Fe^{2+}$ producing acidity. Several options are available for bioleaching including heap leaching, bioslurry reactors, and in situ processes. Anoxic sediments are more suitable for treatment since the bacteria can solubilize the metal compounds without substantially decreasing the pH. Copper, zinc, uranium, and gold have been removed by *Thiobacillus* species in biohydrometallurgical processes (Karavaiko et al. 1988). Another fungus *Aspergillus niger*, which can produce citric and gluconic acids has a potential for remediation of metal contaminated soil. They can act as acids (pH 3.5) and chelating agents for the removal of metals such as copper from oxide mining residues (Mulligan et al. 1999b). Mercury and cadmium can be oxidized, while arsenic and iron can be reduced by microorganism. Cr (VI) can be oxidized to Cr (III) that is less mobile and toxic. Bacteria such as *Bacillus subtilis* and sulfate reducing bacteria in the presence of sulfur can perform this reaction.

### *17.4.3 Biosorption*

Biosorption is the process of binding of metals to cell surfaces (Vidali 2001). It is a biological treatment method, which involves the adsorption of metals into biomass of algal or bacterial cells that can be dead or alive. With the use of *Trichoderma reesei* adsorption and desorption of cadmium and copper were analyzed by Kim et al. (2003). Pb(II) and Cd (II) were recovered employing biomass of *Amanita rubescens* from aqueous solution using the ability of the macrofungus by Sari and Tuzen (2009). If large scale, inexpensive production techniques for the biomass are developed, this heavy metal treatment is promising (Hazardous waste consultant 1996).This method is only applicable for low concentrations of metals in water. Therefore, the cells could potentially be placed in permeable barriers for adsorption of metals in ground water.

### *17.4.4 Biodegradable Biosurfactants*

Surfactants are a class of natural chemicals, which are amphiphilic in nature, that promote the solubilization and emulsification of various types of organic and inorganic contaminants. Bio-surfactants are produced by bacteria and yeast. Biodegradable biosurfactants (surfactin, rhamnolipid and sophorolipid) are used to remove heavy metals from an oil contaminated soil (Mulligan et al. 1999a). The first two agents are produced by bacteria, while the last is produced by yeast. Biosurfactants are also able to remove metals from the sediments. Caustic surfactant could be used for removing the organically associated metals, while foam surfactant can be employed for extracting metals bound to carbonates and oxides (Dermont et al. 2008; Wang and Catherine 2004). Since these agents are biodegradable, they are able to enhance hydrocarbon removal, and can potentially be produced in situ, as they have a great potential for soil washing and soil flushing. This technology yet needs to be performed on commercial scale.

### *17.4.5 Bioventing*

This technique can be applied in situ with a source of oxygen necessary to initiate the processes. It injects air into the contaminated media necessary to run the process at a rate designed to maximize in situ biodegradation. It eliminates the off-gassing of volatilized contaminants to the atmosphere (Khan et al. 2004). The simulation of decontamination of several organic pollutants including variety of petroleum refinery products by bioventing was performed by Sui et al. (2007). Unlike biosparging, which involves pumping air and nutrients into the saturated zone, bioventing pumps the air only into the unsaturated or vadose zone (USEPA 1998). Bioventing also degrades less volatile organic contaminants and, because a reduced volume of air is required, it allows for the treatment of less permeable soils. During the application of bioventing in volatile solute transportation in soils, volatilization has an important role in the first day followed by biodegradation after this period (Suko et al. 2006). Baker and Moore (2000) have reported the optimized performance and effectiveness of in situ bioventing. Diele et al. (2002) have discussed numerical models and their applications in bioventing system design and operation. Any aerobic degradable substance can be treated by bioventing and ultimately leading to biodegradation. Bioventing is most successful on mid-weight petroleum products like diesel since lighter products tend to volatilize quickly, while the heavier products generally take longer time to biodegrade. If the contaminant has to be cleaned to a level lower than 0.1 ppm or if total petroleum hydrocarbon (TPH) has to be reduced to greater than 95 %, bioventing at that site may not be effective, and some other method may be needed for this saturated zone (USEPA 1998).

### *17.4.6 Phytoremediation*

In the past few years, green plants have shown several response patterns to the presence of potentially toxic concentrations of heavy metal ions. Most are sensitive even to very low concentrations; others have developed resistance and tolerance and accumulate toxic metals within roots and above-ground tissues, such as shoot, flower, stem, and leaves, etc. (Barcelo and Poschenrieder 2003). Such extraordinary ability of plants to accumulate heavy metals is described as hyperaccumulators. Hyperaccumulators are able to accumulate Zn concentration higher than 1 % and Cu, Pb, and Ni higher than 0.1 % of the tissue weight. The current criterion used to define a hyperaccumulator is a plant that can accumulate metal to a concentration that is 100 times greater than "normal" plants growing in the same environment (Brooks 1977; Reeves and Brooks 1983). This particular capacity to accumulate and tolerate large metal concentrations has opened up the possibility to use for remediation of polluted soils and waters. The use of hyperaccumulator plants to remove, destroy, or sequester hazardous toxic heavy metals is termed phytoremediation (Schnoor 1997).

Hyperaccumulator plants such as *Thlaspi*, *Utrica*, *Chenopodium*, *Polygonum sachalase,* and *Alyssim* have the capability to accumulate cadmium, lead, nickel, and zinc (Baker et al. 1991). In addition to hyperaccumulator, plants such as trees (Poplar) and grasses (Vetiver) are now being actively evaluated though, their metal bioconcentrating capability is well below that of hyperaccumulator plants (Burken and Schnoor 1998; Sebastiani et al. 2004). Decontamination of soil from radioactive contaminants by phytoremediation has been reported (Van denhove 2013). Two novel approaches, the use of agrobacterium transformed plant roots and mycelia cultures of fungi have been reported as research tool in the study of remediation of contaminated soil by Wenzel et al. (1999).

Phytoremediation is often also referred as botanical bioremediation or green remediation (Chaney et al. 1997). It involves the repeated cropping of plants on heavy metal contaminated soils until the soils metal concentrations have reached acceptable levels. After each cropping, the plant biomass is removed from the area and may be washed to reduce its volume where upon it can be stored in an appropriate area that does not pose a risk to the environment (Raskin et al. 1994; Chaney et al. 1997). Currently phytoremediation is used for treating many classes of contaminants including elemental (heavy metals and radionuclides) as well as organic pollutants (PCBs, PAHs, nitroaromatics) (Cunningham et al. 1996; Dushenkov 2003). This is most applicable to shallow soils with low levels of contamination. The main disadvantage is that longer times are required compared to other methods. Phytoremediation can be classified according to the mechanism and nature of contaminant (Table 17.1).

#### 17.4.6.1 Phytoextraction

It is the biological approach to remove the contamination primarily from soil and isolate it, without destroying the soil structure and fertility. It is also called phytoaccumulation. It is the process that involves the uptake and translocation of heavy metals by roots into the above ground portions of "hyperaccumulator" plants (Brown et al. 1994) (Table 17.2).

**Table 17.1** Phytoremediation—on the basis of mechanism and nature of contaminant (Sheoran et al. 2012)

| No. | Process | Mechanism | Contaminant |
|---|---|---|---|
| 1. | Phytostabilisation | Complexation | Inorganics |
| 2. | Phytoextraction | Hyperaccumulation | Inorganics |
| 3. | Phytovolatilization | Volatilization by leaves | Organics/inorganics |
| 4. | Phytodegradation/ phytotransformation | Degradation in plant | Organics |
| 5. | Rhizofilteration | Rhizosphere accumulation | Organics/inorganics |
| 6. | Rhizodegradation | Rhizosphere degradation | Organics |

In phytoextraction practice, metal accumulating plants are seeded or transplanted into metal polluted soil, and are cultivated using established agricultural practices. The roots of established plants absorb metal elements from the soil and translocate them to the above-ground shoots where they accumulate. After sufficient plant growth and metal accumulation, the above-ground portions of the plant are harvested and removed, resulting in the permanent removal of metal from the site. Following harvesting of pollutant-enriched plants the weight and volume of contaminated material can be further reduced by washing or compositing. Metal enriched plants can be disposed of as hazardous material or, if economically feasible, used for metal recovery (Cunningham and Ow 1996). Phytoextraction of metals for commercial gain is called phytomining (Au, Tl, Ni) (Chaney et al. 1998). This approach is suitable to remove most metals (such as Pb, Cd, Ni, Cu, Cr) and excess nutrient from contaminated soils. Examples of plant species (Table 17.2) used are plants belonging to Brassicaceae family, such as *Thlaspi* sp., *Brassica* sp., (Kumar et al. 1995a, b), and *Alyssum* sp. (Kramer et al. 1996). Radioactive contaminants have also been decontaminated by phytoextraction (Van denhove 2013) (Fig. 17.3).

There are two basic strategies of phytoextraction namely continuous phytoextraction and chelate assisted or induced phytoextraction. Continuous phytoextraction is the removal of metals, which depends on the natural ability of the plant to extract extraordinarily metal concentration from metal contaminated soil. Natural hyperaccumulators have the ability to solubilize readily available metals from the soil matrix, efficiently absorb them into the root, and translocate them to the shoot and storage in a non-phytotoxic form in the aerial portions (Pollard et al. 2002). Some of the natural metal accumulating plants secrete metal chelating compounds such as “phytosiderophores” (mugenic acid) to the rhizosphere and some secrete organic acids (citric, malic, and oxalic acid), which act as metal chelators and decrease the rhizosphere pH, thus increase the bioavailability of metals that are tightly bound to the soil and help to carry them into plant tissues (Kinnersely 1993; Nascimento and Xing 2006). The mycorrhizal fungi associated to rhizosphere also play important role in metal (Chen et al. 2005; Khan 2005; Abou-Shanab et al. 2006).

**Table 17.2** Some of the plants with potential for phytoextraction of various metals (Sheoran et al. 2011, 2012)

| Metal | Plant species | References |
|---|---|---|
| Cadmium | *Chamomilla recutita* | Kral'ova and Masarovicova (2003) |
| | *Helianthus annus* | Fenus and MacNeil (2003) |
| | *Arabidopsis halleri* | Macnair (2002) |
| | *Brassica juncea* | Kumar et al. (1995a), Salt et al. 1995b, Ebbs and Kochian (1998), Huang et al. (1997) |
| | *Thlaspi caerulescens* | Escarre et al. (2000), Lombi et al. (2001), Basic et al. (2006), Keller et al. (2006) |
| | *Salsola kali* | De la Rosa et al. (2004) |
| | *Hypericum perforatum* | Kral'ova and Masarovicova (2003) |
| | *Medicago sativa* | Drazic et al. (2006) |
| | *Zea mays* | |
| Copper | *Commelina communis* | Tang et al. (1997) |
| | *B. juncea* | Ebbs and Kochian (1998) |
| | *Ipomea alpina* | Malaisse et al. (1979), Baker and Walker (1990) |
| | *Erica andevalensis* | Asensi et al. (1999) |
| | *Elsholtzia splendens* | Jiang et al. (2002) |
| | *Pelargonium species* | Krishnaraj et al. (1999) |
| | *Silene vulgaris* | Song et al. (2004) |
| | *Hirschfeldia incana* | |
| | *Haumaniastrum katangense, Crepidorhopalon perennis, Acalypha cupricola* | Faucon et al. (2007) |
| Chromium | *Helianthus annus* | Davis et al. (2001) |
| | *Brassica juncea* | Kumar et al. (1995a), Huang et al. (1997), Han et al. (2004) |
| | *Convolvulus arvensis* | Gardea-Torresdey et al. (2004a, b) |
| | *Pelaronium species* | Krishnaraj et al. (1999) |
| | *Prosopis species* | Aldrich et al. (2003) |
| | *Salsola kali* | Gardea-Torresdey et al. (2005) |
| | *Sutera fodina, Dicoma niccolifera, Leptospermum scoparium, Genipa americana* | |
| | *Typha spp.* | Barbosa et al. (2007) |
| | *Amaranthus viridis* | Dong et al. (2007) |
| | *Miscanthus* | Zou et al. (2006) |
| | *Oryza sativa* | Arduini et al. (2006), |
| | *Convonvulus arvensis* | Bhattacharyya et al. (2005) |
| | *Leucaea leucocephalla* | Gardea-Torresdey et al. (2004a, b) |
| | *Willows (Salix sp.)* | Rout et al. (1999) |
| | *Loilium perenne* | Yu and Gu (2008) |

(continued)

**Table 17.2** (continued)

| Metal | Plant species | References |
|---|---|---|
| | | Vernay et al. (2007) |
| Mercury | *Eichhornia crassipes* | Riddle et al. (2002) |
| Nickel | *Psyshotria douarrei* | Davis et al. (2001) |
| | *Brassicae juncea* | Ebbs and Kochian (1998) |
| | *Thlaspi goesingense* | Reeves and Baker (1984) |
| | *Streptanthus polygaloides* | Reeves et al. (1981) |
| | *Alyssum bertoloni* | Minguzzi and Vergnano (1948) |
| | *Berkheya codii* | Robinson et al. (1997a) |
| | *Alyssum murale* | Robinson et al. (1997b) |
| | | Bani et al. (2007), Chaney et al. (2008) |
| | *Alyssum narkgrafii* | Vinterhalter and Vinterhalter (2005) |
| | | Perrier et al. (2004) |
| | *Sebertia acuminate Phyllanthus species, Euphorbia helenae, Leucocroton flavicans, L. linearifolius* | Berazain et al. (2007a, b) |
| Lead | *Dittrichia viscose* | Melendo et al. (2002) |
| | *B. pekinesis, B.campetris, B. carinata, B. juncea, B. napus, B. nigra, Helianthus annus, Pisum sativum* | |
| | *Thlaspi rotundifolium Zea mays* | Blaylock et al. (1997), Ebbs and Kochian (1998) |
| | *Sesbania drummondii* | Reeves and Brooks (1983) |
| | *Pelargonium species* | Huang and Cunningham (1996) |
| | *Vetiveria zizaniodes* | Sahi et al. (2002) |
| | *Pelargonium crispum* | Krishnaraj et al. (1999) |
| | *Helianthus annus, Triticum aestivum L., Trifolium respens L.* | Chen et al. (2000), Boonyapookana et al. (2005), Krishnaraj et al. (2000) |
| | *Vicia faba* | Yang et al. (1996) |
| | *B. juncea* | Srivastava et al. (2005) |
| | *Hemidesmus indicus* | Liu et al. (2000), Clemente et al. (2005) |
| | | Chandra Sekhar et al. (2005) |
| Zinc | *Sedum alfredii* | Long et al. (2002), Yang et al. (2002) |
| | *B. juncea, B.napus, B.rapa, Hordeum vulgare, Avena sativa,* | Ebbs and Kochian (1997), (1998), |
| | *Arabidopsis halleri* | Dahmani-Muller et al. (2000), |
| | *Viola calaminaria, Thlaspi calaminare* | McGrath et al. (2006) |
| | | Baumann (1885) |
| | *Thlaspi careulescens* | Baker and Walker (1990), Li et al. (2006) |
| | *Polygonium aviculare* | |
| | | Gonzalez and Gonzalez-Chavez (2006) |

(continued)

**Table 17.2** (continued)

| Metal | Plant species | References |
|---|---|---|
| Selenium | *B.napus, Festuca arundianacea, Hibiscus cannabinus* | |
| | *Astragalus racemose* | Banuelos et al. (1997) |
| | *Sinapis arvensis* | Rosenfeld and Beath (1964) |
| | *Astragallus bisulcatus* | Hambuckers et al. (2008) |
| | *Grindelia squarosa, Stangeria pinnata* | Smrkolj et al. (2007) |
| | *Larrea tridentate, Salvia roemeriana* | Goodson et al. (2003) |
| | *Dryopteris fern, Pteris genera* | Cruiz-Jimenez et al. (2005) |
| | *Typha spp.* | Srivastava et al. (2005) |
| | | Pollard et al. (2007) |
| Uranium | *B. chinensis, B. juncea, B. narinosa, Amaranthus species* | Huang et al. (1998) |
| | *Uncinia leptostachya, Coprosma arborea* | Whiting et al. (2004), Chang et al. (2005) |
| | *Picea mariana* | Babula et al. (2008) |
| Thallium | *Iberis intermedia, Biscutela laevigata* | Anderson et al. (1999), Leblanc et al. (1999) |
| | *Zea mays, B. napus* | |
| | *Hirschfeldia incana, Diplotaxis catholica* | Madejon et al. (2007) |
| | *Lolium perenne, B. napus, Phaseolus vulgaris* | |
| | *B. oleracea acephala,* | Makridis et al. (1996) |
| | *Iberis intermedia* | Al-Nazar et al. (2005) |
| Cobalt | *Haumaniastrum roberti* | Brooks (1977) |
| | *Haumaniastrum katangense, Crepidorhopalon perennis, Acalypha cupricola* | Faucon et al. (2007) |
| | *Anisopapus chinesis* | |
| Arsenic | *B. junceae* | Pickering et al. (2000) |
| | *Pteris vittata(Brake fern)* | Ma et al. (2001), Caille et al. (2004) |
| | *Eleocharis spp.,* | Flores-Tavizon et al. (2003) |
| | *Pityrogramma calomelanos* | Francesconi et al. (2002) |
| | *Pteris cretica, Pteris longifolia, Pteris umbrosa* | Zhao et al. (2002) |
| Gold | *B. junceae,* | Anderson et al. (1999) |
| | *B. codii, Chicory* | Lamb et al. (2001), Msuya et al. (2000) |
| | *C. linearis* | |
| | | Gardea-Torresdey et al. (2005) |

(continued)

**Table 17.2** (continued)

| Metal | Plant species | References |
|---|---|---|
| Silver | *B. juncea, Medicago sativa* | Harris and Bali (2008) |
| | | Borovicka et al. (2007) |
| | *Amanita strobiliformis* | |
| Manganese | *Macadamia neurophylla* | Brooks (1997) |
| | *Phytolacca acinosa* | Xue et al. (2004) |
| Platinum | *Sinapis alba* | Alt et al. (1998), (Kologziej et al. 2007), Babula et al. (2007) |
| | *Lolium perenne* | |

**Table 17.3** Some of the plants with potential for phytostabilization of various metals

| Plant species | Metals | References |
|---|---|---|
| *Agrostis tenuis*, *Festuca rubra* L. | Pb, Zn, Cu | Smith and Bradshaw (1992) |
| *Sesbania rostrata* | Pb, Zn | Yang et al. (1997) |
| *Cynodon dactylon* and *Festuca rubra*, *Typha latifolia, Phragmites australis* | Pb, Zn, Cu | Wong, (1982), Ye et al. (1997, 1998) |
| *Paspalum notatum*, *C. dactylcon*, *Imperata cyclindrica* | Pb, Zn | Shu et al. (2000) |
| *Lolium italicum, Festuca arundinaceae* | Pb, Zn | Rizzi et al. (2004) |
| *Hyparrhenia hirta*, *Zygophyllum fabago* | Pb, Zn, Cu | Conesa et al. (2006) |
| *Horedeum vulgare, Lupinus angustifolius, Secale cereale* | As | Mains et al. (2006a, b) |
| *B. juncea* | Cd<br>Zn, Cu, Mn, Fe, Pb, Cd | Bolan et al. (2003),<br>Clemente et al. (2003, 2006) |
| *Anthyllss vulneraria, Festuca arvernensis, Koeleria vallesiana, Armeria arenaria* | Zn, Cd, Pb | Frerot et al. (2006) |
| *H. hirta, Z. fabago* | Pb, Zn, Cu | Conesa et al. (2006) |

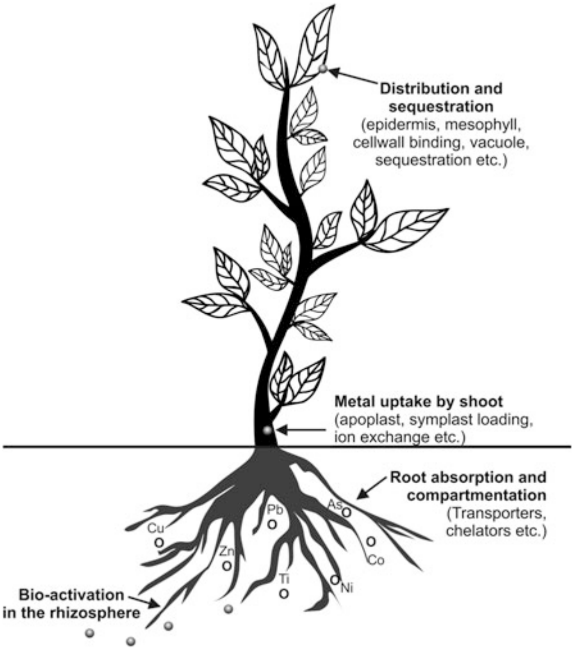
#### 17.4.6.2 Phytostabilization

Phytostabilization, also known as phytorestoration, is a plant-based innovative remediation technique that stabilizes wastes and prevents exposure pathways via wind and water erosion; provides hydraulic control, which suppresses the vertical migration of contaminants into ground water, and physically and chemically immobilizes contaminants by root sorption and by chemical fixation with various soil amendments (Cunningham et al. 1995; Salt et al. 1995a; Berti and Cunningham 2000). It may also serve as an interim strategy to reduce risk at sites where complications delay the selection of the most appropriate technique for the site (Fig. 17.4 and Table 17.3).

**Table 17.4** Some of the plants with potential for phytovolatilization of Hg and Se

| Plant species | Metals | References |
|---|---|---|
| *Arabidopsis thaliana* | Hg | Rugh et al. (1996) |
| *Liriondendron tulipifera* | | Rugh et al. (1998) |
| *Nicotiana tabacum* | | |
| *Astragalus racemosus* | Se | Evans et al. (1968) |
| *Brassica juncea* | | Pilon-Smits (2005) |
| *Salicornia bigelowii* | | Pilon-Smits et al. (1999) |
| *Typha latifolia* | | |

**Fig. 17.3** Schematic diagram showing mechanism of phytoextraction



For phytostabilization, the normal practice is to choose drought-resistant, fast growing crops or fodder, which can grow in metal contaminated and nutrient deficient soils. Plant should also be poor translocator of metal contaminants to above-ground plant tissues that could be consumed by humans or animals, the lack of appreciable metals in shoot tissues also eliminates the necessity of treating harvested shoot residue as hazardous waste. Metal tolerant plant species (Table 17.4) immobilize heavy metals through adsorption and accumulation by roots, absorption on to roots, or precipitation within the rhizosphere (Flathman and Lanza 1998). Phytostabilization also involves soil amendments (organic matter) to promote the formation of insoluble metal complexes that reduce biological availability and plant uptake, thus preventing metals from entering the food chain (Berti and Cunningham 2000).

**Fig. 17.4** Schematic diagram showing mechanism of phytostabilization

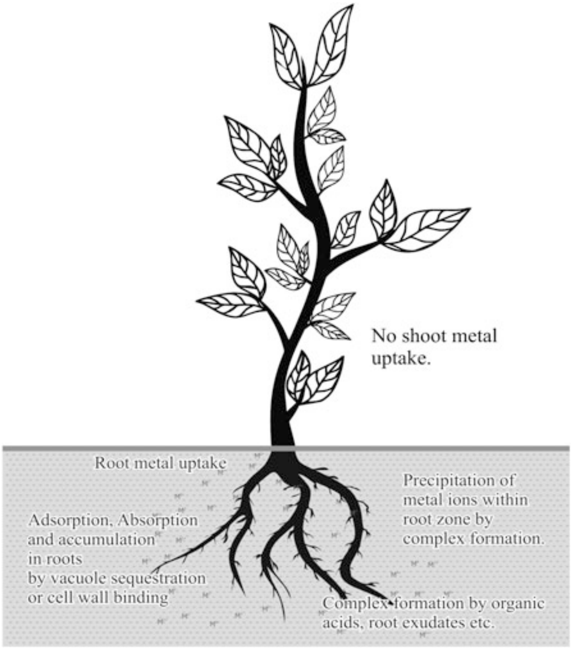


**Table 17.5** Some of the plants with potential for rhizofilteration of various metals

| Metals | Plant species | References |
|---|---|---|
| As, Cd, Cr, Ni, Pb, Zn | *Eichnornia crassipes*<br>*Populus sp., Thlaspi* sp. | Zhu et al. (1999), Mangabeira et al. (2004), Salt et al. (1995a, b) |
| Fe, Cu, Cr | *Lemna minor, Azolla pinnata* | Jain et al. (1989) |
| Cr | *Hydrocotyle umballata* | Yong-pisanphop et al. (2005) |
| Cr | *Bacopa monnieri* | Mangabeira et al. (2004), |
| Pb, Cu, U, Sr, Cs, Co Zn | *Helianthus annus* | Dushenkov et al. (1995) |
| Cr | *Spirodela polyrhiza* | Appenroth et al. (2000) |
| Pb, Ni, Cd, Zn, Cd, Cr, Cu | *Brassica juncea* | Raskin et al. (1997) |
| Pb | *Hemidesmus indicus* | Sekhar et al. (2004) |

### 17.4.6.3 Phytovolatilization

This involves use of naturally occurring or genetically modified plants that are capable of absorbing elemental forms of metal contaminants of subgroups II, V, and VI of the periodic table, such as As, Hg, and Se from the soil, and biologically converting them to gaseous species in the plant and releasing them into the

**Table 17.6** Plant enzymes that have a role in transforming organic compounds (Susarla et al.2002)

| Enzymes | Plants known to produce enzymatic activity | Application |
|---|---|---|
| Dehalogenases | Hybrid poplar (*populus* spp.), algae (various spp.), Parrot feather (*Myriophyllum aquaticum)* | Dehalogenates chlorinated solvents |
| Laccase | Stonewort (*Nitella spp.),* parrot-feather (*Myriophyllum aquaticum*) | Cleaves aromatic ring after TNT is reduced to triaminotoluene |
| Nitrilase | Willow (*Salix spp*.) | Cleaves cyanide groups from aromatic rings |
| Nitroreductase | Hybrid poplar (*Populus spp*.), Stonewort (*Nitella spp*.), parrot feather (*Myriophyllum aquaticum*) | Reduces nitro groups on explosives and other nitroaromatic compounds, and removes nitrogen from ring structures |
| Peroxidase | Horseradish (*Armoracia rusticana* P.Gaertner, Meyer & Scherb) | Degradation of phenols (mainly used in wastewater treatment) |
| Phosphatase | Giant duckweed (*Spirodela polyrhiza*) | Cleaves phosphate groups from large organophosphate pesticides |

atmosphere (LeDuc et al. 2004). The well-known example of genetic manipulation is the transfer and expression of a modified *E. coli* $Hg^{2+}$ reductase gene (*merA9pe*) in transgenic *Arabidopsis thaliana* plants (Rugh et al. 1996). Bacteria possessing *merA* are capable of converting highly toxic, $Hg^{2+}$ to less toxic elemental Hg. Thus, expression of *merA* in transgenic plants helps the removal of elemental Hg as vapors through natural mechanisms of respiration. Rugh et al. (1998) also examined the ability of yellow poplar (L*iriondendron tulipifera*) tissue cultures and plantlets to express modified mercuric reductase (*merA*) gene constructs (Table 17.4).

Phytovolatization potentially offers a low cost alternative for Se removal from soil and water. During the process of Se volatilization, plants metabolize various inorganic species of Se [e.g., selenate, selenite, and Se-Met (Met)] into a gaseous form dimethyl selenide, the major volatile form of Se, is more than 600 times less toxic than inorganic forms (Evans et al. 1968; Berken et al. 2002; Neumann et al. 2003). Terry et al. (1992) reported that members of Brassicaceae are capable of releasing up to 40 g Se/ha/day as various gaseous compounds. Indian mustard (*Brassica juncea*) has a high rate of Se accumulation and volatilization, and a fast growth rate, making it a promising species for Se remediation (Pilon-Smits 2005). Some aquatic plants, such as cattail (*Typha latifolia L*.), have potential for Se phytoremediation (Pilon-Smits et al. 1999). Volatilization of arsenic (As) as dimethylarsenite has also been postulated as a resistance mechanism in marine algae (Salt et al. 1995a, b). Phytovolatilization has been successful in tritium (3H), a radioisotope of hydrogen; it is decayed to stable helium with a half-life of about 12 years reported by Dushenkov (2003). This remediation method has the added benefits of minimal site disturbance, less erosion, and no need to dispose of contaminated plant material (Heaton et al. 1998). However, phytovolatilization should be avoided for sites near population centers and at places with unique meteorological conditions that promote the rapid deposition of volatile compounds. Hence, the consequences of releasing the metals to the atmosphere need to be considered carefully before adopting this method as a remediation tool (Suko et al. 2006; Padmavathiamma and Loretta 2007).

#### 17.4.6.4 Rhizofilteration/Phytofilteration

Plant assisted technique, which involves the use of both terrestrial and aquatic plants, to absorb, concentrate, and precipitate contaminants in the aqueous system has low contaminant concentration in their roots or seedlings (blastofilteration) (Dushenkov et al. 1995; Prasad and Frietas 2003). Mechanisms involved in rhizofilteration include chemisorption, complexation, ion exchange, micro precipitation, hydroxide condensation onto the biosurface, and surface adsorption (Gardea-Torresdey et al. 2004a, b). Root exudates and changes in rhizosphere pH also may cause metals to precipitate onto root surfaces. As they become saturated with metal contaminants, roots or whole plants are harvested for disposal (Flathman and Lanza 1998). Rhizofilteration can partially treat industrial discharge, agricultural runoff, or acid mine drainage. It can be used for Pb, Cr, Cd, Ca, Cu, Ni, and Zn, excess nutrients, and radionuclides (U, Cs, Sr), which are primarily retained with the roots (Ensley 2000) (Table 17.5).

#### 17.4.6.5 Phytodegradation

It involves the breakdown of organics to simpler molecules that are incorporated into the plant tissues. Plant contains enzymes or enzyme cofactors that can breakdown and convert ammunition wastes, chlorinated solvents such as trichloroethylene and other herbicides (Newman and Reynolds 2004). Various plant species that can degrade aromatic rings in the absence of microorganisms have been described by Dec and Bollag (1994) and Singh and Jain (2003). Polychlorinated biphenyls (PCBs) have been metabolized by sterile plant tissues. Phenols have been degraded by plants, such as horseradish, potato (*Solanum tuberosum*), and white radish (*Raphanus sativus*) that contain peroxidases (Roper et al. 1996). Poplar trees (*populus* species) are capable of transforming trichloroethylene in soil and ground water (Newman et al. 1997). The enzymes are usually dehalogenases (transformation of chlorinated compounds), peroxidases (transformation of phenolic compounds), nitroreductases (transformation of explosives and other nitrated compounds), nitrilase (transformation of cyanated aromatic compounds), and phosphatases (transformation of organophosphates pesticides (Boyajian and Carriera 1997) (Table 17.6).

#### 17.4.6.6 Rhizodegradation

Rhizodegradation is a biological treatment of a contaminant by enhanced bacterial and fungal activity in the rhizosphere of certain vascular plants. The rhizosphere is a zone of increased microbial density and activity at the root surface, and was described originally for legumes. Plants and microorganisms often have symbiotic relationships making the root zone or rhizosphere an area of very active microbial activity (bacteria and fungi) (Kirk et al. 2005). Plant litter and root exudates provide nutrients such as nitrate and phosphate that reduce or eliminate the need for costly fertilizer additives. Plant roots penetrate the soil, providing zones of aeration and stimulate aerobic biodegradation (Anderson et al. 1993).

Many plant molecules released by root dies and this exudation resembles common contaminants chemically and can be used as co-substrates. For example, phenolic substances released by plants have been found to stimulate the growth of PCB degrading bacteria (Fletcher and Hegde 1995). Recent studies have described enhanced degradation of pentachlorophenol in the rhizosphere of wheat grass (*Agropyron cristatum*), increased initial mineralization of surfactants in soil-plant cores, and enhanced degradation of TCE in soils collected from the rhizospheres (Knabel and Vestal 1992; Ferro et al. 1994).

### *17.4.7 Biochar*

It is environmental friendly, carbon rich, fine grained, and porous substance, which is produced by thermal decomposition of several kinds of biomass under oxygen-limited conditions and at a relatively low temperatures, and have the capability of moisture and nutrients retention (Tang et al. 2013). It can also mitigate climate change by sequestrating C from atmosphere into the soil (Marris 2006) and also improve soil properties and enhance recycle of agricultural and forestry waste (Luo et al. 2011), and also microbial activity (Lehman et al. 2011). Amendment by adding biochar in the soil with poor fertility can improve the crop yield. It has been reported by various studies that biochar acts as an efficient sorbent of various organic and inorganic contaminants because of its increased surface area and special structure. Biochar can also be used for heavy metal removal from contaminated soils. Several kinds of organic waste like animal manure, woodchips, and crop waste can serve as source materials of biochar, thus showing a relationship among biochar, waste recycle, and soil decontamination.

Surface adsorbtion and partition of pollutant molecules in the micropores of biochar enhances the bioremediation process .However, from different point of view, further studies on the safety uses of biochar is needed to be carried out (Beesley et al. 2011).

## 17.5 Special Techniques

### 17.5.1 Electrokinetic Enhanced Phytoremediation

Electro-kinetic remediation is an environmental restoration technique, which involves energy application of a low DC current or a low potential gradient, in the order of mA/cm$^2$, to the two electrodes that are inserted into the sediments and encompass the contaminated zone. The application of the electric potential causes the ions to move to their respective electrodes designated as cathode and anode for subsequent removal out of the contaminated soil. It is especially designed for the in situ remediation of the contaminated soils (Cameselle et al. 2013). The electrokinetic technology has been researched for over last two decades for the decontamination of soil. It helps in removal of heavy metals, recalcitrant, and hydrophobic organic contaminants.

Cameselle et al. (2013) reported the development of new coupled technology of electro-kinetic enhanced phytoremediation. This technology may lead to more effective and efficient remedial strategy as compared to the sequential use of these individual technologies (Fig. 17.5).

Basically, the coupled phytoremediation–electrokinetic technology consists of the application of a low intensity electric field to the contaminated soil in the vicinity of growing plants. The electric field may enhance the removal of the contaminants by increasing the bioavailability of the contaminants by desorption and transport of contaminants, even over short distances (Cameselle et al. 2013).

Variables that affect the coupled technology are: the use of AC or DC current, voltage level and mode of voltage application (continuous or periodic), soil pH evolution, and the addition of facilitating agents to enhance the mobility and bioavailability of the contaminants.

In the coupled phytoremediation-EK technology, the removal or degradation of the contaminants is performed by the plants; where as the electric field enhances the plant activity by increasing the bioavailability of the contaminants. Since the

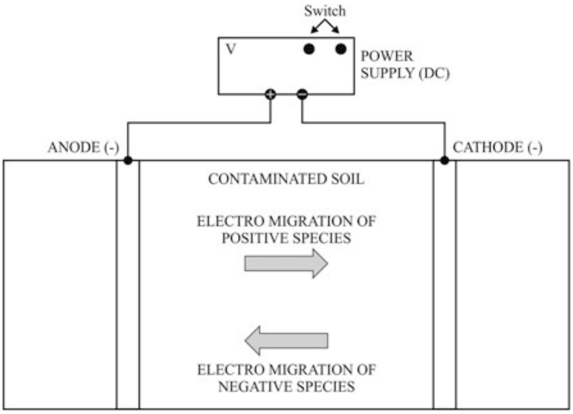


**Fig. 17.5** Schematic principle of electro-kinetic soil remediation

electric field efficiency drives increased amount of soluble heavy metals toward plant roots, which results in stress conditions for the plants, hyperaccumulator plant with a rapid growth period are considered the best candidates for use in combination with EK technique .Phytoremediation can be applied after EKR to remove residual concentration of contaminants, and to achieve cleaner soil (Wan et al. 2012). The coupled EK–phytoremediation technology has showed very promising results for the restoration of heavy metal contaminated soils, and may lead to more effective and efficient remedial strategy as compared to the sequential use of these technologies (Cameselle et al. 2013).

## 17.6 Conclusion and Future Scope

Soil contamination is a global concern and disrupts the health of the biosphere in numerous ways; as a result reduces the capacity of the soil to meet the needs of future generation. There is an urgent need to develop an effective and affordable technological solution. There are physical, chemical, and biological methods available for such remediation, but effective remediation of polluted soils requires accurate information on the distribution and behavior of contaminants as they interact with soil and broader environment. The selection of each technique is site specific. On site with a range of organic and inorganic pollutants present, combination of different treatment approaches may offer the best prospect for effective remediation. Physical treatment process is an inexpensive comparison to chemical treatment, but most methods of physical treatments remove pollutants from the complex polluted form for further treatment or disposal. Chemical process converts the pollutant into less toxic form, or to extract them, or to immobilize them. This is highly scientific and technical process, and requires expert manpower with technological resources. Chemical additives increase the remediation cost and in situ application also increases the chances of leaching of pollutant to the other uncontaminated area and ground water. More field demonstrations are required to match reactive media with contaminants, model lifetime performance, optimize retention times, and develop methods for regeneration of reactive media. Biological methods include microorganisms (bacteria), soil invertebrates, and plant. Various field of research are needed to optimize the efficiency of biological methodology including identification of microorganisms capable of promoting their degradation, and better systems for delivering microbes, and nutrients to pollutants. Phytoremediation is environment friendly and cost-effective emerging new technology for remediation of low to moderate area of contamination as well as have important role in ecology restoration. The majority of the research for phytoremediation has been conducted in laboratories under relatively controlled conditions for short period of time.

Finally, to optimize the ecologic and economic efficiencies, it must be recognized that we need to focus more on ecological engineering approach, which is more sustainable. Assessing remediation progress and efficiency is also important, especially because pollutants are rarely completely destroyed or removed from polluted soils and evaluation of remediation has focused on the extent to which they achieve acceptable reductions in the risks posed by pollutants. Although it is clear that remediation of environment contamination is important, the need of the hour is to shift the focus from remediation to prevention for sustainable future.

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