Chapter 8
Low-Cost Technology for Heavy Metal Cleaning from Water

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Abstract Uncontrolled and rapid industrialization and excessive anthropogenic activities have caused extensive pollution in the waterbodies. Water contamination has been a major concern especially in the developing world. The high number and level of pollutants in the wastewaters are hazardous to human health and the environment. Among major pollutants found in the wastewaters are heavy metals. Many conventional methods such as membrane filtration, adsorption, electrochemical treatment, and bio-sorption have been applied to remove and remediate the heavy metal contamination from wastewaters. Although some of the approaches are found to be successful, a number of these are not economical and time consuming. Among the new technologies, nanotechnology, emerging membrane technology, low cost sorbents technology, use of zeolites and metal organic frameworks have been developed as efficient and economical techniques for heavy metals removal from wastewaters. Biotechnological methods have great potentials to lower the cost of wastewater treatment for contamination removal. This chapter outlines the conven-

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tional wastewater treatment techniques and highlights the potential low cost methods for successful removal and remediation of toxic heavy metals from the wastewaters.

Keywords Water contamination · Type of pollutants · Sources of heavy metals · Conventional wastewater treatment · Advanced wastewater treatment · Remediation · Biotechnological strategies

8.1 Introduction

The demand for clean water in recent years has increased manifold due to the increase in the population (Pendergast and Hoek 2011). The World Health Organization (WHO) report estimates that, since 1990, only 2.5 billion people have access to the facilities of clean water, and in 2015, nearly 663 million people still do not have access to clean water. Water pollution has been caused by rapid urbanization, development in agriculture, and industrialization. The pollutants can be classified into organic, inorganic and biological pollutants. Heavy metal ions, viruses, organics, and bacteria are present in waste water. As freshwater availability is still a major issue for socio-economic development, the WHO has set a limit to the quantity of heavy metals allowable in aqueous solution (Machell et al. 2015). Inorganic metals can be beneficial for human health, but when the amount exceeds permissible limit, they become poisonous. Heavy metals have the ability to penetrate into the living beings and persist in the environment as they are non-biodegradable (Hashim et al. 2011) and eventually affects human health (Zou et al. 2016), causing nervous breakdown, cancer, and organ rupture. Toxic heavy metals such as Hg^{2+}, Cd^{2+}, As^{3+}, Pb^{2+}, and Cr^{6+} are carcinogenic and hazardous (Meng et al. 2014) when released in huge amount into the environment (Yin et al. 2018). Iron, cadmium, cobalt, mercury, zinc, nickel, lead, and manganese can cause toxicity in the groundwater, surface water, and the soil. Pollutants that enter the soil can be linked to their active sites (mineral clays, hydroxides and oxides of manganese and iron, and organic material). The activities will subsequently change, either increased or decreased, which will determine the degree of their harmful effects. Large amount of biological waste containing lead (Pb) is often found with its salts. In soil, lead makes stable complex composite with organic ligands which may become less harmful as compared to the free metal ions (Linnik and Nabinvaets 1986).

To ensure that the impact of exposure is not hazardous to public health, the removal of harmful metals from aqueous media and the reduction in the number of impurities is important (Atkovska et al. 2018). In this review article, the sources of different types of heavy metal pollutants, the routes of contamination, and different strategies for their removal from the environment are highlighted.

8.2 Sources and Impact

Metals having atomic weight higher than 50 are termed as heavy metals (Orlov et al. 1985; Orlov et al. 2002). The common ones are the 19 elements (Mn, Cr, Co, Ni, Fe, Zn, Cu, Ge, Cd, Sb, Sn, Ga, Mo, W, Pb, Te, Bi, Tb, and Hg). The list does not include Ba, actinides, and lanthanides, and several elements are considered as the highly distinctive polluting noxious metals - Cd, Cu, Pb, Ni, Co, Sn, Mo, V, Zn, and Hg. Heavy metalloids, also called as semi-metals, are also grouped as poisonous metals. Uranium, at molecular weight 238, is radioactive. The heavy metals in the environment are assembled, and are not easily degraded and can enter human food chain. The origins of heavy metals may come from the traffic and building material, sewage water and emission from atmospheric deposits (Sörme and Lagerkvist 2002). The sources can be categorized as households, drainage water, businesses, pipe sediments, release from the atmosphere, road, and construction materials and pipe sediment. Examples of other different sources are overflow through the rooftops, food, tires' wear, or car washing. Contaminated water containing chromium, zinc, nickel, cadmium, mercury, and copper, may come from different industries (Evanko and Dzombak 1997). Heavy metals like nickel, vanadium, silver and titanium are produced in electroplating, milling, and coating industries. Other heavy metals like tin, lead and nickel are generated from Printed-Circuit Board (PCB) manufacturing. Wood industry produces arsenic waste, pigment production industries produce chromium sulphide, petroleum industry produces used catalysts such as vanadium and chromium. All these industries produce large amount of residues and waste water that can be harmful, requiring extensive waste water treatment. Recycled water may contain as high as 30% of metals and metalloids (Fig. 8.1). Some types of metals can be detected and tracked like copper, zinc, nickel and mercury, and some may be undetected such as chromium, cadmium and lead. The biggest source of copper metal are roofs and tap water. For zinc, the largest sources are car washing and galvanized material; for nickel, the major source can be from drinking water itself and the chemicals in the wastewater treatment plant; and in the case of mercury, from amalgam in teeth.

Figure 8.2 shows the natural and anthropogenic sources of heavy metal ions. Volcanic eruptions, comets, erosions and weathering of minerals are some of the natural sources of the heavy metals which enter the atmosphere (Ayangbenro and Babalola 2017). Heavy metals that exist naturally are influenced by particle size, soil organic carbon, and mineral composition. Soil heavy metals may be modified by the external sources, weathering, or erosion (Herngren et al. 2005). Naturally occurring quantity of heavy metals may not be a cause for concern, but the anthropogenic activities may have disrupted their safe level in the environment. The main anthropogenic sources include mining activities, chemical and metallurgical industries, smelting process, and plastic manufacturing, cement industry, pesticides, fertilizers, transport and agriculture. (Yadav et al. 2017). Toxic heavy metals present naturally are not easily available for plants and microorganism, as they are in insoluble forms such as complexes, precipitates, or minerals. Such heavy metals also

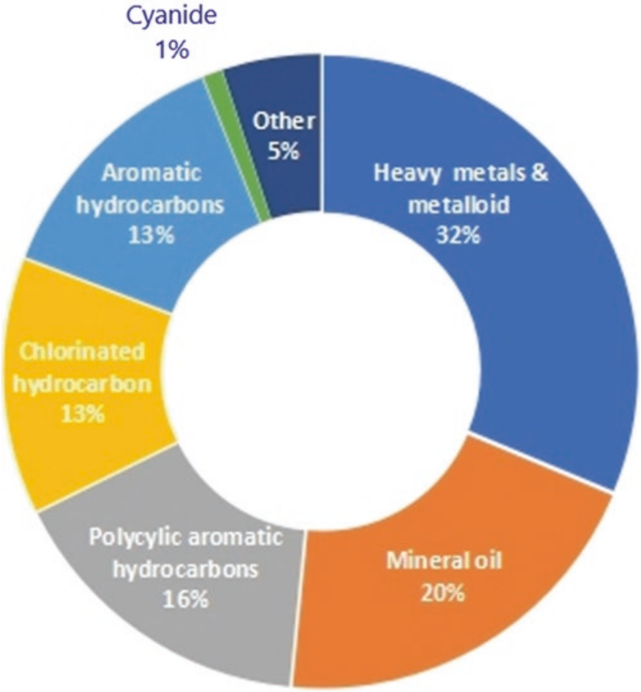

Fig. 8.1 Composition of water contaminants in recycled water. In recycled water 32% comprised of heavy metals and metalloids, 20% of mineral oil, 16% of polycyclic aromatic hydrocarbons, 13% of chlorinated hydrocarbon, 13% of aromatic hydrocarbon, 1% of cyanide, and 5% of other contaminants. (Modified from Bolisetty et al. 2019)

have strong interaction with the soil and the binding energy of these heavy metals and the soil is quite large.

Heavy metals coming from anthropogenic resources have high solubility and are very reactive due to which their bioavailability is very much higher than that of the heavy metals coming from the natural resources. Therefore, they are more dangerous to the biota. Anthropogenic sources of the heavy metals are diverse which include manufacturing of explosives; improper handling of industrial wastes, sewage and biosolids; electroplating industries and battery production; pesticides and phosphate fertilizers; dyes, printing and photographic materials; mining and smelting; and leather tanning, wood preservatives and textile industries (Fig. 8.3). The parameters which influence the accumulation of the toxic metals in the life cycle include soil characteristics, level of poisonous metals in the ground, limit of absorption by animals and limit of plant uptake. The pollution of the ground from the noxious metals can be caused by the ore processing and mining. Mining processes change the environment through the release of heavy metals and the accumulation of large quantity of heavy metals could take several decades for their recovery from the environment (Ayangbenro and Babalola 2017).

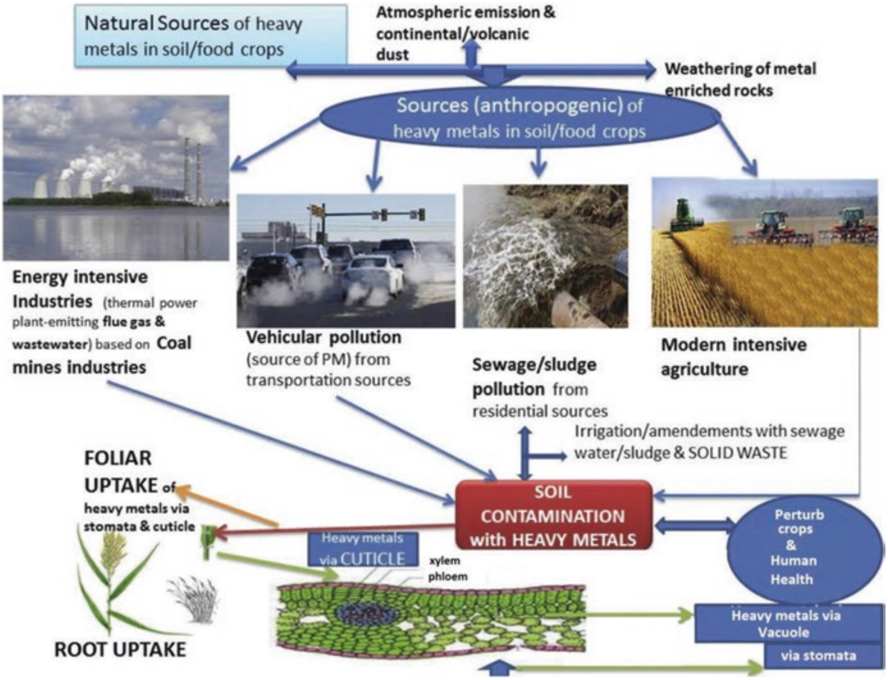

Fig. 8.2 Natural and anthropogenic sources of heavy metal ions. Two sources of heavy metals consist of natural sources i.e., atmospheric emission, volcanic dust, weathering of metals enriched rocks, and metals found in atmospheric condition, and anthropogenic sources i.e., energy intensive industries, road and water vehicles, sewage and sludge pollution from domestic areas, and modern intensive agriculture. These sources contribute significantly towards soil contamination with heavy metals. (Reprinted with the permission of Heavy metals in food crops: Health risks, fate, mechanisms, and management, Creative commons attribution, Rai et al. 2019)

Soil is the main base for harmful metallic ions to be released into the environment and atmosphere. Unlike organic contaminants, heavy metals are not biodegradable and the level will remain high in the ground for a long period of time before being released from any natural or anthropogenic activities (Bolan et al. 2003). The bioavailability and changes in the chemical structures are made possible by these release and interactions, and the biodegradability of some organic contaminants may be inhibited by the toxic metals present in the ground. The accumulation of heavy metal natural concentrations in the ground can be transported by carrier such as water and weathering pattern (Osman 2014). Soil rich in noxious metals not only risks polluting the groundwater, but also causes phyto-toxicity, and reduces the land use potential for agricultural productions (Maslin and Maier 2000).

Micronutrients are required by the plants and animals in an amount below the threshold limit. When the quantity increases, it becomes hazardous (Ojuederie and Babalola 2017). Pollutants such as heavy metals could severely affect animals, plants and human health and the productivity of crops (Rashid et al. 2019). Heavy metals are toxic depending on time of exposure, dose and heavy metal type. Each

Fig. 8.3 Anthropogenic sources of heavy metals. The main anthropogenic sources are attributable to urbanization, mining, modern agricultural practices, volatilization through different routes, fertilizer contamination with time, and mainly from modern industries. (Modified from Verma and Sharma 2017)

type has its own adverse effect on human body (Masindi and Muedi 2018). Heavy metals may get into the human body by inhalation and ingestion, causing genetic mutations (mutagenicity), damage of neural tissues (neurotoxicity), and affecting normal embryonic development (teratogenicity). As it is non-degradable, heavy metal ion attached to the cells may cause cell damage and increase the risk of cancer. Chromium, arsenic, nickel, cobalt, copper, lead and mercury are known to affect the circulatory, digestive and nervous system, leading to brain damage, blindness, cancer and death. Cadmium poisons the liver and kidney due to similar chemical properties, and interchanges with minerals like iron, zinc and copper and competes at the binding sites. Lead accumulates mainly in bones, brain and kidney. Arsenic poisoning causes gastrointestinal or nervous disorders. In plants, heavy metal contamination leads to reduction in water potential and protein oxidation, nucleic acid damage, cell death, enzyme and growth inhibition, and decrease in photosynthesis (Ashfaque et al. 2016).

8.3 Different Routes of Contamination

Many sources have caused the release of heavy metals in soil, waterbodies and eventually the food chain (Islam et al. 2018a, b). Ground water reservoir represents major total fresh water sources, and the pollution of toxic metallic ions in basewater and the impurities as contaminants in ground water will limit its use (Sun et al. 2018). Half of the world may be facing the harmful effects of ground water pollution where an estimated 100 million people are consuming heavy metals contaminated water every year (Rashid et al. 2019). Heavy metals may contaminate the ground water through natural sources (lithogenic sources) including disintegration of rocks, degradation of soil and precipitations, while the combustion of fuel, underground corroded pipes, mining, urbanization, industrial and agriculture wastes represent the anthropogenic routes (Rajeshkumar et al. 2018; Saleem et al. 2019). The natural routes involving weathering of rocks and minerals, erosion, surface water degradation and leaching are slow and are influenced much by climatic conditions, but the anthropogenic activities are fast and pose serious threats due to increasing population and industrial activities (Titilawo et al. 2018). Metal smelting and lead removal from paints and petroleum industries also have significant effect on the soil contents, and vegetative propagation (Alloway 2013) which could render the ground water unsuitable for consumption.

Other source of groundwater contamination include overabundance of sulphides, arsenic, manganese and other metals, the most common ones, being iron and manganese that occur naturally in the soil. Radioactive decay is the source of heavy metal contamination in rocks and sediments. Uranium decay, particularly, results in the release of radon and other harmful gases. In coastal regions, saltwater intrusion and the contamination with metal remnants of ship wreckage or plastic residues especially pose serious threats. Abandoned mine areas is not only unsuitable for crop production but also constantly release the toxic heavy metals and sulfide minerals such as FeS_2 (pyrite), FeAsS (arsenopyrite), PbS (galena), $CuFeS_2$ (Chalcopyrite) and (FeZn)S (Sphalerite), to the environment as sulphuric acid or metals from the ores and minerals. The acidity causes further release of more toxic heavy metals from the mineral sources and metal such as arsenic may be released from mine drainage. These toxic metals and pollutants continuously change their states and undergo various redox reactions, where their movement increase the risk of contamination to the ground water and surrounding areas (Karaca et al. 2019). Sediments may contain toxic elements such as cadmium, copper, lead, and chromium from sewage and industrialization water sediments which are discharged into the water bodies, leading to serious health hazards and deterioration of the water quality, which eventually causing harmful effects on aquatic life (Rajeshkumar et al. 2018). The wastes from smelting, electroplating and industrial processes and effluents could also contaminate drinking water, food and the surroundings (Chowdhury et al. 2016; Sakshi et al. 2019). The thermal power plant wastes from the combustion of coal generates large amount of solid ashes, which are sometimes dumped near the area of large ponds and water reservoir, resulting in the soil surrounding the area and the pond having high level of lead, molybdenum, astatine, chromium, manganese, nickel, cobalt, copper, vanadium (Sakshi et al. 2019).

The untreated solid and liquid wastes from agricultural crop land can be another major source of ground water contamination. Heavy metals, pesticides, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls which are present in the soil as contaminants, are toxic, mutagenic and carcinogenic (Sakshi et al. 2019). Fungicides, pesticides, insecticides, and phosphate-containing fertilizers have caused contamination of Zn, Cd, and Cu in the agricultural soil. To lower the contamination and for its prevention, it is pertinent to identify and apply multivalent approaches to measure the variety and probable origins of heavy metal accumulation in the soil (Chai et al. 2015). Positive-matrix-factorization (PMF) has been applied to locate and simplify the identification of the origin of soil pollution (Hu et al. 2013). The levels significantly affect the movability and availability of heavy metals in the soils. Greater quantity of cadmium and copper have been detected in the soil for industry and construction as compared to the soils without sewage irrigation (Yang et al. 2018). Leaching of metals from pipes of water distribution system is another anthropogenic route of ground water contamination (Chowdhury et al. 2016). Urbanization, untreated discharged wastes, agricultural activities, rapid industrialization and toxic metal leaching are deteriorating the groundwater quality (Rashid et al. 2019), where leaching of metals from pipes of water distribution system has contributed towards ground water contamination (Chowdhury et al. 2016). These different routes including deposition, industrial discharge and sewage waste as depicted in Fig. 8.4, may render the natural ground water reservoir as unfit for utilization (Singh et al. 2018; Titilawo et al. 2018; Varol 2019).

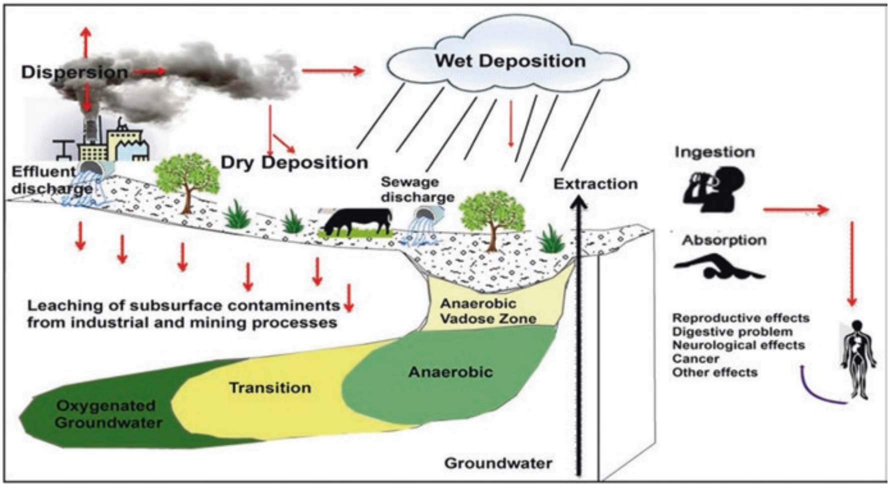

Fig. 8.4 Anthropogenic routes to contaminate the ground water quality with toxic metals. Industrial discharge and sewage discharge in water and soil not only leachout into soil and ground water, but also eventually disperse in air. The formation of dirty wet deposition in the atmosphere results in the down-pouring of dirty water into the ground and waterbodies, thereby leading to the contamination of groundwater with heavy metals. (Reprinted with the permission of Groundwater chemistry and human health risk assessment in the mining region of East Singhbhum, Jharkhand, India, Elsevier publisher, Singh et al. 2018)

8.4 Conventional Water Treatment Methods

The processing of surface water may involve the Drinking Water Treatment Plants (DWTPs), and the Waste Water Treatment Plants (WWTPs), both having to comply to the standards established by the World Health Organization (WHO) and Environmental Protection Agency (EPA). The organic, heavy metals and inorganic compounds and impurities need to be removed and eliminated before can be deemed safe for release into the environment and fit for human consumption. Toxic metal ions removal from aqueous medium can be treated by various conventional and advanced methods. As shown in Figs. 8.5 and 8.6, these primarily consist of sorption (Song et al. 2019), chemical precipitation and coagulation (Yu et al. 2017a, b), oxidation-reduction (Sheng et al. 2016), solvent extraction, photocatalytic degradation (Kumar et al. 2018), membrane filtration (Mikušová et al. 2014), and ion exchange (Radchenko et al. 2015). Figure 8.7 shows the merits and demerits of various techniques for the removal of hazardous substances from the contaminated water. There are major considerations to be made such as economical process, can be operated in industrial scale, no complex chemistry involved and the method can be tuned to achieve better results by functionalization (Xu et al. 2018). Adsorption is an effective and reliable way for the uptake of heavy metals. The advantages of adsorption include wide pH range, low cost and simple operation while the disadvantages are weak selectivity and waste product excretion. Similarly, chemical precipitation is low cost, and requires simple operation but it produces waste products and ineffective for the removal of trace ions (Pinakidou et al. 2016).

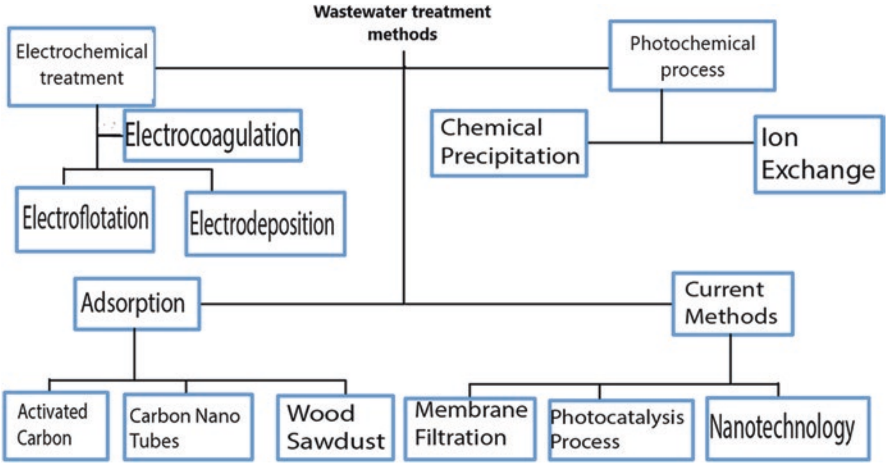

Fig. 8.5 Water treatment methods. The water treatment techniques mainly consist of adsorption (i.e., through wood sawdust, activated carbon, and carbon nanotubes), electrochemical (i.e. electroflotation, electrodeposition, and electrocoagulation), photochemical (i.e. chemical precipitation and ion exchange), and advanced method (i.e. membrane filtration, photocatalysis, and nanotechnology) to treat contaminated water and remove heavy metals. (Modified from Bolisetty et al. 2019)

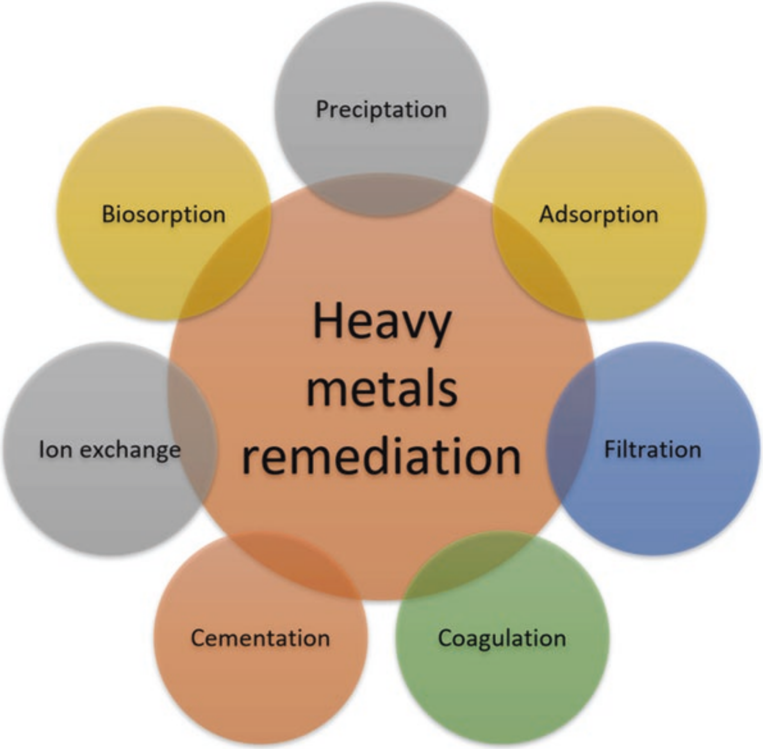

Fig. 8.6 Remediation of heavy metals. The methods like precipitation, adsorption, biosorption, ion exchange, filtration, coagulation, and cementation are mainly used to remove heavy metals from water. (Reprinted with permission of Environmental Contamination by Heavy Metals, Creative commons attributions 3.0, Masindi and Muedi 2018)

8.4.1 Preliminary Treatment

The large sized and coarse solids in waste water must be removed and this is the basis of preliminary treatments. The units should be maintained, and the impurities are removed during the process. This treatment includes coarse screening, grit removal and removal of larger objects in some cases. The flowrate of water in the grit chamber is maintained high and some organic solids are prevented to settle by the air flow. The organic and inorganic materials can settle down by sedimentation. Those that float will be removed by skimming. The treatment could achieve the removal of 50–70% suspended solids, 25–50% biological oxygen demand (BOD) along with 65% oil/grease. However, dissolved and colloidal particles are not separated. In primary sedimentation, nitrogen, heavy metals and organic phosphorous which are linked to the solids may be separated, and the wastes are known as primary effluents. In the small wastewater treatment plants, the grit removal is not the

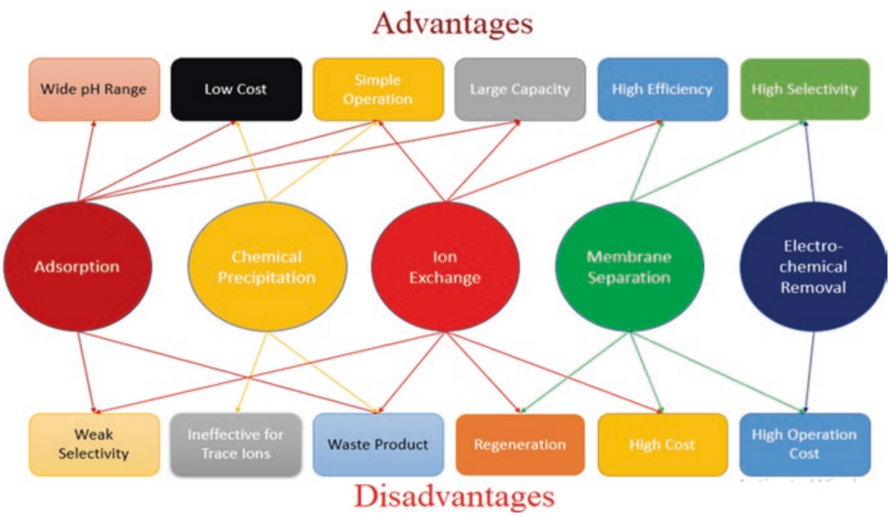

Fig. 8.7 Techniques for elimination of heavy metals and their advantages and disadvantages These techniques mainly involve adsorption, chemical precipitation, ion exchange, membrane filtration, and electrochemical removal of heavy metals. (Reprinted with permission of A review of functionalized carbon nanotubes and graphene for heavy metal adsorption from water: Preparation, application, and mechanism, Commons creative attributions (3.0), Xu et al. 2018)

first step. Comminutors are used to minimize the size of the large materials. In this way, the waste in the form of sludge will be obtained.

Toxic metals can be removed by specific adsorbents which exhibit significant affinity (Xiao et al. 2016). Activated carbon is a common adsorbent used to treat water and waste water for the removal of organic and inorganic impurities. Activated carbon has large meso and micropores, and greater surface area to remove heavy metals ions such as lead, nickle and zinc (Kuroki et al. 2019). The next steps may involve screening, centrifugation, chemical precipitation, microfiltration, coagulation, flocculation and gravitational methods. Flocculation, coagulation, microfiltration and chemical filtration are used when there is a high level of the metals, but these are less effective as compared to the tertiary treatment. The heavy metal removal in industries is primarily done by chemical precipitation where water insoluble materials are formed when the heavy metals react with different reagents. The pH variation of heavy metals also form insoluble materials which can be separated by sedimentation. The main advantages of chemical precipitation are it is easy to handle and cheap but the main drawback is that the heavy metals may not be at such amount of concentration that are acceptable to be removed or discharged. Large-scale treatment should be carried out for the heavy metals to be disposed off.

8.4.2 Secondary Water Treatment

Microorganism is capable of remediating the pollutants in the safe manner, using simple natural bioprocesses. In the aerobic treatment, micro-organisms are present with oxygen supply to convert the pollutants into carbon dioxide and biomass. Wastewater is combined with the oxygen which is supplied by the air compressor and circulated around the tank for good mixing. In anaerobic treatment, biogas is produced from the pollutant in the absence of oxygen. The methane produced can be used as energy source. These processes mostly involve the removal of organic pollutants. About 90% pollutant removal efficiency can be achieved with anaerobic process. The industrial wastewater containing heavy metal may be treated with the bio-adsorbent such as the activated carbon. The sequestration of Hg can be achieved by utilizing the bacterial biofilms, and zinc, copper, manganese and iron can be removed by using immobilized yeast. However, the industrial treatment with specific and genetically modified microbes is not widely used as yet although the potential is great for future application (Bolisetty et al. 2019).

8.4.3 Tertiary Water Treatment

Chemical precipitation is used in industry and is simple to operate to eliminate heavy metals from the inorganic waste. The dissolved heavy metals and the chemicals introduced react in the solution producing insoluble precipitates of metals. The size of the precipitate can be increased by coagulation, and the large size particles are removed as sludge. By varying the reaction conditions such as temperature, pressure, ions concentration and pH, the metal ion removal can be increased. The hydroxide treatment is commonly used as it is cheap, simple and easily atomized (Bolisetty et al. 2019). Crystallization and thermal treatment are a part of the tertiary water treatment. Thermal method, such as evaporation and distillation, provides energy to water which brings it to boiling temperature and the the steam is collected as a pure water. Crystallization of pollutants is achieved by adding the amount of seed for nucleation. Nitrogen, ammonia and phosphorous are crystallized by the process of struvite crystallization. (Bolisetty et al. 2019). Photocatalysis involving oxidation and reduction make use of the catalyst like titanium oxide (TiO_2) and ultravoilet light to produce free radicals that could degrade the pollutants (Bolisetty et al. 2019). Electrochemical treatment may involve electrocoagulation, electroflotation, electrodeposition and electrooxidation, making use of anode and cathode plate, where current is passed through the effluent containing the metal ions. The precipitation of metals in acid and base neutralization reaction could recover the metals (Gunatilake 2015).

8.4.4 Membrane Filtration

Membrane filtration technologies could remove heavy metals, total dissolved solids (TDS), algae, microorganisms, bacteria and micro-pollutants. Different materials are used such as polymer or ceramic, and the separation is on the basis of pore size and weight of impurities utilizing different size-based membrane processes such as nanofiltration or ultrafiltration. The pore size of the micro-filtration is the largest (100–1000 nm) (Bolisetty et al. 2019). Ultrafiltration is used to remove particles ranging in the microsize category where 90% of the heavy metals could be removed from the solution, requiring small space because of its compact size (Gunatilake 2015). Nanofiltration, which lies in between the size of ultrafiltration and reverse osmosis, can remove solute particles ranging in sizes from 100 to 1000 Da. Sufficient pretreatment steps must be taken as the small pore size of the nanofiltration membrane may get clogged easily. Although nanofiltration is considered less effective in removing ions, it shows better capability of removing the pharmaceutical active compounds.

Reverse osmosis involves the separation where the solution is forced through a membrane due to the applied pressure to overcome the osmotic pressure, allowing only the pure solvent to pass through. The semipermeable membrane however stops the impurities like the bacteria and metals from passing through. The separation depends on the pressure, water flux and concentration as it is a diffusive process (Gunatilake 2015). Ion exchange method (Fig. 8.8) is effective in converting a number of liquid phase impurities into solid state. The ion exchanger exchanges the cations and the anions that the metal ions at low quantity can be removed, and it

Fig. 8.8 Ion Exchange Filtration setup. (Reprinted with permission of Ion Exchange Filtration, MAA Chem, CC BY 4.0 (Open access), MAA Chem)

commonly involves economical material as synthetic organic ion exchanger and simple protocols but very effective to remove metals from the solution. The -SO_3H group present in the cation exchange resin has good selectivity, reversibility and ion exchange capacity for the lead ion. The mercury ion can be removed from the waste water by the Immobilized metal affinity chromatography (Imac TMR resin), ALM-525 resin and sarfion resin. The Imac TMR has microporous copolymer structure which could bind with Hg due to the presence of SH group. Cadmium can be removed by cationic resins Doweex50 W-X4 and purolite S-950 (Zhang et al. 2019).

8.5 Advanced Technology for Heavy Metal Ion Removal

8.5.1 Nano-Adsorption

Nanotechnology has been developed to purify drinking water, and provide efficiency through minimal generation of waste. Nano-magnetic oxides (NMO) are extensively used in the waste water treatments. The high surface area, stability and the nanostructures are advantageous to remove metal ions, but the adsorption properties are dependant upon the conditions of the operating unit. Zeolites-based water treatment plants have also been applied for the removal of toxic metals. Zeolites are negatively-charged lattice, composed of alumino-silicate with porous surface and cavity structure in a three-dimensional frame work. The negatively-charged mineral is balanced by the positive charge ions such as Na^+, K^+, Ca^{2+}, and Mg^{2+}. The zeolites can easily replace the cations present in water. The low cost and high surface area make zeolites one of the most efficient water treatment materials especially for heavy metal ions removal. The ion exchange properties of zeolites commonly exhibit the sorption order of $Pb^{2+} > Cu^{2+} > Ni^{2+}$. The Pb^{2+} and Cu^{2+} removal from aquatic system depend upon the composition of alumino-silicate framework, while the Ni^{2+} sorption mainly depends upon the size and shape of the micro-pores present on the surface of the lattice (Hong et al. 2019) (Fig. 8.9).

8.5.2 Molecularly-Imprinted Polymers

Ion printing is one of the advanced methods for the preparation of adsorbents, with high selectivity and affinity for ions. Ion printing polymers (IIP) bear the same properties as that of the molecularly-imprinted polymers which can detect metal ion and differentiate between the types of ions. Suitable monomers having cross-linkage properties and proper ion templates are pre-requisites for the synthesis of IIP. The ion templates and the monomers are the basic components to form the metal-ligand

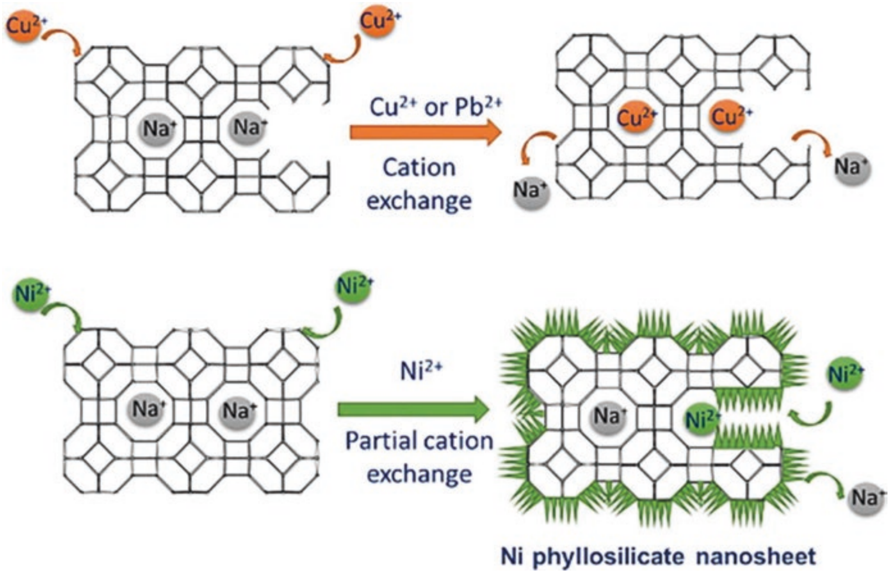

Fig. 8.9 Effect of zeolites on copper and lead sorption. Zeolites take up the heavy metal ions such as copper and nickel by exchanging with the lighter metal ion such as sodium to remove the ions from the sample. (Reprinted with permission of Heavy metal adsorption with zeolites: The role of hierarchical pore architecture, Elsevier, Hong et al. 2019)

complex where the coordination bond or electrostatic attractions are the main factors. Copolymerization of metal-ligand complex and the initiators are necessary to obtain the final product. The resultant polymers are washed with appropriate solution to obtain a polymer with three-dimensional specific cavities due to the removal of the template ions (Zhang et al. 2019).

8.5.3 Layered Double Hydroxides (LDH) and Covalent-Organic Framework (COF)

Apart from the noxious metallic ions present in cationic form, different types of anions are also present in the waste water or in air. Layered double hydroxides (LDHs) are active adsorbents used to remove these anions. (Dai et al. 2019). Another development is the specifically designed covalent organic frameworks (COFs) under defined conditions. COFs are divided on the basis of the monomers that are the basic component making up the specific COFs, with specific pore size to capture the desired heavy metal. Amide-based COFs could be recycled for several cycles of usage (Li et al. 2019).

8.5.4 Emerging Membrane Technologies

Different types of micro-porous membranes have been used for the removal of high molecular weight pollutants like colloides and dissolved particles from waste water. Specific pressure from 0.1 to 5 bars is commonly applied. Many types of polymer membrane such as Complexation-enhanced ultra-filtration (CEUF), simple polymer ultra-filtration, polyelectrolyte ultra-filtration and polymer supported ultra-filtration use the same working principle. *Saccharomyces cerevisiae*, sodium alginate, and seaweed-extracted polysaccharides are initially used in the synthesis and polymerization of CEUF. Metal ions are attached to the functional group of the polymers through ligand formation or electrostatic interaction (Abdullah et al. 2019). The complex formation of the polymers is achieved with the heavy metals utilizing chelation process as the basic mechanism of the CEUF.

In electro-dialysis, ionic-exchanger membranes (IEMs) comprising of anionic and cationic membranes are placed in parallel stacks. In between the stacks, a dilute feed stream along with the electron stream flows through the IEMs. The electric current is applied to the electrodes to allow the current flow in the solution feed through which the positive metal ions move towards the cathode. These ions then pass across the negatively charged membranes and halted by the positive membranes. Similarly, the negative ions move towards the anode, crossing the positive membrane and stopped by the negative membrane. Small amount of hydrogen gas is released at the cathode and chlorine and oxygen are removed at the anode as represented by the equations (Abdullah et al. 2019):

$$2e^{-} + 2H_2O \rightarrow H_2(g) + 2OH^{-}$$

$$H_2O \rightarrow 2H^{+} + 1/2O_2(g) + 2e^{-} \ or \ 2Cl^{-} \rightarrow Cl_2(g) + 2e^{-}$$

8.6 Low-Cost and Biotechnological Approaches

8.6.1 Biosorption

Biosorption has been increasingly used for heavy metal ion sorption utilizing agro-biomass and natural microorganism like fungi, algae and bacteria. The method is attractive for industrial scale application as it is cheap, efficient, can be regenerated, utilizes less chemicals, and the metals can be recovered (Joshi 2017). The biosorbent may be pretreated chemically for process improvement on the sorptive capability, and different types of biosorbents sorb the metal ions to a different capacity. Coal, coconut shells, wood have been turned into activated carbon (Joshi 2017). Clay is the potential alternative to the activated carbon especially the zeolites which have high surface area and negatively-charged functionalities to attract the metal

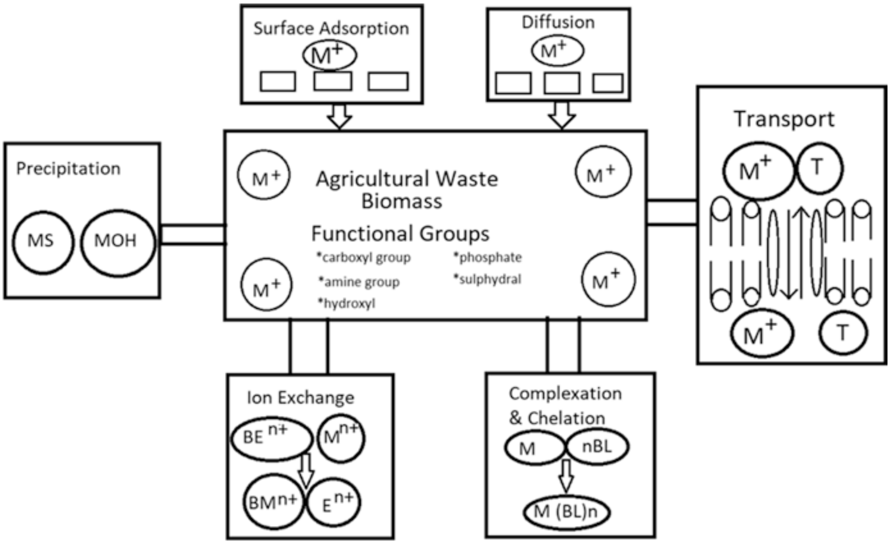

Fig. 8.10 Mechanism of biosorption. The heavy metals present in soil are sorbed via precipitation, ion exchange (Biomolecules with Exchangeable ions (BE), Biomolecules with Metal ions (BM)), complexation and chelation, and ion transfer, in order to remove heavy metal ions using agricultural biomass waste. (Reprinted with permission of A review on heavy metals uptake by plants through biosorption, Attribution international (CC BY 4.0), Sao et al. 2014)

ions. Chitosan which has versatile metal binding capacities, is also more cost-effective than the activated carbon. The raw materials can be sourced from the fishery wastes such as lobsters, shrimp and crab shells. Figure 8.10 illustrates the mechanism of biosorption for metal ion removal.

8.6.2 Microbial Remediation

Microbial remediation removes heavy metals by precipitation, reduction, oxidation, absorption and adsorption (Fig. 8.11). The uptake into the microbial metabolic pathways allows the heavy metals to be utilized for metabolism, respiration, fermentation and growth. Microorganisms such as algae, yeasts, bacteria and fungus have been utilized as biosorbents for the removal or recovery of heavy metals (Ayangbenro and Babalola 2017; Igiri et al. 2018). These may involve processes such as bioaccumulation, biosorption, and biomineralization (Ayangbenro and Babalola 2017). Bioaccumulation uses living cells to actively accumulate and transport the ions into the cells (Fig. 8.12). Biosorption can be passive but occurs very fast where the metal ion binds to the surface of the organisms. Then, the ion slowly perforates the cell membrane and enters the cell. Metal ions can be reduced to lower the reduction state to make them less harmful and converted into water soluble forms. It is the specific

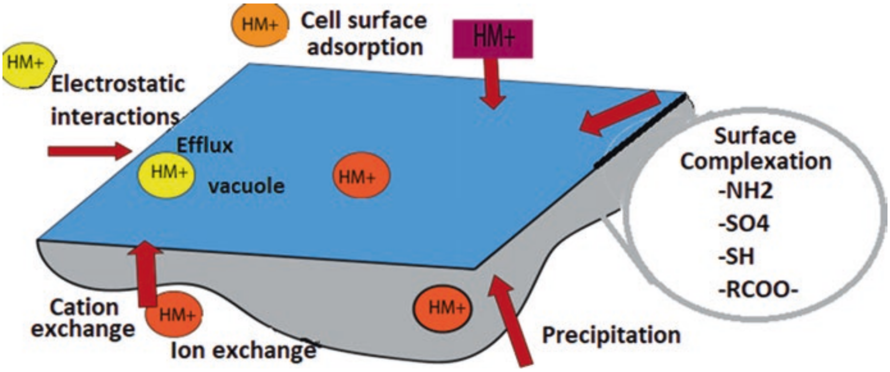

Fig. 8.11 Mechanism of heavy metal ion uptake by the microorganisms by electrostatic interaction, cation exchange, precipitation, or adsorption. (Reprinted with permission of Toxicity and bioremediation of heavy metals contaminated ecosystem from tannery wastewater: a review, Hindawi, CC BY 4.0, Igiri et al. 2018)

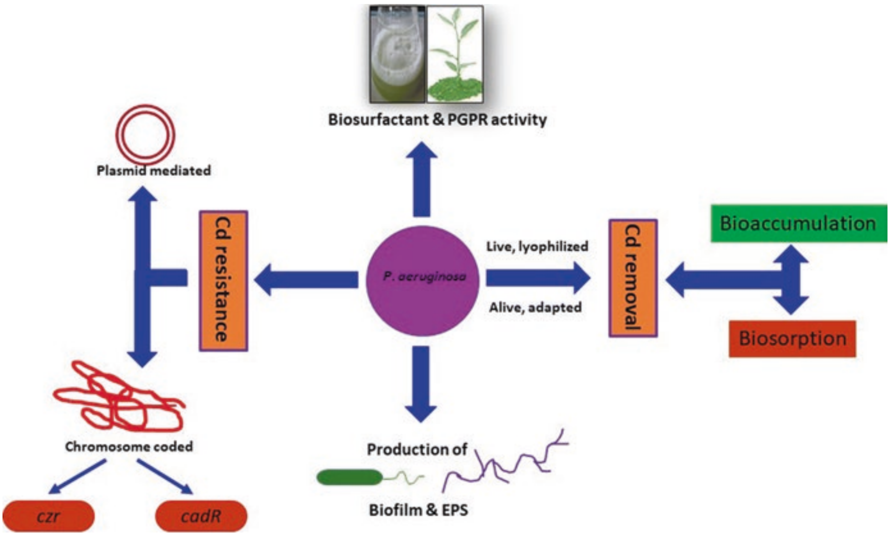

Fig. 8.12 Mechanism of bioaccumulation for cadmium. (Reprinted with permission of Cadmium (heavy metals) bioremediation by *Pseudomonas aeruginosa*: a minireview, Common Creative attributions, Chellaiah 2018)

characteristic of the microbial cells that converts the oxidation state of the metal ion from one form to another, thereby lessening the ion toxicity. Different metals and metalloids are used as electron donor or contributor by the bacteria for energy production. Some metals, also in oxidized form, act as acceptor of electrons in anaerobic respiration of bacteria. Metal ions can be reduced by enzymatic reactions to generate less harmful chromium or mercury. Through bioleaching (Fig. 8.13), metal

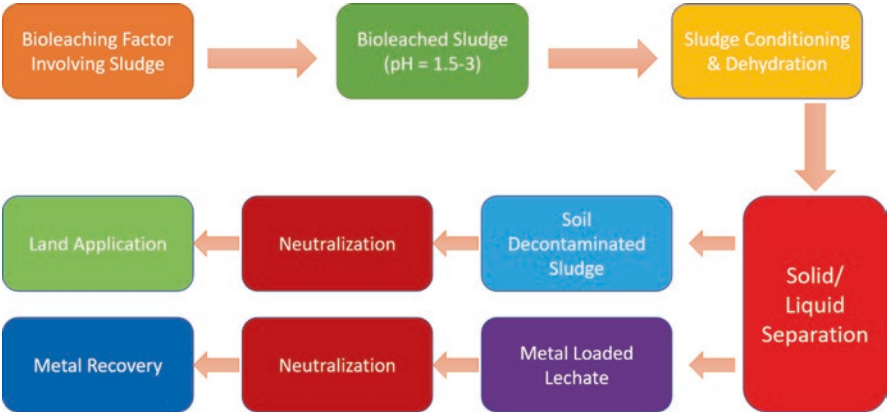

Fig. 8.13 Process of bioleaching. Bioleached sludge is conditioned and dehydrated leading to solid and liquid separation, thereby neutralizing it to obtain metal recovery. (Reprinted with permission of Bioleaching of heavy metals from sewage sludge: A review, Attribution international (CC BY 3.0), Pathak et al. 2009)

ions can be dissolved naturally and removed from the soil (Bahafid et al. 2017). Fungi have been used for biomonitoring of the toxic metal ions as the fungal cell wall contains proteins and polysaccharides that could bind the metal ions. Fungi, algae and yeasts such as *Yarrowia, Pichia and Candida* have high tolerance towards heavy metal ions. In the case of algae, this may depend on the internal structure and the environment or habitat of the species (Yadav et al. 2017). Different defence mechanisms such as ion complexation or binding protein formations have been used by the microorganisms to cope with the heavy metal stress. Metal toxicity due to the complex formation of metal ions and the biomolecules can block the metabolic activities and inhibit growth. There are however threshold limits beyond which the microbial tolerance towards toxicity may be reduced (Yadav et al. 2017).

8.6.3 Biotechnological Strategies

Biofilms can be applied as stabilizer, and used for bioremediation or biotransformation of persistent organic pollutants, pharmaceuticals/personal care products, and heavy metals (Edwards and Kjellerup 2013). Biofilms possess the characteristic of emulsifier or surfactant properties and could tolerate large amount of toxic metal aggregation. Encapsulating or immobilizing the biomass in polymeric matrix also improves the chemical and physical stability especially in cases where the level of heavy metal ions removal are not satisfactory. To increase the efficiency of remediation, recombinant deoxyribonucleic acid (DNA) technology is used to change the genome of microorganisms or specific enzyme pathway such as ligases by metabolic or genetic engineering. Heavy metals like arsenic, cadmium, and mercury can be removed using the genetically-modified microorganisms but the rate of decontamination still depends on the enzyme catalytic activity (Ojuederie and Babalola 2017). *Chlymadomonas reinhardtii* strain has been engineered to tolerate cadmium toxicity, and *Escherichia coli* is genetically engineered to specifically target As^{+3} removal. Over expression of arsenic-resistance (*ars*) operons in *Cyanobacterium glutamicum* has been developed as a strategy to remediate arsenic contaminated sites (Igiri et al. 2018).

In the cell cytoplasm, there is a mixed amount of metal ions that could be sequestered intracellularly by the biomolecules. These include the polysaccharides, lipids and peptidoglycan, with ligands and functional groups on the cell surface such as hydroxyls, carboxyls (-COOH), $-PO_4$, thiols, and amino group that are metal binding. Zinc ions for example are transported from the cytoplasm and get accrued in the periplasm, where the influx or efflux of ions take place with the physiological changes within and outside the cells. Different kinds of bacteria have the ability to remove metals by extracellular sequestration of metal ions, allowing precipitation of the metals and converting them into nontoxic elements. Examples are the sulphur-reducing bacteria which include *Desulfromonas* and *Geobacter* species. An anaerobe, *G. metallireducens,* has the capacity to reduce Mn^{4+} to Mn^{2+}, and Cr^{6+} to Cr^{3+}. The bacteria that reduces sulphur, produces large quantity of H_2S, causing the precipitation of metal ions that are positively charged. With *P. aeruginosa* strain, the precipitation of cadmium could take place in aerobic condition. Another economical biotechnological approach is phytoremediation, utilizing plants for the removal or remediation of toxic pollutants from groundwater, ground, and wind (Fig. 8.14). It is eco-friendly and could work in symbiosis with the microbial biomass. The phytoremediating plants maybe hyper or non-hyper accumulators. The hyper type does not require any enzymes for the removal of toxic metallic ions. Phytoextraction may include direct extraction of the metal ions into the plant vacuole, and rhizoremediation uses microbes in rhizosphere to remove toxic ions (Ojuederie 2017). As shown in Fig. 8.15, the biotechnological and biological approach, though may be time consuming and limited to specific contaminated sites, is more cost effective and environmentally-friendly to achieve long term remediation of the toxic pollutants.

8.7 Conclusion

Adsorption, biosorption electrochemical treatment and membrane filtration are conventional methods to reduce water contamination and to produce clean water. However, advanced methods for heavy metal removal from waste water including nanotechnology and emerging membrane technology, can be costly. Lower cost sorbent technology utilizing zeolites and metal organic frameworks have been applied to achieve reasonable economical treatments of heavy metals. Remediation of heavy metals from wastewaters via biotechnological strategies have attracted considerable interest not only because of the economics, but because these are more eco-friendly for long term use. The future direction may involve the application of biofilms and

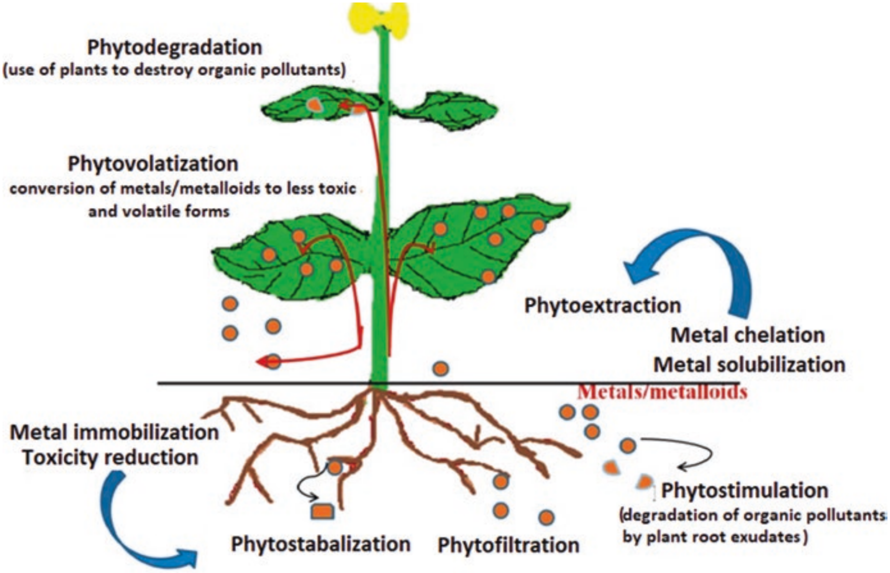

Fig. 8.14 Phytoremediation in plants. Phytovolatization converts metals into volatile form, phytodegradation degrades metals via enzymes, phytofiltration filters metal ions, phtyoextraction extracts the accumulated metals, phytostabilization limits the movement of metal ions, and phytostimulation degrades the metal ions *via* extruders. (Reprinted with permission of Microbial and Plant-Assisted Bioremediation of Heavy Metal Polluted Environments: A Review, Attribution international (CC BY 3.0), Ojuederie 2017)

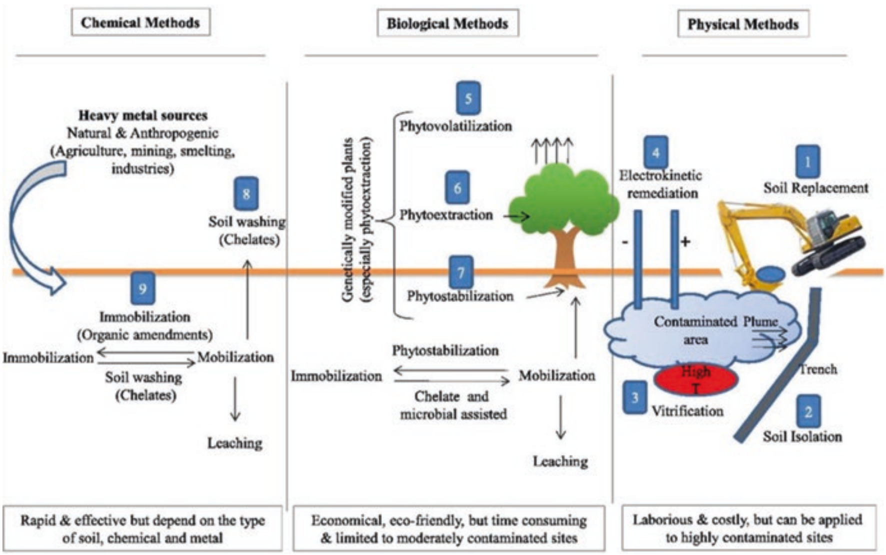

Fig. 8.15 Comparison of the technologies for toxic heavy metal remediation involving chemical, biological, and physical methods. (Reprinted with permission of A comparison of technologies for remediation of heavy metal contaminated soils, Creative Common Attribution (CC BY 4.0), Khalid et al. 2017)

surfactants in combination with microbial remediation and phytoremediation to achieve higher efficiency with long term reduction of environmental impact.

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