

Review

Remediation of heavy metals in drinking water and wastewater treatment systems: Processes and applications

Akpor O. B.* and Muchie M.

Institute for Economic Research on Innovation, Tshwane University of Technology, 159 Skinner Street, Pretoria 0001, South Africa.

Accepted 27 September, 2010

In small quantities, certain heavy metals are nutritionally essential for a healthy life. The heavy metals linked most often to human poisoning are lead, mercury, arsenic and cadmium. Other heavy metals, including copper, zinc and chromium are actually required by the body in small amounts, but can also be toxic in larger doses. They have the ability of dissolving in wastewaters and when discharged into surface waters, they can be concentrated and travel up the food chain. They can also seep into groundwater, hence contaminating drinking water, thereby harming the consumers of that water. The enactment of several water legislations and guidelines worldwide coupled with the need for environmental sustainability has necessitated the need for several stringent regulations for drinking water supply and wastewater discharge. To achieve unpolluted drinking water distribution and wastewater discharge, several technologies and processes for heavy metal remediation are currently in use. This review was therefore aimed at elucidating the major available technologies for heavy metal remediation in water, with emphasis on their processes and applications. Currently, no one of the existing technologies for heavy metal remediation (chemical remediation, phytoremediation or microbial remediation) is without some form of merits and demerits. There is therefore a proposed need for the utilization of safe and economical multiple/integrated approach for heavy metal remediation. The application of this may offer enormous public health, environmental and cost benefits.

Key words: Heavy metals, remediation, water.

INTRODUCTION

Heavy metals (elements with an atomic density greater than 6 g/cm^3) are one of the most persistent pollutants in water. Unlike other pollutants, they are difficult to degrade, but can accumulate throughout the food chain, producing potential human health risks and ecological disturbances. Their presence in water is due to discharges from residential dwellings, groundwater infiltration and industrial discharges. The discharge of wastewater containing high concentrations of heavy metals to receiving water bodies has serious adverse environmental effects. Their occurrence and accumulation in the environment is a result of direct or

indirect human activities, such as rapid industrialization, urbanization and anthropogenic sources (EPA, 2000; Hussein et al., 2005; Gardea-Torresdey et al., 2005; Martin-Gonzalez et al., 2006).

Heavy metal pollution is a global issue, although severity and levels of pollution differs from place to place. At least 20 metals are classified as toxic with half of them emitted into environment in concentrations that pose great risks to human health. The common heavy metals that have been identified in polluted water include arsenic, copper, cadmium, lead, chromium, nickel mercury and zinc. The release of these metals without proper treatment poses a significant threat to public health because of their persistence, biomagnification and accumulation in food chain. Severe effects include reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases,

*Corresponding author. E-mail: akporbo@tut.ac.za. Tel: +27(0) 12 382 3046. Fax: +27(0) 12 382 3071.

Table 1. Main effect of heavy metals in plants.

Metal	Effects
Cadmium (Cd)	Decreases seed germination, lipid content, and plant growth; induces phytochelatin production
Chromium (Cr)	Decreases enzyme activity and plant growth; produces membrane damage, chlorosis and root damage
Copper (Cu)	Inhibits photosynthesis, plant growth and reproductive process; decreases thylakoid surface area
Mercury (Hg)	Decreases photosynthetic activity, water uptake and antioxidant enzymes; accumulates phenol and proline
Nickel (Ni)	Reduces seed germination, dry mass accumulation, protein production, chlorophylls and enzymes; increases free amino acids
Lead (Pb)	Reduces chlorophyll production and plant growth; increases superoxide dismutase
Zinc (Zn)	Reduces Ni toxicity and seed germination; increases plant growth and ATP/chlorophyll ratio

(Source: Gardea-Torresdey et al., 2005)

death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system (Rajendran et al., 2003; Johnson and Hallberg, 2005; Silvia et al., 2006; Oelofse et al., 2007).

The danger of heavy metal pollutants in water lies in two aspects of their impact. Firstly, heavy metals have the ability to persist in natural ecosystems for an extended period. Secondly, they have the ability to accumulate in successive levels of the biological chain, thereby causing acute and chronic diseases. For example, cadmium and zinc can lead to acute gastrointestinal and respiratory damages to brain, heart and kidney damages (Fuggle, 1983; Nelson and Campbell, 1991; Nomanbhay and Palanisamy, 2005; Lon et al., 2008).

The use of domestic and industrial effluents, which may contain high concentrations of heavy metals on agricultural lands, is a common practice in some parts of the world. These toxic metals, when concentrated on plant tissues can have damaging effects on the plants themselves and may also pose health hazards to man and animals (Athar and Ahmad, 2002). Table 1 shows the main effects of heavy metals on plants. Although copper contributes to several physiological processes in plants, including photosynthesis, respiration, carbohydrate distribution, nitrogen and cell wall metabolism, seed production and disease resistance, higher concentration may account for suppressed root growth and leaf chlorosis. As an example, excess copper is known to be highly toxic to sweet potato, with concentrations as low as 5 μM in the root zone being sufficient to cause significant growth reduction. At concentrations above 20

μM , prevention root growth and death of the transplanted cutting may result (Alva et al., 1995).

Also, cadmium is reported to be strongly phytotoxic, disturb enzyme activities and inhibit the DNA-mediated transformation in microorganisms. It is also known to interfere in the symbiosis between microbes and plants, as well as increase plant predisposition to fungal invasion. Toxicity to plants, microorganisms and aquatic organisms has been reported in the presence of nickel and lead (Kuzovkina et al., 2004; Boonyapookana et al., 2005; Khan and Moheman, 2006; Jada and Fulekar, 2009).

With the enactment of several water legislations and guidelines worldwide (South Africa Water Act, US Clean Water Act, Australian Water Quality Guidelines, etc) coupled with the need for environmental sustainability (Goal 7 of the Millennium Development Goals), several stringent levels of water quality in domestic and industrial water and wastewater are required (Holtzman, 1994; Pivetz, 2001). Because heavy metal pollution affects the quality of drinking water supply and wastewater discharge, great efforts have been made in the last two decades to reduce pollution sources and remedy polluted water resources. This paper was therefore aimed at reviewing the different technologies with emphasis on processes and applications for the remediation of heavy metals pollutants in drinking water and wastewater treatment systems.

PHYSICOCHEMICAL REMEDIATION PROCESSES AND APPLICATIONS

The common physicochemical treatment processes for metal remediation in water include: Precipitation, ion

exchange and reverse osmosis.

Chemical precipitation

This is a widely used technology for the removal of heavy metals from water. It has long been the primary method of treating metal-laden industrial wastewater. The process involves the transformation of dissolved contaminants into insoluble solids, thereby facilitating the contaminant's subsequent removal from the liquid phase by physical methods, such as clarification and filtration (NEESA, 1993; Nomanbhay and Palanisamy, 2005). In a precipitation process, chemical precipitants (also known as coagulants and flocculants) are used to increase particle size through aggregation. The amount of chemical that is required during treatment is dependent on pH and alkalinity of the water. Usually, heavy metals in water are precipitated by adding sodium hydroxide or lime during neutralization. However, the results of this process are far from satisfying in many cases. A complete hydroxide precipitation does not take place especially in the presence of complexing agents (NEESA, 1993; EPA, 2000; Xu and Xu, 2008).

The precipitation of heavy metals in water has been practiced as a prime method of treatment in industrial waters for many years. Chemical treatment of contaminated groundwater to remediate heavy metals has been performed in column and pilot scale experiments. In one such study, granulated lime and calcium carbonate were used as coagulants (Lee et al., 2007). In the result, through the use of granulated lime as coagulant, more than 98% of arsenic and nickel were removed from artificially contaminated water. On the other hand, with granulated calcium carbonate, the removal efficiencies of arsenic and nickel were more than 97% but arsenic removal efficiency was lower than 5% (Lee et al., 2007). Furthermore, some investigators have developed and selectively used 1, 3-benzenedaimidoethathiol dianion (commercially known as Metx) to irreversibly bind soft heavy metals in aqueous solution. In a study by Matlock et al. (2002), Metx was found to remove over 90% of several toxic heavy metals from acid mine drainage samples. At pH 4.5, the concentrations of metals such as iron were found to be reduced from 194 ppm to below 0.009 ppm.

A combination of precipitation with other chemical treatment techniques, such as ion exchange has been reported to be effective in heavy metal removal in polluted waters. In South Africa, acid mine water from gold mine has been treated by the precipitation of heavy metals with lime and sulphides, followed by ion exchange. The process was reported to generate very pure water from acid mine water with a great flexibility and an acceptable cost. In the report, the oxidation and precipitation of heavy metals with lime and subsequent sulphide-carrier magnetic separation was observed to be

particularly suitable for the removal of heavy metal ions from the effluent of the particular gold mine that was investigated (Feng et al., 2000).

Precipitation with sulfide is reported to be the most efficient precipitation technique. This is because of its low solubility to destabilize soluble complexes. The simplest sulfur compounds are sodium sulfide salts (Na_2S and NaSH). Despite their simplicity, they are not recommended for use since they release toxic when pH is acidic, hence presenting great risks in case of accidental release or over-dosages. The best suggested alternative to the traditional sulfide treatment is the dithiocarbonate precipitation (METALSORB, 2004).

Chemical precipitation of metals can be justified by their low costs and can be performed by a simple pH adjustment. Other advantages include:

1. It is a well-established technology with ready availability of equipment and many chemicals.
2. Because it is a completely enclosed system, it is convenient, self-operating and requires low maintenance since only replenishment of chemicals is needed, with no need for sophisticated operators.

Despite the above advantages, chemical precipitation of metals in water still has the following disadvantages:

1. The precipitates are in the form of light tiny flocs requiring an extra coagulation/flocculation.
2. Large volumes of sludge are generated, inducing additional waste-disposal costs. The addition of treatment chemicals may increase the waste sludge up to 50% (EPA, 2000).
3. Regulation requirements are not always met using hydroxide and carbonate precipitation alone. Each dissolved metal has its own distinct pH level for maximum hydroxide precipitation.
4. Because metal hydroxides are increasingly soluble above or below their individual maximum precipitation point, even a slight pH adjustment to precipitate one metal may put another back into solution.
5. It requires working with corrosive chemicals, thereby increasing safety concerns. (EPA, 2000; METALSORB, 2004).

Ion exchange

Ion exchange is a reversible chemical reaction wherein an ion from water or wastewater solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. It is a process that is very similar to biosorption whereby the latter is known to actually function predominantly on the basis of ion exchange. Ion exchange uses mainly hydrocarbon-derived polymeric resins (Vaca et al., 2001; Volesky et

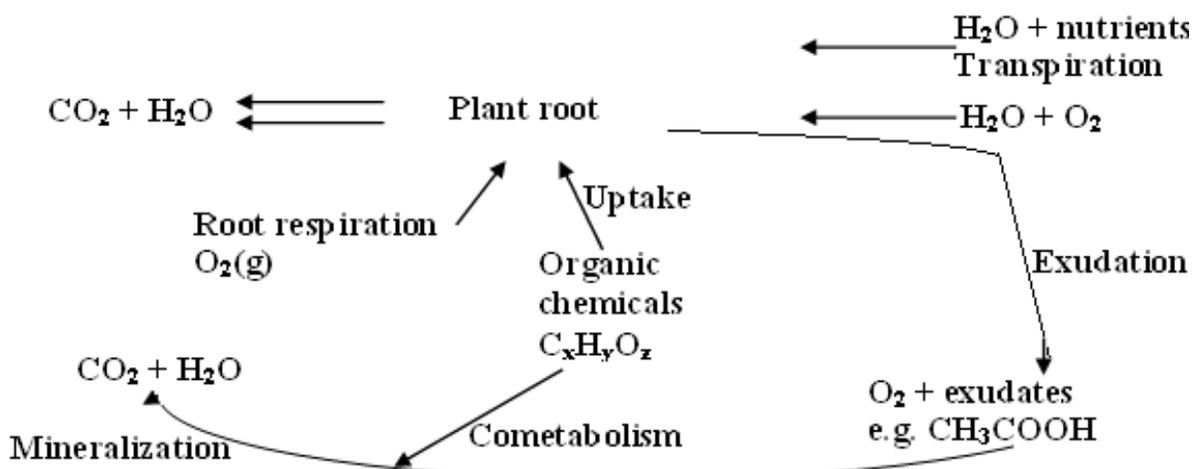


Figure 1. Schematic oxygen, water, and chemical flows through a woody tree (Schnoor, 1997).

al., 2003). This technique has been successfully used in the removal of several heavy metals from water. Vaca and co-workers have reported on the interactions of lead, cadmium and chromium, when competing for ion-exchange sites in naturally occurring clinoptilolite. Their study revealed effective removal of dissolved lead and cadmium removed within 18 h in batch reactors, with higher removal efficiencies that was greater than 95% in the acidic pH range (Vaca et al., 2001).

Reverse osmosis

Reverse Osmosis is a membrane process that acts as a molecular filter to remove over 99% of all dissolved minerals. In this process, water passes through the membrane while the dissolved and particulate matter is left behind. The process is very effective for removal of ionic species from solution. The resulting concentrated by-product solutions make eventual recovery of metals more feasible.

Despite the effectiveness, the membranes are relatively expensive both to procure and operate. The use of elevated pressures makes this technique costly and sensitive to operating conditions. A significant advantage of reverse osmosis over other traditional water treatment technologies is the ability to reduce the concentration of other ionic contaminants, as well as dissolved organic compounds (Volesky et al., 2003; Pawlak et al., 2005). Reverse osmosis had been applied in heavy metal removal both in small and large scales. For examples, in a study by Pawlak et al. (2005), when carrying out a pilot study conducted over a 30-day period on verification testing of a reverse osmosis membrane module, the total arsenic concentration in a feed water which was averaged 60 ppb during the test period was observed to reduce to an average of 1 ppb in the treated water.

PHYTOREMEDIATION PROCESSES AND APPLICATIONS

Phytoremediation is a remediation process that entails the use of plants to partially or substantially remediate selected substances in contaminated soil, sludge, sediment, groundwater, surface water and wastewater. It is also referred to as green remediation, botanoremediation, agro-remediation or vegetative remediation (Pivetz, 2001). Depending on the type of contaminant and underlying process, phytoremediation is broadly categorized into the following main areas: phytodegradation/phytotransformation, phytoaccumulation/phytoextraction, phytostimulation/rhizostimulation, phyto-volatilization, rhizofiltration and phytostabilisation. The removal of metal contaminants from water through phytoremediation occurs by any of three mechanisms: Phytoextraction, *rhizofiltration* and phytostabilisation (Lasat, 2000; UNEP, 2010).

Phytodegradation

Phytodegradation is the degradation or breakdown of organic contaminants by internal and external metabolic processes driven by the plant. It involves the use of plants to uptake, store and degrade contaminants within its tissue. During the process, plants actually metabolize and destroy contaminants within their tissues. Some contaminants can be absorbed by the plant and are then broken down by plant enzymes (Newman and Reynolds, 2004). As shown in Figure 1, during phytodegradation, the plants are able to take-up metal contaminants directly from the soil water or release exudates that help to degrade pollutants via cometabolism in the rhizosphere. For environmental application, it is vital that the metabolites which accumulate in vegetation are non-toxic

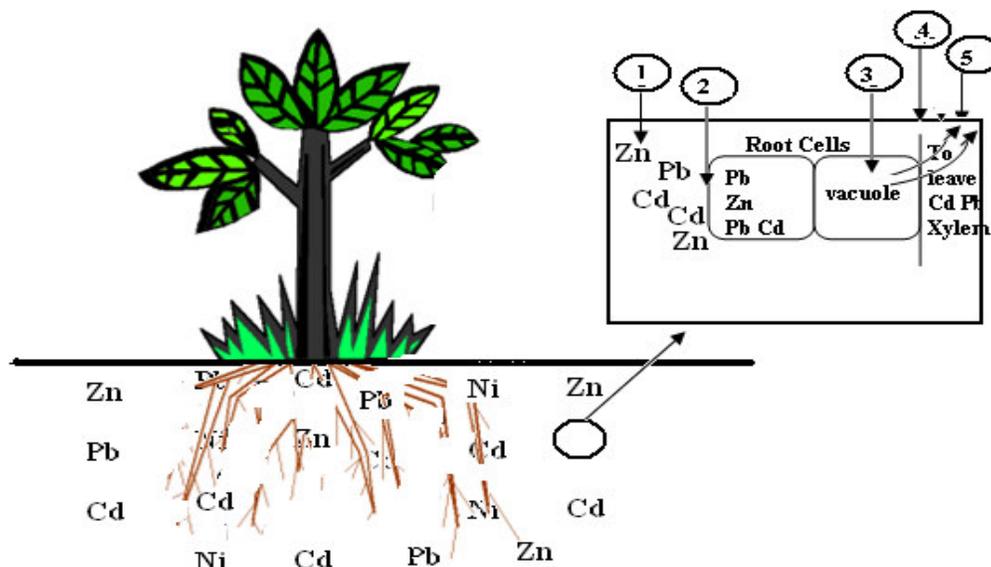


Figure 2. Metal uptake and accumulation in plants: (1) metal fraction is sorbed at root surface, (2) bio-available metal moves across cellular membrane into root cells, (3) fraction of the metal absorbed into roots is immobilized in the vacuole, (4) intracellular mobile metal crosses cellular membranes into root vascular tissue (xylem), (5) metal is translocated from the root to aerial tissues (stems and leaves)] (Lasat, 2000).

or at least significantly less toxic than the parent compound (Schnoor, 1997).

Phytoextraction

Phytoextraction is a phytoremediation process whereby plant roots absorb, translocate and store contaminants along with other nutrients and water. This method is used primarily for wastes containing metals. Figure 2 shows a schematic representation of metal uptake and accumulation in plants. Because different plants have varying abilities to uptake and withstand high levels of pollutants, many different plants may be used. Metal compounds that have been successfully phytoextracted include, zinc, copper, and nickel, but there is promising research being completed on lead and chromium absorbing plants (Lasat, 2000; UNEP, 2010). Because of the large quantities of specific metals hyperaccumulators are able to accumulate, they have been suggested for phytoextraction. The process of phytoextraction is known to occur either continuously (natural) using hyperaccumulators or induced through the addition of chelates to increase bioavailability (Utmazian and Wenzel, 2006).

Phytostimulation

During this process, plants release natural substances through their roots, thereby supplying nutrients to microorganisms, which in turn enhance biological

degradation (Figure 3). It is a symbiotic relationship between plants and microorganisms for the degradation of contaminants (Miller, 1996; Lasat, 2000). During phytostimulation, there is the release of organic substances and oxygen by plant roots, which stimulates microbial activity in the rhizosphere compared to bulk soils. This leads to increased microbial activity, which in turn results in a stimulation of natural degradation of organic contaminants (Meers and Tack, 2004).

Rhizofiltration

This process is similar to phytofiltration. The only difference is that the plants for remediation are raised in greenhouses with their roots in water. It is the breakdown of organic contaminants in water via enhanced microbial activity in the plant root zone or rhizosphere. The process is concerned with the remediation of contaminated groundwater rather than the remediation of polluted soils. The contaminants are either adsorbed onto the root surface or are absorbed by the plant roots. Plants used for this are not planted directly *in situ* but are first acclimated to the pollutant (Figure 4) (Miller, 1996; Lasat, 2000). A suitable plant for rhizofiltration applications can remove toxic metals from solution over an extended period of time with its rapid-growth root system. A variety of plant species have been found to be effective in removing toxic metals such as Cu^{2+} , Cd^{2+} , $\text{Cr} (6+)$, Ni^{2+} , Pb^{2+} and Zn^{2+} from aqueous solutions (EPA, 1998; Dushenkov and Kapulnic, 2000).

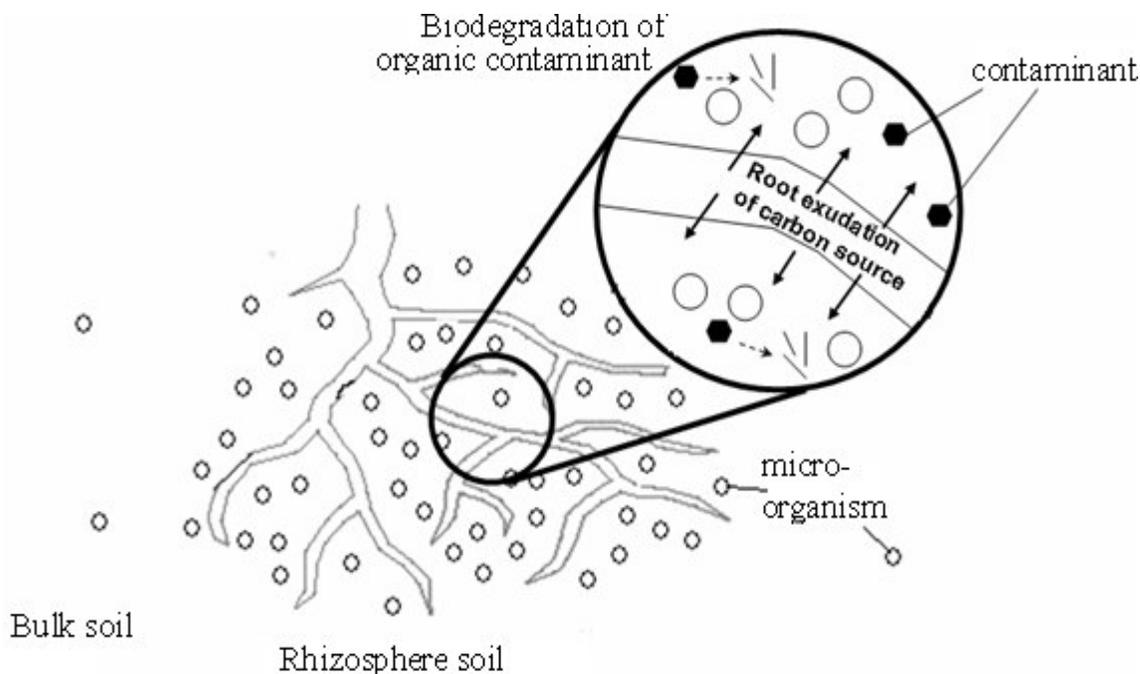


Figure 3. Schematic representation of phytostimulation (Meers and Tack, 2004).

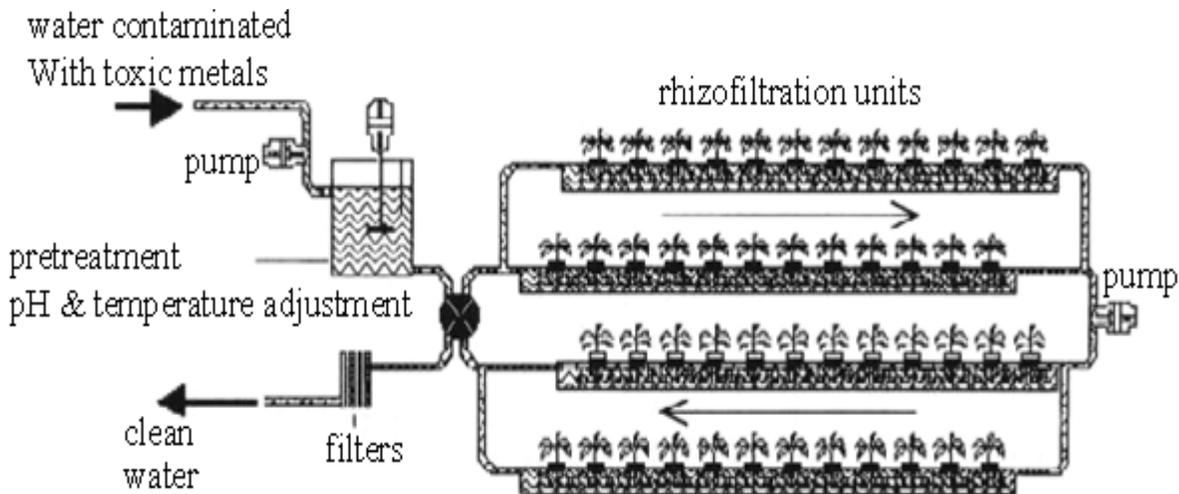


Figure 4. Schematic representation of an aerated rhizofiltration system (Dushenkov and Kapulnik, 2000).

Phytovolatilization

This process makes use of the ability of a plant to take up contaminants from the growth matrix and subsequently transform and volatilise them into the atmosphere through its leaves. The contaminant may become modified along the way, as the water travels along the plant's vascular system from the roots to the leaves, whereby the contaminants evaporate or volatilize into the air surrounding the plant (Figure 5). Some of these

contaminants can pass through the plants to the leaves and volatilize into the atmosphere at comparatively low concentrations (Ghosh and Singh, 2005). The process of phytovolatilization depends heavily on the physical characteristics of the contaminant itself. In order to get into the plant, the contaminant must have the proper chemistry to pass through the root membrane. Once inside the plant it can then be phytovolatilized into the atmosphere through the stomata (Scheper and Tsao, 2003).

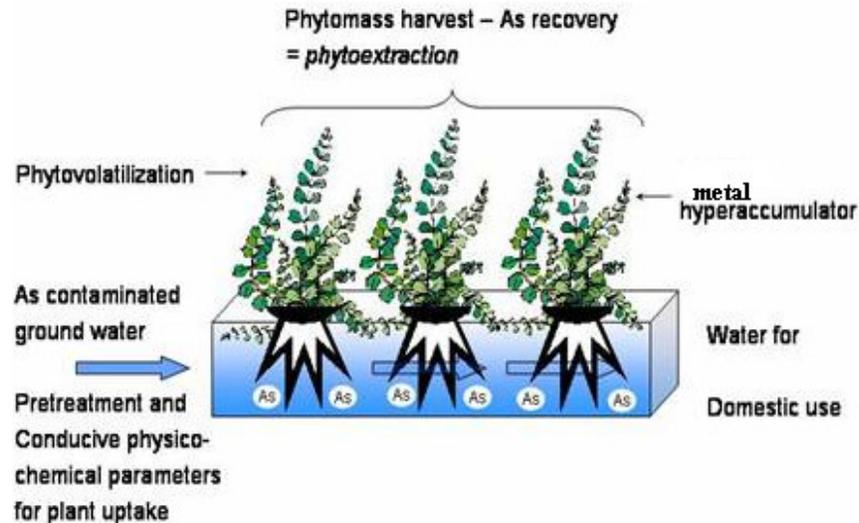


Figure 5. Metal removal from ground water using macrophytes by phytovolatilization (Aksorn and Visoottiviset, 2004).

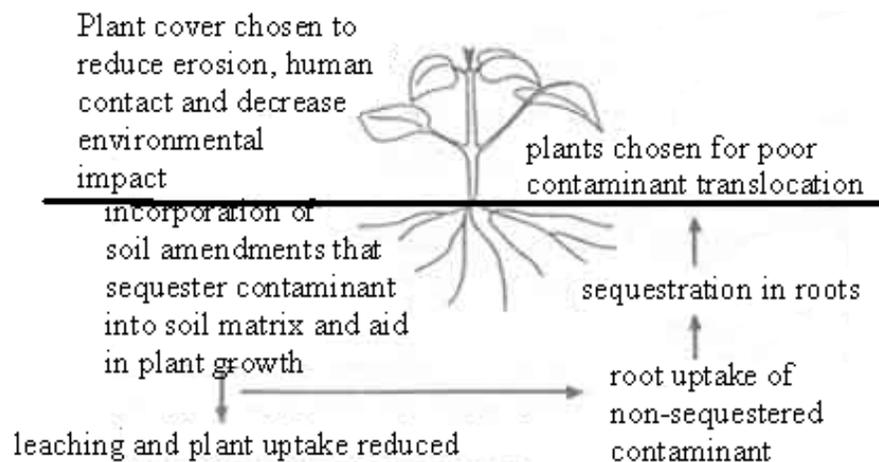


Figure 6. Processes involved in the phytostabilization of contaminants (Scheper and Tsao, 2003).

Phytostabilization

Phytostabilization, also referred to as in-place inactivation, is primarily used for the remediation of soil, sediment, and sludges (EPA, 2000). It is the use of plant roots to limit contaminant mobility and bioavailability in the soil. During the process, contaminants are absorbed and accumulated by roots, adsorbed onto the roots, or precipitated in the rhizosphere (Figure 6). When this happens, there is the prevention of mobility of the contaminants, hence reducing their availability in the food chain (Lasat, 2000; Jada and Fulekar, 2009). The process of phytostabilization depends on the tolerance ability of a plant to a contaminant. Even if the plant physically remove little or no contaminant, they are useful

as phytostabilization agents as long as they tolerate and grow under the contaminated conditions (Scheper and Tsao, 2003).

As it is with any technology, phytoremediation has several advantages and disadvantages. When compared to conventional remediation processes, the advantages of phytoremediation include:

1. Economical and low cost technology.
2. Less disruptive to the environment and does not involve waiting for new plant communities to decolonize the site.
3. No need for disposal sites, hence reducing risk of spread of contaminants.
4. More aesthetically pleasing than traditional methods.

5. Potential to treat sites polluted with more than one type of pollutant.

Despite the above advantages, some of the disadvantages include:

1. Dependent on the growing conditions (climate, geology, altitude, temperature) required by the plant, hence success depends on tolerance of the plant to the pollutant.
2. Requires access to agricultural equipment and knowledge to operate at large scale.
3. Risk of release of contaminants collected in senescing tissues being released back into the environment.
4. Contaminants may be collected in woody tissues used as fuel.
5. Since it is dependent on plant growth, when compared to other technologies, remediation time is long.
6. Possibility for environmental damage due to leaching of soluble contaminants.
7. Because of shallowness of plant roots, there is the problem of depth limitation, hence effectiveness can only be achieved within zone of influence of plant roots (Hinchman and Negri, 1997; Pivetz, 2001; Gardea-Torresdey et al., 2005).

Since phytoremediation is known to be more cost-effective and have fewer side effects than physical and chemical approaches, it has gained increasing popularity in both academic and practical circles. Studies have demonstrated that plants such as *Brassica juncea*, *Salsola kali*, and *Prosopis* species cultivated in hydroponics and agar are able to uptake significant amounts of heavy metals, which indicates their possible utilization in phytoremediation processes. Also, a wide variety of plants have demonstrated the ability to grow and uptake heavy metals from severely polluted sites. Several species of *Thlaspi*, *B. juncea*, *Salix* spp., and *Populus* species have been tested for remediation ability in pilot studies or are currently in commercial application. Researchers have also realized that phytoextraction can be used for the recovery of precious metals such as gold, silver, platinum, and palladium, which indicates the wide possibilities of the phytoremediation technology with regards to mining (Gardea-Torresdey et al., 2005).

Presently, over 400 species of plant are identified to have potential for remediation of water sources (Lone et al., 2008). The ability of water hyacinth (*Eichhornia crassipes*) to absorb and translocate cadmium lead, copper, zinc, and nickel in wetlands has been investigated by Liao and Chang (2004). They defined translocation ability as the quantity of copper, lead, cadmium, nickel, and zinc translocated in the plant's tissues, which was expressed as a root/shoot ratio. The ratio results they obtained were in the order of copper>lead>cadmium>nickel>zinc. In their investigation, water hyacinth plants had a high bio-concentration of

these trace elements when grown in water environments with low concentrations of the five elements. Their result revealed that, the concentration of these five elements in the roots was 3 to 15 times higher than those in the shoots. The concentrations in the root tissue were found in the order of copper>zinc>nickel>lead>cadmium. Also, the absorption capacity for water hyacinth was estimated at 0.24 kg/ha for cadmium, 5.42 kg/ha for lead, 21.62 kg/ha for copper, 26.17 kg/ha for zinc, and 13.46 kg/ha for nickel (Liao and Chang, 2004).

In addition, phytoremediation of heavy metal in water accumulated by aquatic macrophytes have been investigated in recent years (Kumar, 2008). The study used roots, stems and leaves of native aquatic plants (biomonitors) represented by seven species: *Ipomoea aquatica*, *Eichhornia crassipes*, *Typha angustata*, *Echinochloa colonum*, *Hydrilla verticillata*, *Nelumbo nucifera* and *Vallisneria spiralis* L. The result showed greatest and lowest accumulation of heavy metals in *N. nucifera* and *E. colonum*, respectively. The detected values of cadmium and lead fall within normal range, while that of cobalt and nickel were within the critical range. However, zinc and copper showed the highest accumulation with alarming toxicity levels (Kumar et al., 2008).

MICROBIAL REMEDIATION PROCESSES AND APPLICATIONS

Microbial bioremediation is defined as the process by which microorganisms are stimulated to rapidly degrade hazardous organic contaminants to environmentally safe levels in soils, subsurface materials, water, sludge, and residues. Microbes deal with poisonous chemicals by applying enzymes to convert one chemical into another form and taking energy or utilizable matter from this process. The chemical transformations generally involve breaking of large molecules into several small molecules in simpler form. In view of the interest in water and wastewater treatment, the response of microorganisms towards toxic heavy metals is of importance. In some cases the by-products of microbial remediation are not only harmless but may prove useful (Gupta et al., 2003).

Microbial activity is thought to play a key role in the detoxification of metals in water. For example, wastewater treatment systems are known to rely on microbes to perform the function of the breakdown of sewage influent. The microbes live in the sludge of the treatment plants, digest the solids and breakdown various compounds. As these microbes are living organisms, they require certain nutrients and environments to survive, multiply and perform. In any wastewater treatment system there is a vast array of microbes present, that is aerobic, anaerobic and facultative, each performing specific functions in their respective parts of the system. Each of these microbial species has a

tolerance of ecological minimums and maximums with regard to various conditions such as pH, temperature, dissolved oxygen levels and nutrient levels (Kosolapov et al., 2004).

Studies on the interactions of microorganisms with heavy metals have had increasing interest in recent years. Some of these studies have dealt on elucidation of different metal resistance mechanisms, interactions and processes, especially those used by bacteria, protozoa and fungi. The cost effective and eco-friendly newer biotechnological processes viz. bioremediation and bio-beneficiation through microbial metal re-absorption have been widely accepted. Bioleaching/biosolubilization of metal sulfide ores is an ideal alternative for the mitigation of pollution even at mining sites. It has been found that maximum rates and yields of metal extraction can be enhanced at elevated temperatures. There is however the ultimate is that there is a need to search such metal tolerant, metal absorbent as well as moderate thermophilic acidophilic organisms for biogeotechnological applications (Martin-Gonzalez et al., 2006; Umrana, 2006).

Microbial metal uptake can either occur actively (bioaccumulation) and/or passively (biosorption). Studies conducted in large-scale systems have shown that, biosorptive processes are more applicable than the bioaccumulative processes. This is because living systems (active uptake) often require the addition of nutrients and hence increase biological oxygen demand or chemical oxygen demand in the effluent (Hussein et al., 2005). On the other hand, biosorption is reported to be quite effective for the removal of metal ions from contaminated solution in low cost and environmental friendly manner (Rani et al., 2009). Since immobilised microorganisms provide a potential system for the treatment of metal contaminated waters, the efficiency of rotating biological contactors in the treatment of waters contaminated with cadmium, copper and zinc in multiple sorption–desorption cycles have been investigated. In rotating biological contactors, metals are removed by biosorption onto the microbial biofilm and the metal-loaded biomass may either be periodically removed for controlled disposal or suitably treated to recover sorbed metals such that the biofilm may be reused in multiple cycles (Hutchins et al., 1986; Costley and Wallis, 2001).

Different species of bacteria, fungi and protozoa have been reported to show resistance to high concentrations of heavy metals in wastewaters (Munner, 2005). Studies have shown that these potential microbial consortia are versatile for remediation of heavy metals contaminated water and wastewater, thus have high significance for environmental cleanup. Several scales-up process techniques have been used to expose them at varying concentrations of heavy metals. The study carried out by Sharma et al. (2000) revealed that *Klebsiella pneumoniae* has potential to bioaccumulate heavy metals at high concentrations (15 mM), thus showing the potential of

this bacterium in remediating heavy metals from contaminated environment.

Also, the survival of *Euplotes mutabilis* (a ciliate protozoa) in industrial wastewater containing high concentrations of heavy metals (cadmium, lead copper and chromium) have been evaluated in the past (Rehman et al., 2008). In their report, Rehman et al. (2008) observed that the ciliate, *E. mutabilis* showed tolerance against cadmium ($22 \mu\text{gml}^{-1}$), chromium ($60 \mu\text{gml}^{-1}$), lead ($75 \mu\text{gml}^{-1}$) and copper ($22 \mu\text{gml}^{-1}$). In addition, it was observed that after 96 h inoculation of the *E. mutabilis* in the medium containing $10 \mu\text{gml}^{-1}$ of metal ions, the live protozoan could remove 97% of lead and 98% of chromium from the medium. The acid digestion of ciliate revealed 89% of lead and 93% of chromium ions being accumulated in the organism. In general, the metal uptake ability of *E. mutabilis*, was evidenced by its survival and growth in water containing $10 \mu\text{gml}^{-1}$ of metal ions. By using the heat-killed organism, no metal uptake was observed (Rehman et al., 2008).

Similarly, the remediation of aqueous lead and cadmium ions by the fungus *Fusarium oxysporum* have been investigated in the past (Sanyal et al., 2005). In the report of Sanyal et al. (2005), it was observed that in the presence of the *F. oxysporum*, metal carbonates are formed by the reaction of the heavy metal ions with carbon dioxide produced by the fungus during metabolism, thus providing a completely biological method for production of crystals of metal carbonates. The major advantage of this approach is that the reaction leads to detoxification of the aqueous solution and could have immense potential for bioremediation of heavy metals. Under conditions of their study, the metal ions were not observed to be toxic to the fungus, which readily grows after exposure to the metal ions (Sanyal et al., 2005).

Furthermore, the use of immobilized non-living algae biomass (bioresins) for the stripping of metals from solution has also been studied (Brown, 1996). In a study, which involved a bench-scale setup, cultures of algae biomass were isolated and sufficient material to produce bioresins was generated. A total of four bioresin materials were tested, including materials derived from two different species of microalgae. In the result, bioresins derived from one biomass type were found to be highly effective in binding copper, nickel and lead ions in water (Brown, 1996).

As mentioned in chemical remediation and phytoremediation processes, microbial remediation has several advantages and disadvantages. Some of the advantages of microbial remediation include:

1. It uses relatively low-cost, low-technology techniques, hence requires moderate capital investment. When compared to other remediation processes, it is fairly inexpensive.
2. Since it is a natural process, it is environmental safe,

hence usually perceived by the public as an acceptable treatment process.

3. It does not generate waste, hence less wasted groundwater.
4. It is self-sustaining since the microbes able to degrade the contaminant increase in numbers when the contaminant is present; and decreases when the contaminant is degraded.
5. The residues for the treatment are usually harmless products and include carbon dioxide, water, and cell biomass.
6. It can be used alongside other technologies.
7. It can be carried out on site, often without causing a major disruption of normal activities.

Some of the disadvantages are:

1. It is not always suitable, however, as the range of contaminants on which it is effective is limited, the time scales involved are relatively long, and the residual contaminant levels achievable may not always be appropriate.
2. Bioremediation is limited to those compounds that are biodegradable. Not all compounds are susceptible to rapid and complete degradation.
3. There are some concerns that the products of biodegradation may be more persistent or toxic than the parent compound.
4. Biological processes are often highly specific, since success is dependent on the presence of metabolically capable microbial populations, suitable environmental growth conditions, and appropriate levels of nutrients and contaminants.
5. It is difficult to extrapolate from bench and pilot-scale studies to full-scale field operations, for research is needed to develop and engineer bioremediation technologies that are appropriate for sites with complex mixtures of contaminants that are not evenly dispersed in the environment.
6. Although the methodologies employed are not technically complex, considerable experience and expertise may be required to design and implement a successful bioremediation program, due to the need to thoroughly assess a site for suitability and to optimize conditions to achieve a satisfactory result, (Viladi, 2001; Humar and Pohleven, 2006; Golden Environmental Services, 2007).

CONCLUSION

Heavy metal contamination of distributed water and discharged wastewater is a constant area of concern. Nationally and internationally, there is the challenge to remediate hazardous metal-containing water and wastewater. The removal of heavy metals from domestic and industrial waters has become an important application in water and wastewater treatment systems. This is because legislations and guidelines have created

strict distribution and discharge limits, which has compelled plants to add or upgrade metal removal processes.

The minimization of the health and environmental impacts of the presence of heavy metals in aquatic systems requires the application of different treatment processes. This has necessitated the need for economically viable and effective technologies, in order to supply safe drinking water and discharge wastewater that preserves precious natural resources and biological lives. At present, no single technology for heavy metal remediation (chemical remediation, phytoremediation or microbial remediation) is without some form of merits and demerits.

Due to the enormous benefits and drawbacks of each of the existing remediation technologies/processes, there is a need for the implementation of an integrated remediation technology/multiple technology which can have great potential. This can be attained through further heavy metal remediation research, which will help to enhance decisions that are science-based. To achieve a safe and economically viable remediation option for heavy metals in water and wastewater systems, there is need to review and assess the current costs and market share of the established remediation processes. The application of this may offer enormous environmental public health and cost benefits.

REFERENCES

- Aksorn E, Visoottiviseth P (2004). Selection of suitable emergent plants for removal of arsenic from arsenic contaminated water. *Sci. Asia* 30: 105-113.
- Alva AK, Graham JH, Anderson CA (1995). Soil pH and copper effects on young 'Hamlin' orange trees. *Soil Sci. Soc. Am. J.*, 59: 481-487.
- Athar R, Ahmad M (2002). Heavy metal toxicity: effect on plant growth and metal uptake by wheat, and on free living *Azotobacter*. *Water Air Soil Poll.*, 138: 165-180.
- Boonyapookana B, Parkpian P, Techapinyawat S, Delaune RD, Jugsujinda A (2005). Phytoaccumulation of lead by Sunflower (*Helianthus annuus*), Tobacco (*Nicotiana tabacum*) and Vetiver (*Vetiveria zizanioides*). *J. Environ. Sci. Health. Part A: Toxic/Hazardous Substances Environ. Eng.*, 40: 117-137.
- Brown LM (1996). Removal of heavy metals from water with microalgal resins 1: process development. *Water Treatment Technology Program Report No. 74*. US Department of the Interior Bureau of Reclamation.
- Costley SC, Wallis FM (2001). Bioremediation of heavy metals in a synthetic wastewater using a rotating biological contactor. *Water Res.*, 35(15): 3715-3723.
- Dushenkov S, Kapulnik Y (2000). Phytoremediation of metals. In: Raskin I, Ensley BD (Eds.). *Phytoremediation of toxic metals: using plants to clean up the environment*. John Wiley and Sons Inc., New York, pp. 89-106.
- EPA (2000). Wastewater technology sheet: chemical precipitation. United State Environmental Protection, EPA 832-F-00-018. Available from http://www.epa.gov/own/mtb/chemical_precipitation.pdf. Accessed 07/07/2010.
- Feng D, Aldrich C, Tan H (2000). Treatment of acid mine water by use of heavy metal precipitation and ion exchange. *Miner. Eng.*, 13(6): 623-642.
- Fuggle RF (1983). Nature and ethics of environmental concerns. In: *Environmental Concepts in South Africa*, Fuggle RF and Rabie MA.

- Juta, Cape Town.
- Gardea-Torresdey JI, Peralta-Videa JR, Rosa GD, Parsons JG (2005). Phytoremediation of heavy metals and study of the metal coordination by X-ray absorption spectroscopy. *Coord. Chem. Rev.*, 249(17-18): 1797-1810.
- Ghosh M, Singh SP (2005). A review on phytoremediation of heavy metals and utilization of its byproducts. *Appl. Ecol. Environ. Res.*, 3(1): 1-18.
- Golden Environmental Services (2007). Natural processes: bioremediation. Available from <http://www.goldenenviro.ca/bioremediation.html>. Accessed 12/06/2010.
- Gupta AK, Yunus M, Pandey P (2003). Bioremediation in ecotechnology for the present century. *Inter. Soc. Environ. Botanists Environnews*, 9(2).
- Hinchman RR, Negri MC (1997). Providing the Baseline Science and Data For Real-Life Phytoremediation Applications – Partnering for Success, Chapter 1.5. In, *Proceedings of the 2nd Intl. Conference on Phytoremediation*, Seattle WA, June 18-19, 1997.
- Holtzman A (1994). Cyanide and heavy metal removal: comparison of different chemistries with emphasis on an innovative new treatment method. *Advanced Chemical Technology, Inc.* Available from http://www.actglobal.net/products_wastewater_heavy_metals.htm. Accessed 07/07/2010.
- Humar M, Pohleven F (2006). Bioremediation of waste wood -Overview of advantages and disadvantages. Available from <http://www.bfaifh.de/inst4/45/ppt/bioremd.pdf>. Accessed 10/06/2010.
- Hussein H, Farag S, Kandil K, Moawad H (2005) Resistance and uptake of heavy metals by Pseudomonads. *Process Biochem.*, 40: 955-961.
- Hutchins SR, Davidson MS, Brierley JA, Brierley CL (1986). Microorganisms in reclamation of metals. *Ann. Rev. Microbiol.*, 40: 311-336.
- Jada CD, Fulekar MH (2009). Phytoremediation of heavy metals; recent techniques. *Afr. J. Biotechnol.*, 8(6): 921-928.
- Johnson DB, Hallberg KB (2005). Acid mine drainage remediation options: a review. *Sci. Total Environ.*, 338: 3-14.
- Khan SU, Moheman A (2006). Effect of heavy metals (Cadmium and Nickel) on the seed germination, growth and metals uptake by chilli (*Capsicum frutescens*) and sunflower plants (*Helianthus annuus*). *Pollut. Res.*, 25(1): 99-104.
- Kumar JIN, Soni H, Kumar RN, Bhatti I (2008). Bhatti1Macrophytes in Phytoremediation of Heavy Metal Contaminated Water and Sediments in Pariyej Community Reserve, Gujarat, India. *Turk. J. Fish. Aquat. Sci.*, 8: 193-200.
- Kuzovkina YA, Knee M, Quigley MF (2004). Cadmium and copper uptake and translocation in five Willow (*Salix L.*) species. *Int. J. Phytoremediat.*, 6: 269-287.
- Lasat MM (2000). Phytoextraction of metals from contaminated soil: a review of plant/soil/metal interaction and assessment of pertinent agronomic issues. *J. Hazard. Subst. Res.*, 2(5): 1-25.
- Lee M, Paik IS, Kim I, Kang H, Lee S (2007). Remediation of heavy metal contaminated groundwater originated from abandoned mine using lime and calcium carbonate. *J. Hazard. Mater.*, 144(1-2): 208-214.
- Liao S, Chang W (2004). Heavy metal phytoremediation by water hyacinth at constructed wetlands in Taiwan. *J. Aquat. Plant Manage.*, 42: 60-68.
- Lone MI, HE Z, Stoffella PJ, Yang X (2008). Phytoremediation of heavy metals polluted soils and water: progress and perspectives. *J. Zhejiang Univ. Sci. B* 9(3): 210-220.
- Martin-Gonzalez A, Díaz S, Borniquel S, Gallego A, Gutierrez JC (2006). Cytotoxicity and bioaccumulation of heavy metals by ciliated protozoa isolated from urban wastewater treatment plants. *Res. Microbiol.*, 157: 108-118.
- Matlock MM, Howerton BS, Atwood DA (2002). Chemical precipitation of heavy metals from acid mine drainage. *Water Res.*, 36(19): 4757-4764.
- Meers E, Tack FMG (2004). The potential of foliar treatments for enhanced phytoextraction of heavy metals from contaminated soil with *Helianthus annuus*. *Remediat. J.*, 14: 111-123.
- METALSORB (2004). Heavy metal chelating agents. Available from http://www.snf-group.com/IMG/pdf/Heavy_Metal_-METALSORB_E.pdf. Accessed 09/07/2010.
- Miller R (1996). Phytoremediation, technology overview report. *Ground-Water Remediation Technologies Analysis Center, Series O, Vol. 3.*
- Munner B (2005). Role of microorganisms in remediation of heavy metals in the wastewater of Tanneries. *Doctoral Thesis Submitted to the Department of Zoology, University of Punjab, Pakistan.*
- NEESA (1993). Precipitation of metals from ground water. *NEESA Document Number 20.2-051.6, Novel Energy and Environmental Support Activity, Port Hueneme, CA.*
- Nelson WO, Campbell PGC (1991). The effects of acidification on the geochemistry of Al, Cd, Pb and Hg in fresh water environments: a literature review. *Environ. Pollut.*, 71: 91-130.
- Newman LA, Reynolds CM (2004). Phytodegradation of organic compounds. *Curr. Opin. Biotechnol.*, 15(3): 225-30.
- Nomanbhay SM, Palanisamy K (2005). Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electron. J. Biotechnol.*, 8(1): Issue 15.
- Oelofse SHH, Hobbs PJ, Rascher J, Cobbing JE (2007). The pollution and destruction threat of gold mining waste on the Witwatersrand - A West Rand case study. *Symposium on Environmental Issues and Waste Management in Energy and Mineral Production (SWEMP 2007)*, 11-13 December, Bangkok.
- Pawlak Z, Zak S, Zablocki L (2005). Removal of hazardous metals from groundwater by reverse osmosis. *Pol. J. Environ. Stud.*, 15(4): 579-583.
- Pivetz BE (2001). Phytoremediation of contaminated soil and groundwater at hazardous waste sites. *EPA Ground Water Issue, EPA/540/S-01/500.*
- Rajendran P, Muthukrishnan J, Gunasekaran P (2003) . Microbes in heavy metal remediation. *Indian J. Exp. Biol.*, 41(9): 935-944.
- Rani MJ, Hemambika B, Hemapriya J, Kannan VR (2009). Comparative assessment of heavy metal removal by immobilized and dead bacterial cells: a biosorption approach. *Afr. J. Environ. Sci. Technol.*, 4(2): 077-083
- Rehman A, Shakoori FR, Shakoori AR (2008). Heavy metal resistant freshwater ciliate, *Euplotes mutabilis*, isolated from industrial effluents has potential to decontaminate wastewater of toxic metals. *Bioresour. Technol.*, 99(9): 3890-3895.
- Sanyal A, Rautaray D, Bansal V, Ahmad A, Sastry M (2005). Heavy-metal remediation by a fungus as a means of production of lead and cadmium carbonate crystals. *Langmuir*, 21(16): 7220-7224.
- Scheper T, Tsao DT (2003). *Advances in Biochemical Engineering Technology: Phytoremediation.* Springer-Verlag Berlin Heidelberg, New York.
- Schnoor JL (1997). *Phytoremediation. Ground-Water Remediation Technology Analysis Centre technology Evaluation Report Series, TE-98-01.*
- Sharma PK, Balkwill DL, Frenkel A, Vairavamurthy MA (2000). "A new Klebsiella planticola starin (Cd-1) grows anaerobically at high cadmium concentrations and precipitates cadmium sulfide". *Appl. Environ. Microbiol.*, 66(7): 3083-3087.
- Umrana VV (2006). Umrana, Bioremediation of toxic heavy metals using acidothermophilic autotrophes, *Bioresour. Technol.*, 97: 1237-1242.
- UNEP (2010). *Phytoremediation, an environmentally sound technology for pollution prevention, control and remediation: an introductory guide to decision makers.* United Nations Environment Programme, Newsletter and Technical Publication, Freshwater Management Series No 2.
- Utmazian MN, Wenzel WW (2006). Phytoextraction of metal polluted soils in Latin America. *Environmental Applications of Poplar and Willow Working Party.* Available from: <http://www.fao.org/forestry/11114-1-0.pdf>. Accessed 19/09/2010.
- Vaca MV, Callejas RLP, Gehr R, Cisneros BJN, Alvarez PJJ (2001). Heavy metal removal with mexican clinoptilolite: multi-component ionic exchange. *Water Res.*, 35(2): 373-37.
- Viladi M (2001). Bioremediation: an overview. *Pure Appl. Chem.*, 73(7): 1163-1172.
- Volesky B (2003). *Sorption and Biosorption.* BV-Sorbex, Inc., St. Lambert (Montreal), (ISBN 0-9732983-0-8) Quebec, Canada.
- Xu Y, Xu T (2008). Heavy metal complexes wastewater treatment with chelation precipitation. *IEEE Xplore*, pp. 2789-2793.