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Biological Processes of Heavy Metals-Contaminated Environmental Remediation: A Review

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Abstract

Environmental contamination as a result of utilization of chemicals such as pesticide, fertilizer, radioactive nucleotide and organic substances has serious deteriorating effect to the environmental (soil, water and air) quality. To restore the integrity of our environment, different scientific approaches are put forward including bioremediation, mycoremediation and phytoremediation processes where all of which are eco-friendly. Both bacteria, fungi and plants use extracellular secretion, adsorption and biosorption processes to remove/convert toxic pollutants such as heavy metals into less toxic matter; uptake and bioaccumulate the environmental contaminants and sequester them. bacteria use to sequester heavy metal with the help of low molecular weight cysteine-rich proteins glutathione, fungi use plastocyanin, metallothionein and glutathione, whereas plants use phytochelatins and metallothioneins. This review provides broader focus on involvement of bacteria, fungi and plants in alleviating heavy metals from contaminated environment and mechanisms involves.

Keyword: Heavy metals, Bioremediation, Mycoremediation, Phytoremediation

1 Introduction

Heavy (or trace) metals also refer to any chemical elements that are metallic in nature and has enormous density and are potentially toxic even at low dose. Heavy metals are neither essential elements nor do they have any vital role in the metabolic pathways of cells but are readily uptaken and bio-accumulated in various plant parts (1). Among the heavy metals, Cobalt (Co), Nickel (Ni), Copper (Cu), Vanadium (V), Zinc (Zn), Chromium (Cr), and are non-toxic heavy elements at low concentration. Cadmium (Cd), Silver (Ag), Lead (Pb), Aluminium (Al), Mercury (Hg) and Arsenic (As) are those trace elements that their nutritional function is not yet known and are seemingly more or less toxic to both plants, animal and microorganism (1). Heavy metals form integral part of earth that can neither be degraded nor destroyed. They are really dangerous because of their ability to accumulate in living cells. Bioaccumulation refers to gradual aggregation of a chemical substance within living organisms over time compared to their environmental concentration. Trace metals can get into water and disturb aquatic lives through industrial and consumer waste and / or from acidic rain causing weathering and release of heavy metals into the ground water, river, lakes and stream. Heavy metals and metalloids found in soil are sourced from parent materials of the soil through lithogenic as well as different anthropogenic activities (2). Anthropogenic activities leading increase in heavy metals in the environment include various industrial processes, smelters, mining, foundries, gasoline and combustion of fossil fuel, and waste incinerators. This affects the ability of the environment to foster life and render its intrinsic values. Cd, Hg, and Pb according to European Monitoring and Evaluation Programme (EMEP) are the major heavy metals of immense concerned, because of their highly toxic effects on human health (3). According to Damodaran et al. (4), the way and manner in which heavy metal removal mechanism ensues is a complex process that depend on several factors including chemistry of metal ion, physiology and composition of cell wall of organism as well as the physicochemical factors such as pH, ionic strength of metal, metal concentration, temperature and time. Any environmental product bearing these heavy metals may be lethal to both soil, plants and animal including human health. As reported by Singh and Kalamdhad, (5), plants absorption and subsequent accumulation of heavy metals and transfer of heavy metals to human tissues through food chain is of great concern. Bacteria, fungi and plants interact with both living and non-living components in the ecosystem. In the presence of stress, they tend to adjust metabolically to adopt to the condition where they undergo different processes to ameliorate the toxicity (Figure 1) shown below. Recent review will specifically focus on the environmental contamination resulting from industrialization and other sources and the way living organisms such as plants, fungi

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and bacteria decontaminate environment and the mechanism they adopt in resisting stress and accumulation of heavy metals.

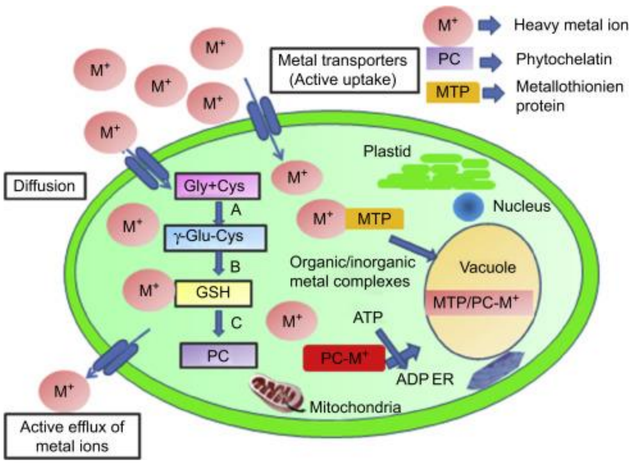

Figure 1: Environmental effects of heavy metals and amelioration process (6)

1.1 Terrestrial effects

The principal basins for heavy metals emitted to the environment via human activities have been reported as soil. According to Singh and Kalamdhad (5), various higher atomic weight metals especially Cd, Pb, Zn, Cu, Cr and Ni are the major soil contaminants whereas Duruibe et al. (7) documented that most of the above mentioned metals have no biological value in human either biochemical and/ or physiology and are highly toxic when consumes even at low concentration. Heavy metals affect soil microbial communities. They negatively affect soil microorganisms by causing significance change in their overall activities, population size and diversity. Calvaruso et al. (8) coins out the imperative roles of microbial community in soil for rock weathering and making use of released element as nutrients. They oblige important part in weathering of mineral, crucially partake in nutrient cycling, formation of soil structure and decomposition of organic matter (9). Heavy metal has been found to affect plant in various ways such as growth and developmental retardation and affect germination process. Most heavy metals affect enzyme activities in plant. As heavy metal concentration reaches certain degree, different cytotoxic symptoms in plants are observed ranging from impairment of growth, green coloration loss in plants' leaves (chlorosis), root blackening and other physiological, anatomical as well as morphological changes. Most heavy metals has no role in plants' metabolic process but do absorbed and accumulate in various parts. Nickel (Ni) is toxic to many plants affecting protease, ribonuclease and amylase enzyme activities thus the rate at which germination, growth and development ensues is slowed down (10). Ahmad and Ashraf (10); Ashraf et al. (11) disclosed that heavy metals has effect on digestion and mobilization of food reserve such as carbohydrate and proteins in germinating seed. According to Ashraf et al. (11), morphological features such as plant height, chlorophyll content, fresh and dry weight, root length, and enzyme carbonic anhydrase activity are reduced, and lipid oxidation leading to raise in malondialdehyde content (MDA) and leakages electrolyte was observed. Bhattacharyya et al. (12) documented that lead (Pb) affect both soil productivity and halt many plant lives processes such as cell division, photosynthetic pathway and absorption of water as well as toxic symptoms including older leaves wilting, dark green leaves, brown, stunted and short foliage leaves and roots. Occurrence of cadmium (Cd) in bioavailable form, interfere with other minerals uptake either directly on available minerals in the soil or through reduction of soil microbes (13). Among the direct effects of Cd to plants are reduction of stomatal opening, transpiration and photosynthesis (14), lipid peroxidation and affecting metalo-enzymes activities.

1.2 Aquatic effects of heavy metals

Both surface water and acidic rain is capable of carrying heavy metals to ocean through washing heavy metal contaminated environment. Heavy metals in aquaculture is poisonous, disturbing aquatic lives especially fishes. Heavy metals are dissolved and react with various water inherent such as organic compounds, sulphate and carbonate to form insoluble complexes and salts that are predictably harmful to aquatic organisms (15). Chemical fertilizers containing some heavy metals application can influence the growth of the fishes. Either chlorinated or organophosphorous pesticides has been confirmed and studied broadly in fishes. Sun et al. (16) reported the effect of xenobiotic on quality and functioning of DNA. According to Lee et al. (17) fishes accumulate Pd and induce oxidative stress which in turn causes synaptic damage and neurotransmitter impairment in fish as neurotoxic. Cadmium is most dangerous heavy metal that stances high toxicity even at very low dose and causing acute and chronic deleterious effects to aquatic animal health and environment. Cd affects kidney, calcium metabolism and triggers abnormal spine development (18). High mortality rate in juvenile fish and drastic decrease in breeding potential of adult upon prolong exposure was reported (19). Khayatzadeh and Abbasi, (15) observed some effects of heavy metal toxicity in fishes and aquatic invertebrates including reduced developmental growth rate, abrupt rise in developmental anomalies, drastical drop of the rate at which fishes survive expressly at the start of exogenous feeding or even set off extinction of entire population of fishes

2 Biological remediation process of heavy metal contaminated environment

Heavy metals are among the most important sorts of contaminant in the environment. Several methods already used to clean up the environment from these kinds of contaminants, but most of them are costly and difficult to get optimum results (20). Biological processes of heavy metals remediation involve the use of organisms such as various bacteria, fungi and plants, and their derivatives or products are applied as a mild environmentally friendly method for elimination of contaminants from the environment. Biological processes process of heavy metal remediation could be active (metabolic and energy dependent) or passive and could involve the use of dead or live organisms/biomass (21). According to Tekere (21) Microorganisms could be introduced straight to contaminated environment or used in designed bioreactors optimized to achieve the remediation goals. In phytoremediation, plants are developed in contaminated location/ site or in wetlands. Both microbial (bioremediation), mycoremediation and phytoremediation are effective and affordable technological solution to heavy metal contaminants that gain more attention worldwide. The main principle of biological process is to degrade and convert pollutants to either mild or non-toxic forms (22).

2.1 Bacterial Bioremediation Process

Bioremediation is the remediating process which employ the use of microorganisms to break, inactivate/transform and render toxic environmental contaminants to less toxic form. In heavily contaminated environment, microorganisms try to adopt and resist toxic effects of heavy metals by various mechanisms. Microorganisms enjoy excellent metabolic pathways that help the adopt to the stress condition in their environment by metabolizing toxic compounds and harness energy for growth and development, by co-metabolism, respiration and fermentation. Characteristically, presence of enzymes with degradative ability for a particular contaminant confer to them broad pathways for resistance to heavy metals and maintaining of homeostasis (23-25). Extracellular polymeric and functionalized compounds found in their cell wall biomass can chelate heavy metals either by microprecipitation or proton exchange (26). The negatively charge of biomass surface is due to the presence of phosphoryl, carboxyl, sulfur, and amino acid groups which serve as potential metal sinks and sites of ion exchange as shown in Figure 2 below.

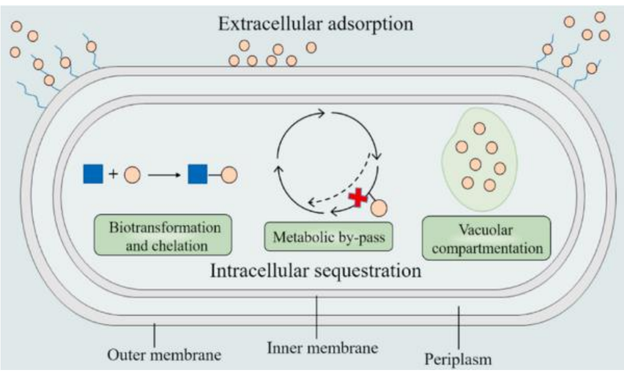

Figure 2: Extracellular adsorption process (27)

Consortium of microbes has been reported to be more resourceful in transforming pollutants to less or nontoxic than pure isolates (28). The major mechanism in which bacteria resist heavy metal toxicity include methylation, metal ligand degradation, efflux pump of metal, intracellular and extracellular sequestration, metal chelators such as metallothioneins and bio surfactants synthesis, complex formation with organic compound, formation of permeable barrier and change in metal state (oxidation/reduction) (29). Bioremediation processes is initiated by redox reactions which involves mobilization/immobilization metal by microorganisms. Meena and Sarita, (31) reported that bioremediation is achieved by changing metal from its insoluble and inactive forms to its soluble active form. Heavy metals like Hg, Cr, As and Fe undertake reduction and oxidation cycle in bacteria. According to Wu et al. (32), bacteria that are resistant to mercury employ organomercurial lyase to demethylate methyl mercury to Hg (II), which is about several-fold less toxic than methylated mercury. Hg (II) is reduced to mercury element and later to its volatile form Hg (0) using the MerA enzyme to catalyze reduction of Hg (II) to volatile Hg (0) (33). The solubility of ions like As (V) and Fe (III) can be improved by microbial reduction via reducing them to As (III) and Fe (II) respectively and facilitate their leaching from soil (34).

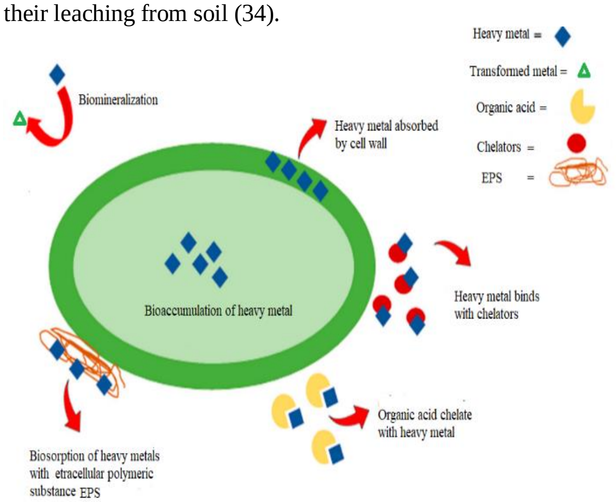

Figure 3: Bacterial bioremediation process (adopted and modified from Rigoletto et al. (30))

Biomethylation of heavy metals is important process that plays significant roles in both the soil and water by modifying their toxicity, converting them to more volatile and enhance their mobility. These processes serve as integral means of detoxification as methylated heavy metals can easily get rid of (35). Indirect metals mobilization mechanism takes into account the decomposition of organic matter to release ions. Bacteria, *Schizophyllum commune* for example dissolves organic matter to release heavy metals (36). However, mobilization process is associated with some deleterious effect when toxic metals are released and redistributed from solid phase to dregs into the solution (37), and this increase metals' bioavailability. It has been evaluated that in employing immobilization process, an element can easily be indifferent and get rid of from its aqueous phase in water (31). Mosa et al. (38) and Gadd, (39) reported that microbes carryout immobilization and serve as basin for metals. Secretion of some metabolites such as amino acids and carboxylic acid by microbes serve vital role in metal ion chelation (31).

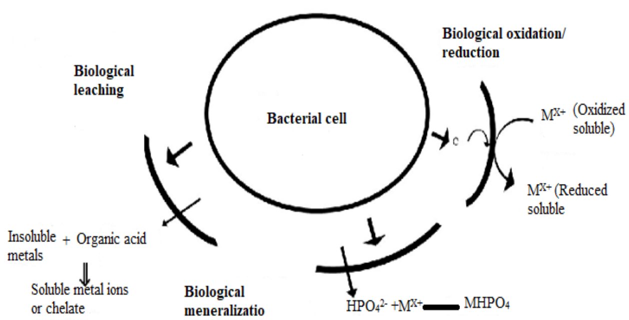

Figure 4: Biomining remediation mechanism (40)

Table 1: Bacteria and their response to heavy metals

Bacteria	Action on Heavy metal	Reference
P. putida	Intracellular sequestration of Copper, Zinc and Cadmium ions	(41)
Rhizobium leguminosarum	Intracellular sequestration of Cd	(42)
G. metallireducens	Reducing Manganese (Mn) to non-toxic	(43)
G. sulfurreducens and G. metallireducens	Reducing Chromium to non-toxic	(44)
Bacillus subtilis, B. megaterium, B. megaterium, Penicillium sp. and *A. niger*	Lead reduction	(45)
Lactococcus, Enterobacter and *Spirochaeta*	Vanadium	(46)
Bacillus subtilis and *B. megaterium*	Reduce Cd	(47)
Klebsiella planticola	Precipitate Cd	(48)
Clostridium spp., Escherichia spp., Pseudomonas spp. and *Bacillus spp.,*	Bio-methylation of Hg, Selenium (Se) and Lead (Pb) to methylated-metal gaseous	(49)
Brevibacterium iodinium Alcaligenes faecalis, B. pumilus and P. aeruginosa,	Bioaccumulation of Cadmium (Cd) and Lead (Pb).	(50)
B. cereus	Remove Cr	(51)
Arthrobacter sp. and Acinetobacter sp.	Remove Cr	(50)
Desulfovibrio desulfuricans	Removes Nickel (Ni), Copper (Cu), and Chromium (Cr^{6+})	(51)
Ganoderma applantus	Utilize Lead, Copper, Mercury	(52,53)
Alcaligenes faecalis	Lead (Pb). Mercury (Hg) and Cadmium (Cd)	(50)
Azotobacter vinelandii	Siderophore production	(54)
Citrobacter spp. and *Zooglea spp.*	Utilize Nickel, Copper, Cadmium, Cobalt, Nickel	(55)
C. vulgaris and Citrobacter spp.	Remove Uranium, Copper, Gold, Cadmium, Lead, Mercury, Nickel.	(56)
Rhizopus arrhizus	Utilize Mercury, Lead, Silver, Calcium and Cadmium	(52,56)
Aspergilus Niger	Uses Thorium, Uranium, Cadmium, Zinc	(56)
Pleurotus ostreatus	Remove Zinc, Copper and Cadmium	(56)
Bacillus spp. and *Pseudomonas aeruginosa,*	Utilize Copper and Zinc	(56)
Stereum hirsutum	Utilize Copper, Nickel, Cobalt and Cadmium,	(52,53)
Pseudomonas syringae	Extracellular sequestration of Cu	(57)
Phormidium valderium	Remove Lead and Cadmium	(52,53)

2.2 Mycoremediation

Is an environmental decontamination technology that involves use of fungi. It is ecofriendly, cheaper, noninvasive that lessen or transform hazards in the environment into non-hazardous and harmless form (58). Fungi are prominent for their competence to inhabit a broader range of heterogenous environments, to acclimatize to the complex matrices of the soil as well as the extreme environmental conditions. Ability to decompose organic matter and inhabit both abiotic and biotic surfaces has been documented by Bharath et al. (59) and Joutey et al. (60). Mycoremediation has a wider role of application in environmental protection. It comprises various intrinsical mechanisms at cellular level that involves synthesis of organic acids and phytochelatins for heavy metal detoxification, and heavy metal stress tolerance. White rot fungi and other esculent mushrooms have the potential to biodegrade xenobiotics (61). In metal stressed environment, mushrooms first respond by producing stress relieve proteinous and nonproteinous compounds. Damodaran et al. (4) evaluated the role of mushroom's cap as site specific for production of stress related compound that enhance metal absorption and detoxification including plastocyanin, metallothionein and glutathione. Fungi are latent heavy metal accumulator most especially *Basidiomycetes* mushroom use their mycelia to biosorbs metals from soil and accumulate them in their fruiting bodies (62). Ali et al. (63) reported some mushroom species like *Boletus Agaricus, Amanita, Phellinus, Cortinarius, Suillus and Leccinum* applicable for heavy metals complexation/mobilization in the soil.

Prado et al. (74) coined out that fungi can immobilize, mobilize, transform/inactivate to tolerate and resist absorbed ionic heavy metal. However, the fungal strategies espoused in mycoremediation encompasses; *Exclusion;* this involve developing of barrier which is selectively permeable, so, the metal ions are reserved far from the spot sites. *Extrusion;* metals within the cell (cytosol) are actively transported (extruded) to vacuolar compartment. *Fixation;* production of metal binding protein to complex with metal ion or other cell components such as enzyme for intra- and extracellular sequestration, de-toxification, acid production to dissolute metal, extracellular metal precipitation of metal and chelation of metal ion. *Biotransformation;* reduction, oxidation, volatilization, methylation and demethylation are the important mechanisms employed by fungi to modify toxic metal to less toxic forms.

2.3 Phytoremediation

The process involves plant utilization to decontaminate environment. Phytoremediation technology is non-destructive and non-invasive processes which leave the soil undamaged and agriculturally productive after remediation (75). Some plant has strength to tolerate substantial amount of heavy metals within their tissues by producing and binding of organic compounds, cellular and sub-cellular levels of metal compartmentalization and some changes in metabolic pathways (76, 77).

Table 2: Fungi and response to heavy metal

Fungi	Effect on heavy metals	Ref.
Aspergillus sp.	Removal of Cr	(64)
Coprinopsis atramentaria	Bioaccumulation of Cd	(65)
Rhizopus oryzae, Aspergillus niger, Penicillium chrysogenum	Reduce Cr (IV) to Cr (II)	(66)
Candida sphaerica and Saccharomyces cerevisiae	Remove Lead (Pb)Iron (Fe) and Zinc (Zn),	(67)
p. guilliermondii, Yarrowia lipolytica, Hansenula polymorpha, Rhodotorula pilimanae, Rhodotorula mucilage and *S. cerevisiae,*	Bioconvertion of Cr (VI) to Cr (III)	(68)
Aspergillus fumigatus, Penicillium rubens, Aspergillus niger	Removal Cd and Cr	(69)
Rhizopus stolonifer	Removal of lead, cadmium, zinc, and copper	(70)
Rhodotorula mucilaginosa	mercury, copper, and lead	(71)
A. niger	Bioleaching of aluminum, iron, lead, and zinc	(72)
Bacillus megaterium	Removal of Nickel	(73)

Various organic compounds are produced by plants to cope and tolerate the heavy metal stress by chelation comprise metallothioneins, phytochelatins, amino acids, organic acids, and cell wall components (proteins/pectins/polyphenols etc.) (78, 79). Various plants species have been successful in absorbing contaminants such as cadmium, lead, arsenic, chromium, and several radionuclides from environment (20). phytoextraction a phytoremediation type, has been used to eliminate heavy metals from soil by plants' ability to absorb metals which are essential for plant growth, (Fe, Ni Mo, Zn, Mn, Mg, and Cu,). Some metals (Hg Cd, Se Cr, Co, Ag, Pb) that has no known biological role in plants could also be accumulated (20, 80). Phytoremediation can be classified into phytostabilization, phytovolatilization phytoextraction, (88), phytovolatilization, phytodegradation, phytostabilization and phytostimulation (Figure 3). Phytoremediators are classified based on their interaction with metals in their environments as: Metal excluders absorbs heavy metals from the contaminated environment into their roots but impede their movement and entry to the aerial parts (89, 90). Metal excluders have low metal extraction potential but good for phytostabilization purposes (91, 92). Metal indicators are such plants use to reflect the extent to which the environment is polluted with heavy metal. Metal indicators absorbs metal in the environment by their roots means and transport to and bio-accumulate in their aerial parts (93). Hyperaccumulators these are plants that has all the necessary potentials to nurture and develop in metalliferous soil, absorb and bio-accumulate exceptionally high concentration of heavy metals in their aerial parts much better than those found in other plant species without showing any heavy metals' phytotoxic effect (94). The mechanism adopted by hyperaccumulators involve bio-sorption and transport of metals transversely membrane of plant root, shuttling and translocation of metals via xylem followed by metals de-toxification and sequestration at both cellular and whole levels of plant (95).

Table 3: Tolerance parameters and their role in phytoremediation process

Tolerance parameter	Uses	Ref.
Organic Acids		
Citrate	Intercede Ni chelation in *T. goesingense* leaves	(81)
Acetic acid and Citric acid	Chelate Cd within the leaves of *S. nigrum*	(82)
Malate	Involved in Zn chelation in *A. halleri*	(83)
Amino Acid		
i. Cysteine	Chelate Cd in *Arabidopsis thaliana*	(84)
ii. Histidine	Detoxification of by chelation Ni	(85)
iii. Proline	Detoxification and osmo-protection in Cd, Cu, Zn, and Pb stress	(86)
Ligands		
Phytochelatin	Chelate Cd in tobacco leaves	(78)
Metallothioneins	Complex with Cu in *Silene vulgaris*	(87)

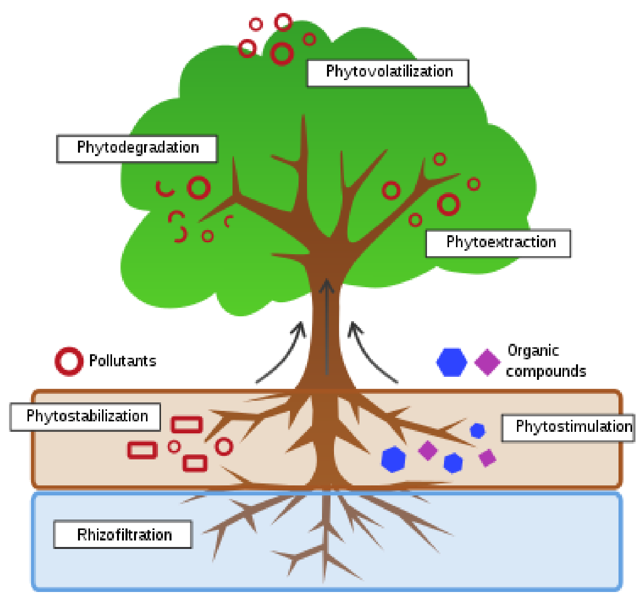

Figure 5: Phytoremediation mechanisms of heavy metals

3 Conclusion

Use of both bacteria, fungi and plants to remediate our immediate environment are modern technologies with high efficiency and very low per cent negative effect to the environment after decontamination hence, are cost effective and eco-friendly compared to the conventional physical and chemical methods. Microorganisms secret organic acids to either mobilize or immobilize heavy metals, uptake and bioaccumulate and detoxify where as phytostabilization in plants is by root organic acid exude and also accumulated and sequester heavy metals. We recommend the genetic engineering process to modify and increase both secretions and exudes and enhancing enzymatic activities to produce and improve the ability of organisms to bioaccumulate.

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Authors'contribution

All authors of this review have a contribution for manuscript writing, reviewing and editing.

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