

HEAVY METAL DETOXIFICATION USING PHYSICO-CHEMICAL AND BIOLOGICAL METHODS: A LITERATURE REVIEW

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ABSTRACT

In the following review an account of the different processes for detoxification of heavy metals has been elaborated. The Physico-chemical methods have been explained with respect to the principle and the process involved. In biological methods both intracellular and extracellular uptake, binding, chelation, biosorption, precipitation, volatilization have been considered. Metal – microbe interaction at the level of cell wall, intracellular accumulation, extracellular interaction have been discussed.

KEYWORDS: Heavy metals, Osmosis, electro dialysis, ion exchange, chemical precipitation, Ultrafiltration, Reduction, Methylation.

INTRODUCTION

Heavy metals released in effluents of many industries is toxic to the ecosystem and thus poses a serious threat to the environment. It has genotoxicity affecting the different life forms and thus the need to neutralize or detoxify it using the different methods at our disposal. An example of this is hexavalent chromium which is more soluble and hence available or mobile in an ecosystem. If it is converted to trivalent chromate, it is precipitated (reduced) out, thus becomes unavailable or immobile. This process of immobilizing chromate can be tried out using a number of physico-chemical or biological methods. In the same manner, mercury can be detoxified using methylation. Similar processes that can control the movement of these metals into different life forms can also result in a check on biomagnifications and its entry into the food chain.

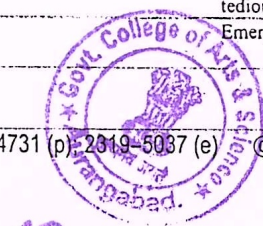
REVIEW OF LITERATURE

Physico-chemical methods involved in detoxification of heavy metals.

Various conventional methods to treat metal pollutants from the effluents are used to control the toxic effect of these metal ions on environmental pollution as well as on various biological systems. The prominent one includes Ion exchange, filtration, precipitation, electrochemical treatment, reduction, chemical reduction, cementation, evaporation recovery (Nyer, 1992). A comparison of various methods used for removal and recovery of metals is given in Table 1 (Iyenger, 2005).

Table 1: Comparison of treatment technologies to remove/recover metals (Iyenger, 2005)

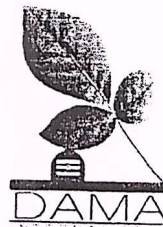
Evaporation	Single /multi stage or vapor compression evaporators	Scaling and/ or fouling	High / Commercial
Distillation	Packed column with heating and concentration device	Scaling and / or fouling	Medium / Commercial
Solvent extraction	Standard procedure	Contaminated solvent requires further processing	Moderately high/ commercial
Adsorption	Batch or continuous adsorption	Limited to low concentration	Medium/ commercial
Ion exchange	Synthetic product	Contaminated solvents required pretreatment.	High / commercial
Membrane processes	Standard manufactured units, with appropriate pretreatment facilities to prevent fouling	Separations are imperfect	Medium/ commercial
Electrochemical processes	DC power and plating apparatus	Impurities upset processes	Medium/ commercial
Starch Xanthate processes	Synthetic product	Preparation is tedious	Medium/ Expt
Biosorption	Live or dead microorganisms.	Emerging technology	Low/recently commercial



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Reverse osmosis

It is a process in which heavy metals are separated by a semi permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater. During the process a high pressure is applied to the effluent side of the membrane to force solvent molecules through the membrane. As a result, membrane separates solvent from solute, and thus effluent becomes more and more concentrated in solutes which can be collected and then recycled. The literature on various methods including reverse osmosis for removal of heavy metals from wastewater has been reviewed by Fujie *et. al.* (1993). The disadvantage of this method is that it is expensive.

Electro-dialysis

In this process, the ionic components (heavy metals) are separated through the use of semi permeable ion selective membranes. Application of an electric potential between the two electrodes causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane (Tiravanti *et. al.* 1996).

Ultra-filtration:

They are pressure driven membrane operations that use porous membranes for the removal of heavy metals. The main disadvantage of this process is the generation of the sludge. Ultra-filtration is the process where membrane is simply used as a filter. Ultra filtration membranes have large pore size and can remove particulates greater than 20 \AA . Some recent work has been done with respect to ultra-filtration to remove metals (Lizzi *et. al.*, 1977).

Ion exchange

Ion exchangers are solid materials which are capable of exchanging cations and anions with their surroundings. A cation exchanger contains exchangeable cations, such as metals or protons. In operation, metal ions in solution are preferentially bound to the insoluble matrix, with the concomitant release of protons or other cations. The toxic metal ion is effectively held within the matrix.

In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resins. The disadvantage includes high cost and partial removal of certain ions. This physico-chemical method is amongst popular method for the removal of chromium from wastewaters. Commonly used matrix for ion exchange is synthetic organic ion exchange resins. (Gadd and White, 1993).

Chemical precipitation

Precipitation of metals is achieved by the addition of coagulants such as, alum, lime, iron salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage.

Electrochemical methods

Treatment of effluents with electrochemical methods depends on changing the formal oxidation state of effluent constituents. With regards to metals, a change in oxidation state via electron exchange brings about a significant change in properties which can be utilized to detoxify effluents. Both the oxidation and reduction of metals are viable effluent treatments. Furthermore, effluents containing more than one metal are also amenable for cleanup. Under the general umbrella of electrochemical methods for waste minimization, there are three broad categories of processes; direct (sulphite oxidation, electro-deposition, dissolution of scrap); indirect (cementation, electro-cementation, electro-precipitation, sulphide oxidation) and electrochemically driven (electro dialysis, electrosorption, electrochemical ion exchange, electro filtration, electro-osmosis) electrochemical processes (Mohammad *et. ai.*, 2003).

In practice electrochemical methods are used mostly for metal recovery in the electroplating industry for effluents which have high metal content like 2000ppm. A simple cell can be used to electrowin the metals with the final effluent concentration of 300ppm. These techniques can be used to recover nickel from acidic and alkaline spent Ni-plating solution (Bershevit *et al.* 1993) recovery of copper from wash water of electroplating industry (Donchenko, 1994), removal of Zinc from waste water by electrode position (Khan and Lutful, 1993), treatment of wastewater of



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galvanizing plant involving the reduction of Cr^{6+} and removal of $\text{Cr}(\text{OH})_3$ with electrolytically generated $\text{Fe}(\text{OH})_2$, recovery of heavy metals from scrap metal pickling wastewater by electrolysis (Huang *et al.*, 1995).

Membranes have applications in electrochemical separation where electro-dialysis is used, it is having higher selectivity for charged particles. This method uses a direct electrical current to transport ions through ion selective membranes. There are two types of ideal membranes:-

- Anionic (permeable to anions and impermeable to cations)
- Cationic (permeable to cations but impermeable to anions)

Precipitation

Precipitation is by far the most common method for dealing with metals-containing waste. Some metal salts are very insoluble; precipitation generates these insoluble salts in the waste stream by the addition of the appropriate counter anion: the precipitate is then filtered off. The anions are usually hydroxide (OH^-), sulfide (S^{2-}) or carbonate (CO_3^{2-}) and metal is usually an alkali or alkaline metal. In most cases the precipitate is lime slurry $\text{Ca}(\text{OH})_2$ which is readily available and inexpensive. Sodium hydroxide can also be used as a solution and generally gives faster precipitation than lime but it is very sensitive to pH and is inefficient at low pH. Carbonates tend to precipitate at lower pH than hydroxides whereas sulphides tend to give complete precipitation with short coagulation time.

The greatest advantage of precipitation is its simplicity; little is needed in terms of extra plant and expertise. The chemicals like lime slurry is abundantly available, generally inexpensive and under correct condition gives reasonable level of clean up. But the disadvantage is that it is unable to treat acidic effluents, it is non selective giving high water content sludge, presence of other salts and organic agents can severely compromises the precipitation efficiency and cannot be used to treat low concentrations of metals (Barkat, M. A., 2011).

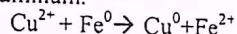
Electro-chemical precipitation

This method utilizes an electrical potential to maximize the removal of heavy metal from contaminated wastewater over the conventional chemical precipitation method (Kurniawan *et al.*, 2006). It is the most common method for removing toxic heavy metals up to (ppm) levels from waste waters.

Although the process is cost effective and its efficiency is affected by low pH and the presence of other salts (ions). The process requires addition of other chemicals, which finally leads to the generation of a high water content sludge, the disposal of which is cost intensive. Precipitation with lime, disulphide or ion exchange lacks the specificity and is ineffective in removal of the metal ions at low concentration.

Cementation

Cementation is a simple metal displacement process used to recover toxic or valuable metals from solution by spontaneous electrochemical reduction to the elemental metallic state, with consequent oxidation of a sacrificial metal by virtue of galvanic cell reaction. A more electropositive metal is used to recover less electropositive metal ion present in the solution. A typical example of this method is the reaction of copper ions with metallic iron. Copper can also be recovered using metallic aluminum.



The process takes place on the surface of Fe, which is anodically dissolved into the solution under open circuit conditions. The advantages of cementation method are the operational simplicity and the use of relatively cheaper reagents.

Solvent extraction

Solvent extraction is a process in which a metal is transferred from aqueous phase to organic phase. The equilibrium stage of this process is termed as liquid partition. One liquid phase is an aqueous solution and the second phase is organic solvent capable of dissolving the distributed at least to certain extent. An extractant is substance with the solvent properties use in a solution of suitable diluents. The main advantages of solvent extraction technique are it is specific with reasonable levels of cleanup upto ppb level, easy modeling and environmentally acceptable alternative to traditional solvent extraction but the disadvantage is it is expensive and requires specialized equipments (Mohammad *et al.*, 2003).



Biological methods

Biological systems have capacity to accumulate metal ions. During growth and metabolism various microorganisms carry out accumulation of various metals, some are essentially required for their metabolic processes. Microbes contain various biochemical processes and efflux processes by which they can deal with different metals. Volatilization is one of the microbial biochemical processes which methylate metals like mercury, selenium, tellurium, arsenic and tin but the processes are complex (Elschenbroich and Salzer, 1992).

Some bacteria have capacity to precipitate metal ions extra-cellularly by the processes of mineralization and the important is by sulfate reducing bacteria, which produce hydrogen sulphide as by product that reacts with metal to produce insoluble metal sulphide. In addition microorganisms possess various mechanisms to accumulate metals intracellularly as well as extracellularly. Extracellular accumulation may be by live cell or by dead biomass. The following table (Table 2) represents comparative performance of various metal recovery technologies.

Table 2: Performance characteristics of heavy metal removal and recovery technologies (Bagdwal *et. al.* 2004)

	pH change	Metal sensitivity	Influence of suspended solids	Tolerance to organic molecules	Working level for appropriate metal(mg l ⁻¹)
Adsorption(e.g. Granulated active carbon)	Limited tolerance	Moderate	Fouled	Can be poisoned	<10
Electrochemical	Tolerant	Moderate	Can be engineered to tolerate Fouled	Can be accommodated	>10
Ion-exchange	Limited tolerance	Chelate resins can be selective	Fouled	Can be poisoned	<100
Membrane precipitation	Limited	Moderate	Fouled	Intolerant	>10
Hydroxide	Tolerant	Nonselective	Tolerant	Tolerant	>10
Sulphide	Limited tolerance	Limited selectively pH dependent	Tolerant	Tolerant	>10
Solvent extraction	Some system tolerant	Metal-selective extractants available	Fouled	Intolerant	>100

Biological methods used in detoxification of heavy metals:

Metal-Microbes interaction

Industrial activities and deliberate and accidental discharges are the major causes due to which microorganisms are increasingly exposed to toxic levels of metal pollutants and may have to acquire resistance to these metals for their survival, for which they detoxify it by using different mechanisms.

Heavy metals can be accumulated by microbial cells by a variety of processes, both physico-chemical and biological. Metabolism-independent binding or adsorption (biosorption) to living or dead cells, extracellular polysaccharides, capsules and slime layers is frequently rapid. Bacterial cell walls and envelopes and walls of algae, fungi and yeasts are efficient metal biosorbent with binding to charged groups frequently being followed by inorganic deposition of increased amount of metal (Burke *et. al.*, 1991). Volesky (1995) has defined utilization of only dead cells as the basis of biosorption and that of living cells as bioaccumulation. I

In practice there are three categories of biotechnological processes for treating liquid wastes containing toxic metals: biosorption; extracellular precipitation and uptake by purified biopolymers and other specialist molecules derived from microbial cells. These processes are not exclusive and several physico-chemical and biological processes may be involved (Gadd and White, 1993). The below mentioned Table 3 contains a comprehensive data of microorganisms and uptake of heavy metals. (Bagdwal *et. al.* 2004)

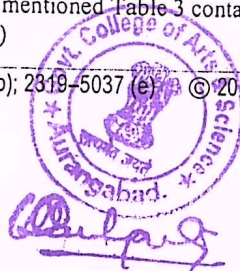


Table 3: Examples of metal uptake by microorganisms.

<i>Streptomyces sp.</i>	Uranium	2-14
<i>Streptomyces viridochromogenes</i>	Uranium	30
<i>Thiobacillus ferrooxidans</i>	Silver	25
<i>Bacillus cereus</i>	Cadmium	4-9
<i>Zoogloea sp.</i>	Cobalt	25
	Copper	34
<i>Citrobacter sp.</i>	Nickel	13
	Lead	34-40
	Cadmium	170
<i>Pseudomonas aeruginosa</i>	Uranium	900
Mixed culture	Uranium	15
<i>Chlorella regularis</i>	Silver	32
<i>Chlorella vulgaris</i>	Uranium	15
<i>Phoma sp.</i>	Gold	10
<i>Rhizopus sp.</i>	Silver	2
	Cadmium	3
	Lead	10
	Uranium	20
<i>Aspergillus niger</i>	Thorium	10
	Thorium	19
<i>Saccharomyces cerevisiae</i>	Uranium	22
	Uranium	10-15
	Thorium	12

The chemical reaction between microorganisms and metals can be divided into six distinct processes.

a) Intracellular accumulation

Concentration of metals within bacteria and other microbial cells can result from interactions with surface legends followed by slow transport into the cell. This may be an important form of detoxification or a means of incorporating specific metals into enzymes (e. g. Cu and Zn). Extracellular or cell wall attached legends are thought to bind toxic metals. These legends transport the metal complexes through the cell wall in a slow transport step. Metals are released inside the cell, incorporated into biochemical pathways or trapped in an inactive form by complexation with another high affinity legend (Wood and Wang, 1985).

Microbial cells can accumulate inter- cellular both metabolically essential metals, such as Ca, K, Na, Fe, and Mg, as well as non- metabolic metals, such as, Ni, Cd, Co. Intracellular accumulation can be energy dependent function requiring active respiration by the microbial cell. Active metal uptake usually requires a specific transport system. Microorganisms have a well-developed transport systems capable of accumulating metals against gradient. When a metal is taken into the cell, ions of an equivalent charge are released by the cell (Brierly *et. al.*, 1985).

b) Cell wall associated metal binding:

Binding of metals to cell or sorption of metals to living or dead cells is considered a practical solution to many metal contamination problems. Algal surfaces contain functional groups that bind to metals competitively with many dissolved legends. Carboxylic amino, thio, hydroxo and hydroxyl-carboxylic groups on the surface of phytoplankton cells interact co-ordinatively with metal ions (Xue *et. al.*, 1988). Bacteria possess lipopolysaccheride (LPS) in their outer membrane. These chemicals are extremely complex consisting of a hydrophobic, phosphorylated section, known as lipid A, a core oligosaccharide; and variable O-specific side chains consisting of a number of unusual sugars. The side chains project out from the cell membrane and contain different functional groups capable of binding metals. Phosphoryl groups of LPS and phospholipids are the most abundant electronegative sites available for metal binding. The polyvalent toxic metals are primarily bound to LPS molecules because of the presence of closely opposed reactive sites (Ferris, 1989). It has been suggested that this may provide a mechanism to immobilize toxic metals and prevent their entry into the cells.

The membranous structure of the Gram negative cell wall results in a more complex interaction with metals. The outer membrane of *Escherichia coli* K-12 binds to the various metals including Na, Ca, Mg, Sr, Ni, Mn, Pb and Fe.



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Approximately 50% of bound metal was usually present in the outer membrane, except for the Mn and Sr. The peptidoglycan layer of Gram negative cell walls also contains sites with which metals can interact. However, the amounts of metal chelated by Gram negative cell walls were less than those chelated by Gram positive cell walls, presumably because the peptidoglycan layer is thinner in Gram negative bacteria and does not contain teichoic acid, a potent chelator of metals (Beveridge, 1981).

Microorganisms can accumulate metabolic and non-metabolic metals by precipitating or binding the metals onto cell walls or cell membranes. Microbial walls are anionic owing to the presence of carboxyl, hydroxyl, phosphoryl, and other negatively charged sites. Cationic metals rapidly bind to these sites by an energy independent reaction. Table 2 comprises the data of metal uptake capacity from effluents by different group of microorganisms.

c) Bacterial cell walls

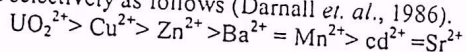
Cell walls of *Bacillus subtilis* are complex polyanion and are likely sites for concentration of metal cations. The isolated cell walls possess select sites, such as diaminopimelic acid residues which retain metals. Isolated cell walls of *Bacillus subtilis* have the greatest preference for Mg, Fe, Cu, Na and K. Lesser amounts of Mn, Zn, Ca, Au and Ni, small amounts of Hg, Sr, Pb and Ag (Beveridge and Murray, 1976).

Fungal cell walls

Like bacteria, both living and non-living fungal biomass can accumulate heavy metals. The uptake of U by *Rhizopus arrhizus* is a three phase process. The first stage involves the formation of a complex between uranyl ions in solution and the nitrogen of the chitin in the fungal wall. In the second stage additional U is absorbed by the three dimensional network of the chitin around the uranyl chitin complex formed in the first stage. In the third stage of the adsorption process the uranyl ion chitin complex hydrolyses precipitating uranyl hydroxide within the chitin network (Sober *et al.*, 1986).

Algal cell walls

Most of what is known regarding algal metal sorption has been determined from studies of freshwater species of *Chlorella*. However, at least one marine alga (seaweed) has been demonstrated to accumulate significant amount of Co (approximately 17 % of the dry weight present.) and the ability of the eluted (non-living) algal material to resorb additional Co was demonstrated for a total of five complete cycles (Kuyucak and Volesky, 1986). Functional groups in algae and other biomass materials include carboxyl, amide, hydroxyl, phosphate amino, imidazole, thiol and thioether moieties that is present in the proteins, carbohydrates and lipids. Algal genera showing significant metal sorption in the non-viable state include species of *Chlorella reguloris*, *Chlamydomonas* and *Ulthrox*. In decreasing order metals are bound selectively as follows (Darnall *et al.*, 1986).



d) Siderophores

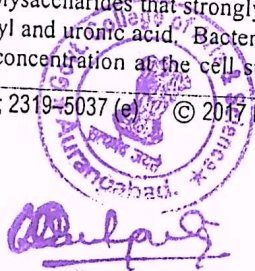
Siderophores are iron complexing, low molecular weight organic compounds. Two major types are generally considered, the hydroxamate and catecholate. Hydroxamate groups strongly bind to ferric iron. It follows that analogs may also be strongly bound by these siderophores for example aluminum, gallium, and chromium form trivalent metal ions of similar size (Raymond *et al.* 1984). Molybdenum and copper have been shown to form strong complexes with catecholate siderophores (Hider, 1984).

e) Extracellular processes

Various bacterial metabolites are responsible to cause mobilization or immobilization of metals which has applications in mining and industrial processes. Organic or inorganic acids produced by microorganisms including genera *Thiobacillus*, *Sulfobolus*, *Serratia*, *Pseudomonas*, *Bacillus* and *Aspergillus*, are able to extract metals from solid substrates (Schinner and Burgstaller, 1989).

Extracellular polymer metal interaction

Many microorganisms produce extracellular polysaccharides that strongly bind metals. Metal binding functional group includes pyruvate, phosphate, hydroxyl, succinyl and uronic acid. Bacterial capsules possess features that suggests that they act as effective modulators of metal ion concentration at the cell surface scavenging metals from solution when



their concentrations are low and serving as impermeable barriers when metals exist at toxic levels in the surrounding environment.

Transformation and volatilization of metals

Toxic metal oxides can be used as electron acceptors and the reduced form is frequently less toxic and may be either more volatile or precipitated. Evidence exists that certain metal tolerant bacteria use toxic metal species as electron acceptors, selenate has been shown to be reduced by anaerobic bacteria (Maiers *et. al.* 1988). Chromate is also reduced under anaerobic condition and it is associated with a soluble chromate reductase protein (Ishibash *et.al.* 1990). Mercury Hg^{2+} is reduced to Hg^0 by mercuric reductase with a subsequent volatilization. A taxonomically diverse group of heterotrophic bacteria utilize metallic cations as terminal electron acceptors under anaerobic conditions. In this process, the metal is reduced to a lower valency which can potentially be utilized in this way by microorganisms. Strain of *Enterobacter cloacae* was isolated from polluted habitat was capable of reducing Cr (VI) To Cr (III) thus reduction of soluble hexavalent chromium to its non soluble trivalent form offers a promising bioremediation strategy (Turick *et. al.*, 1998).

Methylation of metalloids

Conversion of inorganic forms of metals or metalloids to methylated forms may be employed by microorganisms as a detoxification mechanism. Some strains of *Penicillium* were shown to methylate selenite and tellurite ions. The metals Hg, Sn, Pl, Pt, Au, the metalloids As, Se, Te, and S have been postulated to accept methyl group from methyl cobalamine in biological system, but not the metals cadmium, lead, and zinc.

Sulphide precipitation

Hydrogen sulphide is produced by sulphate reducing bacteria like *Desulfovibrio* and *Desulfotomaculum* sp. The solubility products of most metal sulphides are extremely low and they are readily precipitated as sulphides like ZnS, CdS, and FeS. Sulphate reducing activity can occur as a useful auxiliary metal removing mechanism. Table 4 represents uptake capacities of metals under study by microorganisms.

Table4: Metal uptake capacity by some microorganisms (Bagdwal *et. al.* 2004)

		mmol/gm	g/g
Cu	<i>S. cerevisiae</i>	0.68	0.0432
	<i>Rhizopus arrhizus</i>	0.42	0.016
	<i>Chorella fusca</i>	0.05	0.003
	<i>B. subtilis</i>	0.53	0.0033679
	<i>E. coli</i>	0.090	0.005719
Zn	<i>S. cerevisiae</i>	0.47	0.03
	<i>P. chrysogenum</i>	7.83	0.5
	<i>Claviceps paspali</i>	15.30	1.0
	<i>A. niger</i>	0.65	0.042
Cr	<i>R. arrhizus</i>	0.596	0.031
	<i>Candida utilis</i>	0.009	0.0046
	<i>Streptomyces nouresei</i>	0.034	0.0018
Ni	<i>B. subtilis</i>	0.107	0.00628
	<i>E. coli AB264(Envelope)</i>	0.002	0.000117
Mn	<i>B. subtilis</i>	0.801	0.440
	<i>E. coli AB264(Envelope)</i>	0.140	0.00769

CONCLUSION

It is evident from the discussions that these heavy metals can be remediated using various methods. The efficacy of the process would depend on the concentration and type of the heavy metal. The use of physico-chemical methods in metal binding though effective may not be monetarily feasible owing to the higher cost of such materials. In case of biological processes, it may be said that these are in demand as it is a green technology, cheap and is environment friendly. However the selection of the consortium or the pure culture is of utmost importance as metal tolerance and





metal detoxification are two independent characteristics. It has been proved by a number of researchers that organisms that are metal tolerating may not be detoxifying it.

ACKNOWLEDGEMENTS

One of the author Rohini Kulkarni (Pandhare) is grateful to the UGC for granting Teachers fellowship under FIP.

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(Signature)

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