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A Study of Removal of Heavy Metals on Low Cost Biosorbents

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ABSTRACT

The effluent treatment in developing countries is expensive and major cost is associated with the dependence on imported technologies and chemicals. The indigenous production of treatment techniques and chemicals locally, or use locally available non-conventional materials to treat pollutants seems to be the solution to the increasing problem of treatment of effluents. In this regard, there has been a focus on the use of appropriate low cost technology for the treatment of wastewater in developing countries in recent years. Technically feasible and economically viable pretreatment procedures with suitable biomaterials based on better understanding of the metal biosorbent mechanism(s) are gaining importance.

Keywords: Heavy Metals, Waste Water, Low Cost, Biosorbents, Adsorbents

I. INTRODUCTION

Metals, a major category of globally-distributed pollutants, are natural elements that have been extracted from the earth and harnessed for human industry and products for 10 millennia. Metals are notable for their wide environmental dispersion from such activity; their tendency to accumulate in select tissues of the human body; and their overall potential to be toxic even at relatively minor levels of exposure. Today heavy metals are abundant in our drinking water, air and soil due to our increased use of these compounds. They are present in virtually every area of modern consumerism from construction materials to cosmetics, medicines to processed foods; fuel sources to agents of destruction; appliances to personal care products. It is very difficult for anyone to avoid exposure to any of the many harmful heavy metals that are so prevalent in our environment. The distribution of heavy metals in manufacturing industries is given in Table 1

Table: 1 General Distribution of Heavy metals in Particular Industrial Effluents

Industries	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Ti	Zn
General Industry and Mining				X	X	X		X		X			X
Plating			X	X	X				X	X			X
Paint Products				X						X		X	
Fertilizers			X	X	X	X	X	X	X	X			X
Insecticides / Pesticides		X			X		X						
Tanning		X		X									
Paper Products				X	X		X		X	X		X	X
Photographic	X			X									
Fibers					X								X
Printing / Dyeing				X						X			
Electronics	X										X		
Cooling Water				X									
Pipe Corrosion					X					X			

Ag - Silver;, As – Arsenic; Cd – Cadmium; Cr – Chromium; Cu –Copper; Fe – Iron, Hg – Mercury; Mn – Manganese; Ni – Nickel; Pb – Lead; Se – Selenium; Zn- Zinc.

Some metals, such as copper and iron, are essential to life and play irreplaceable roles in, for example, the functioning of critical enzyme systems. Other metals are *xenobiotics*, i.e., they have no useful role in human physiology (and most other living organisms) and, even worse, as in the case of lead and mercury, may be toxic even at trace levels of exposure. Even those metals that are essential, however, have the potential to turn harmful at very high levels of exposure, a reflection of a very basic tenet of toxicology--"the dose makes the poison."

II. TOXICOLOGICAL ASPECTS OF HEAVY METALS

Due to their mobility in aquatic ecosystems and their toxicity to higher life forms, heavy metals in surface and groundwater supplies have been prioritized as major inorganic contaminants in the environment. Even if they are present in dilute, undetectable quantities, their recalcitrance and consequent persistence in water bodies imply that through natural processes such as biomagnifications, concentrations may become elevated to such an extent that they begin exhibiting toxic characteristics. These metals can either be detected in their elemental state, which implies that they are not subject to further biodegradative processes or bound in various salt complexes. In either instance, metal ions cannot be mineralized. Apart from environmental issues, technological aspects of metal recovery from industrial waters must also be considered (Wyatt, 1988).

2.1 Effects of heavy metals on human health

The heavy metals hazardous to humans include lead, mercury, cadmium, arsenic, copper, zinc, and chromium. Such metals are found naturally in the soil in trace amounts, which pose few problems. When concentrated in particular areas, however, they present a serious danger. Arsenic and cadmium, for instance, can cause cancer. Mercury can cause mutations and genetic damage, while copper, lead, and mercury can cause brain and bone damage.

2.2 Effects of heavy metals on aquatic organisms

Aquatic organisms are adversely affected by heavy metals in the environment. The toxicity is largely a function of the water chemistry and sediment composition in the surface water system.

The below illustration (Figure 1) *(Volesky, 2005)* shows how metal ions can become bioaccumulated in an aquatic ecosystem. The metals are mineralized by microorganisms, which in turn are taken up by plankton and further by the aquatic organisms. Finally, the metals by now, several times biomagnified is taken up by man when he consumes fish from the contaminated water.

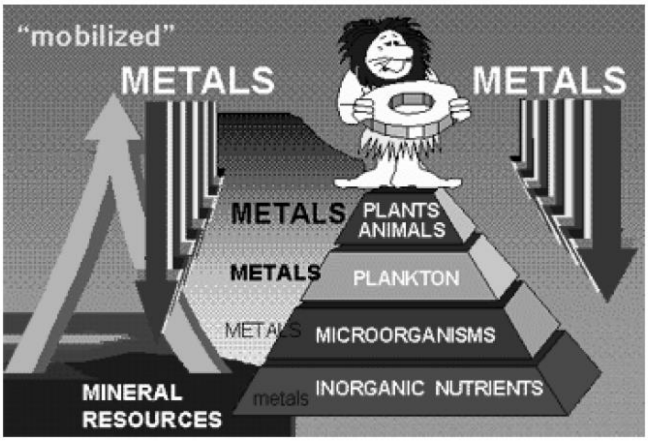

Figure 1. Biomagnifications in natural systems

i. Slightly elevated metal levels in natural waters may cause the following sublethal effects in aquatic organisms: histological or morphological change in tissues;
ii. Changes in physiology, such as suppression of growth and development, poor swimming performance, changes in circulation;
iii. Change in biochemistry, such as enzyme activity and blood chemistry;
iv. Change in behaviour; and
v. Changes in reproduction *(Connell et al., 1984).*

2.3 Irrigation effects of heavy metals

Irrigation water contaminated with sewage or industrial effluents may transport dissolved heavy metals to agricultural fields. Although most heavy metals do not pose a threat to humans through crop consumption, cadmium may be incorporated into plant tissue. Accumulation usually occurs in plant roots, but may also occur throughout the plant *(De Voogt et al., 1980).*

Most irrigation systems are designed to allow for up to 30 percent of the water applied to not be absorbed and to leave the field as return flow. Return flow either joins the groundwater or runs off the field surface (tailwater).

Sometimes tailwater are rerouted into streams because of downstream water rights or a necessity to maintain streamflow. However, usually the tailwater is collected and stored until it can be reused or delivered to another field (USEPA 1993a).

III. NEED FOR THE REMOVAL OF HEAVY METALS

Continuous discharge of industrial, domestic and agricultural wastes in rivers and lakes causes deposit of pollutants in sediments. Such pollutants include heavy metals, which endanger public health after being incorporated in food chain. Heavy metals cannot be destroyed through biological degradation, as is the case with most organic pollutants. Incidence of heavy metal accumulation in fish, oysters, mussels, sediments and other components of aquatic ecosystems have been reported from all over the world (Naimo, 1995; Sayler et al., 1975).

IV. BIOSORPTION

During the 1970's increasing environmental awareness and concern led to a search for new techniques capable of inexpensive treatment of polluted wastewaters with metals. The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on binding capacities of various biological materials. Till date, research in the area of biosorption suggests it to be an ideal alternative for decontamination of metal containing effluents. Biosorbents are attractive since naturally occurring biomass/adsorbents or spent biomass can be effectively used. Biosorption is a rapid phenomenon of passive metal sequestration by the non-growing biomass/adsorbents. Results are convincing and binding capacities of certain biomass/adsorbents are comparable with the commercial synthetic cation exchange resins.

The biosorption process involves a solid phase (sorbent or biosorbent; adsorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (adsorbate, metal). Due to the higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound adsorbate species and its portion remaining in the solution. The degree of adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases.

There are many types of adsorbents; Earth's forests and plants, ocean and freshwater plankton, algae and fish, all living creatures, that including animals are all "biomass/ adsorbents". The renewable character of biomass that grows, fuelled directly or indirectly by sunshine, makes it an inexhaustible pool of chemicals of all kinds.

Biosorption has advantages compared with conventional techniques (Volesky, 1999). Some of these are listed below:

Cheap: the cost of the biosorbent is low since they often are made from abundant or waste material.
Metal selective: the metalsorbing performance of different types of biomass can be more or less selective on different metals. This depends on various factors such as type of biomass, mixture in the solution, type of biomass preparation and physicochemical treatment.
Regenerative: Biosorbents can be reused, after the metal is recycled.
No sludge generation: no secondary problems with sludge occur with biosorption, as is the case with many other techniques, for example, precipitation.
Metal recovery possible: In case of metals, it can be recovered after being sorbed from the solution.
Competitive performance: biosorption is capable of a performance comparable to the most similar technique, ion exchange treatment. Ion exchange is, as mentioned above, rather costly, making the low cost of biosorption a major factor.

Biosorbents intended for bioremediation environmental applications are waste biomass of crops, algae, fungi, bacteria, etc., which are the naturally abundant. Numerous chemical groups have been suggested to contribute to biosorption. A review of biosorption of heavy metals by microorganisms is presented below. Biosorption by microorganisms have various disadvantages, and hence many low cost adsorbents (industrial/agricultural waste products/byproducts) are increasingly used as biosorbents. This chapter also provides review of the low cost adsorbents used for removal of heavy metals (Ahalya et al., 2004).

V. LOW COST ADSORBENTS FOR METAL REMOVAL

The disadvantages of using microorganisms can be overcome by using low cost adsorbents. In general, a sorbent can be assumed to be “low cost” if it requires little processing and is abundant in nature, or is a byproduct or waste material from another industry, which has lost its economic or further processing values. There h been several low cost adsorbents that have been used for the removal of heavy metal.

The following Section presents a detailed discussion on the low cost adsorbents that have been used for the removal of heavy metals. Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing required and local availability. Research pertaining to low cost absorbents is gaining importance these days though most of the work is at laboratory levels. Some of the low-cost sorbents reported so far include: Bark/tannin-rich materials; lignin; chitin/chitosan; seaweed/algae/alginate; xanthate; zeolite; clay; flyash; peat moss; modified wool and modified cotton; tea waste; maize coen cob etc.

5.1 Bark and other tannin – rich materials

Timber industry generates bark a by-product that is effective because of its high tannin content. The polyhydroxy polyphenol groups of tannin are thought the active species in the adsorption process. Ion exchange takes place as metal cations displace adjacent phenolic hydroxyl groups, forming a chelate (Randall *et al*., 1974; Vasquez *et al*., 1994).

Another waste product from the timber industry is sawdust. Bryant *et al*. (1992) showed adsorption of Cu and hexavalent chromium (Cr (VI) by red fir sawdust to take place primarily on components such as lignin and tanin rather onto cellulose backbone of the sawdust. While bark is the most likely choice due to its wide availability, other low cost byproducts containing tannin show promise for economic metal sorption as well.

5.2 Chitosan

Among various biosorbents, chitin is the second most abundant natural biopolymers after cellulose. However, more important than chitin is chitosan, which has a molecular structure similar to cellulose. Presently, chitosan is attracting an increasing amount of research interest, as it is an effective scavenger for heavy metals. Chitosan is produced by alkaline N-deacetylation of chitin, which is widely found in the exoskeleton of shellfish and crustaceans. It was estimated that chitosan could be produced from fish and crustaceans (Rorrer and Way 2002). The growing need for new sources of low-cost adsorbent, the increased problems of waste disposal, the increasing cost of synthetic resins undoubtedly make chitosan one of the most attractive materials for wastewater treatment.

5.3 Zeolites

Basically zeolites are a naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms. During 1970s, natural zeolites gained a significant interest, due to their ion-exchange capability to preferentially remove unwanted heavy metals such as strontium and cesium [Grant et al., 1987]. This unique property makes zeolites favorable for wastewater treatment. The price of zeolites depending on the quality is considered very cheap and is about US$ 0.03–0.12/kg, [Virta, 2001].

5.4 Clay

It is widely known that there are three basic species of clay: smectites (such as montmorillonite), kaolinite, and micas; out of which montmorillonite has the highest cation exchange capacity and its current market price is considered to be 20 times cheaper than that of activated carbon [Virta, 2002]. Therefore, a number of studies have been conducted using clays, mainly montmorillonite, to show their effectiveness for removing metal ions such as Zn2+, Pb2+, and Al3+ from aqueous solutions (Brigatti et al., 1996; Staunton and M. Roubaud, 1997 and Turner et al., 1998). Although the removal efficiency of clays for heavy metals may not be as good as that of zeolites, their easy availability and low cost may compensate for the associated drawbacks.

5.5 Peat moss

Peat moss, a complex soil material containing lignin and cellulose as major constituents, is a natural substance widely available and abundant, not only in Europe

(British and Ireland), but also in the US. Peat moss has a large surface area (>200 m2/g) and is highly porous so that it can be used to bind heavy metals. Peat moss is a relatively inexpensive material and commercially sold at US$ 0.023/kg in the US [Jasinski, 2001]. Peat moss is a good adsorbent for all metals. It is widely known that peat moss exhibited a high CEC and complexities towards metals due to the presence of carboxylic, phenolic, and hydroxylic functional groups.

5.6 Industrial waste

Several industrial by-products have been used for the adsorption of heavy metals. Table 2 summarizes some of the industrial wastes.

Table 2. Adsorption capacities of industrial waste (mg/g)

Material	Sources	Ni^{2+}	Pb^{2+}	Hg^{2+}	Cr^{6+}	Zn^{2+}	Cd^{2+}	Cu^{2+}
Waste slurry	Srivastava *et al.*, 1985		1030	560	640			
	Lee and Davis, 2001						15.73	20.97
Iron (III) hydroxide	Namasivayam and Rangnathan, 1992				0.47			
Lignin	Aloki and Munemori, 1982		1865			95		
Blast furnace slag	Srivastava *et al.*, 1997		40		7.5			
Sawdust	Ajmal *et al.*, 1998							13.80
Activated red mud	Zouboulis and Kydros, 1993	160						
	Pradhan *et al.*, 1999				1.6			
Bagasse fly ash	Gupta *et al.*, 1999				260			

VI. CONCLUSION

The results of many biosorption studies vary widely because of the different criteria used by the authors in searching for suitable materials. Some researchers have used easily available biomass types, others specially isolated strains, and some processed the raw biomass to different extents to improve its biosorption properties. In theabsence of uniform technology, results have been reported in different units and in many different ways, making quantitative comparison impossible. Certain waste products, natural materials and biosorbents have been tested and proposed for metal removal. It is evident from the discussion so far that each low-cost adsorbent has its specific physical and chemical characteristics such as porosity, surface area and physical strength, as well as inherent advantages and disadvantages in wastewater treatment. In addition, adsorption capacities of sorbents also vary, depending on the experimental conditions.

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