

Introduction

The quality of life on Earth is linked inextricably to the overall quality of the environment. Earlier, we believed that we had an unlimited abundance of natural resources viz. water, land, pure air, flora and fauna. The demands of increasing population coupled with the desire of most of the people for a higher material standard of living are resulting in worldwide pollution on a massive scale. All the resources in each and every habitable part of the earth have been polluted to some extent. If this state of affair is allowed to continue, it will prove to be monstrous problem to all living systems on the earth. Various kinds of pollutants are creating special concern to the society to find out the remedial measures to combat this problem of environmental and ecological imbalances.

Exploding population and high standard of living of people are resulting in tremendous growth of industrial sector. In pace with the rise in industrial need of water, wastewater from industries is also going up continuously. Discharge of effluents from the industries to water bodies pollutes large quantity of unpolluted water. Thus, apart from taking measures for saving of water in industrial sector, apparently, there is a need of serious efforts for treatment of industrial effluent to lower the concentration of toxic pollutants in wastewater to the level of permissible limits before discharging into water bodies. For the sustainable development, industries have an important responsibility to practice water conservation and treatment of industrial effluent. The volume of waste water and concentration of various pollutants in industrial discharge vary depending on manufacturing process and other factors such as house keeping, reuse and technology etc.

Organic pollutants impart a high biological oxygen demand (B.O.D.) load to the liquid wastes. Some organic wastes from pharmaceutical and petrochemical industries and coke-ovens contain phenols which are toxic to fish, microorganisms and other aquatic life. Effluents from industries manufacturing drugs, dyestuffs, pesticides and detergents can also be toxic. Usage of anionic detergents which are not biodegradable leads to a lot of foaming and frothing.

Alkalies, acids, inorganic salts and other chemicals formed during processing lead to inorganic pollution. Besides, being the cause of corrosion of metals, these chemicals are toxic to aquatic life. Industries like paper and pulp, tanneries, electroplating, textiles and coke-ovens among many others, discharge these chemicals. Inorganic chemicals such as free chlorine, ammonia, hydrogen sulfide and other sulfides, salts of metals like Cr, Zn, Ni, Cd, Cu, Ag etc. are usually found in metal plating liquid wastes, alkali producing units, polyvinyl chloride, coke-oven and fertilizer industries. Chromates, phosphates, ammonia and urea are typical chemicals found in effluents from fertilizer and electroplating industries.

Heavy metal contamination due to natural and anthropogenic sources is a global environmental concern. Heavy metals are among the most harmful of the elemental pollutants and are of particular concern because of their toxicities at higher levels to humans and other forms of life. The main sources of metal pollution in environment are geological weathering, industrial processing of ores and metals, the use of metal and metal components, leaching of metal from garbage and solid waste dumps. Heavy metals have played a critical role in industrial development and technological advantages. The major water pollution causing industries are electroplating, textile mills, metal processing industries, pulp and paper mills and tannery industries (Niyogi *et al.*, 1998). Metals are among the main environmental concerns because of their unique characteristics unlike organic pollutants; they are non-biodegradable and hence are accumulated by living organisms. Release of heavy metals without proper treatment poses a significant threat to public health because of its persistence, biomagnification and accumulation in food chain (Akar and Tunali, 2005 and Ozcan *et al.*, 2005).

Heavy metal ions such as Cr^{6+} , Zn^{2+} , Cu^{2+} , Ni^{2+} and Fe^{2+} are essential for plants and animals. Essential metals are required for enzyme catalysis, nutrient transport, protein structure, charge neutralization and control of osmotic pressure. But when they are present in excess amount, these and non-essential metals such as Cd^{2+} , Hg^{2+} , Ag^{2+} and Pb^{2+} can be extremely toxic (Axtell and Sternberg, 2003).

These essential metals are required for enzyme catalysis, nutrient transport, protein structure, charge neutralization and control of osmotic pressure. Studies pertaining to the toxicity of trace metals follow the general trend that an undersupply leads to a deficiency, sufficient supply results in optimum conditions, but an oversupply results in toxic effects and lethality in the end. Metal concentration has been linked to birth defects, cancer, skin lesions, retardation leading to disabilities, liver and kidney damage and a host of other maladies (Puranik and Paknikar, 1997; Atkinson *et al.*, 1998; Martins *et al.*, 2004).

Heavy metals in water are compounded by the fact that they are non-biodegradable, vigorous oxidizing agents and strongly bound to many biochemicals especially polypeptides and proteins. Heavy metals pose a high risk in two respects: firstly, these are not usually eliminated from the aquatic systems by natural processes, and secondly, they are enriched in mineral and organic substances. Toxic metals such as mercury, arsenic, chromium, cadmium, zinc, arsenic, copper and many other metal species tend to accumulate in bottom sediments from which they may be released by various processes of remobilization and in changing form can enter the biological chain, thereby reaching human beings where they produce chronic and acute ailments. So, there has been increasing concern over dangerous levels of heavy metals in the aquatic environment and sources of potable water supply, because of heavy metal accumulation and their persistence in nature after they are discharged in small quantities by numerous industrial activities (Zhang *et al.*, 2008).

It is well known that there is a permissible limit for each metal, above which it shows toxic effects (Gadd and White, 1990 and Qian *et al.*, 1999). Several incidents due to heavy metal contamination in aquatic environment have increased the awareness about the heavy metal toxicity. Among these 'Minimata' tragedy due to mercury poisoning, 'Itai-itai' disease in Japan due to cadmium toxicity and 'Arsenic' pollution in West Bengal are well known. In order to reach the full objective of 'Zero pollution', immediate steps have to be taken by adopting alternative technologies which suit the situation of low capital

availability, minimum manpower and can save energy consumption (Siddiqi *et al.*, 1999). A fine balance must be maintained between metals in the environment and human health.

Chromium is naturally occurring element with an atomic number 24 and atomic weight 52.01. It ranks 21st in abundance among the elements and is more abundant than copper, zinc, lead, nickel, mercury etc. Its isotopes present in nature are Cr-50 (4.49%); Cr-52 (83.78%) and Cr-54 (2.3%). It exhibits a wide range of possible oxidation states. The most common oxidation states of chromium are +2, +3 and +6, with +3 being the most stable. Chromium compounds of oxidation state +6 are powerful oxidants. The two major oxidation states viz. +3 and +6 show different biological and toxicological properties (Murthi and Viswanathan, 1991). The permissible limit of Cr (VI) ions in wastewater discharged from industrial and municipal effluent into inland water is 1.0 mg/l (CPCB, 2004).

Chromium metal is extremely resistant to chemical attack (corrosion and oxidation) which accounts for its use in stainless steel for chrome plating (Harie *et al.*, 1993). The major uses of chromium are in the making of alloys such as stainless steel, in chrome plating and metal ceramics. Chromium plating is widely used to give steel a polished silvery mirror coating. Chromium is also used in dyes and paints, its salts colour glass an emerald green and is also used to produce synthetic rubies; as a catalyst in dyeing and in tanning of leather; to make molds of the firing of bricks (Fiol *et al.*, 2008; Kumar *et al.*, 2007; Landis and Yo, 2003). Chromium (VI) oxide (CrO₂) is used in the manufacturing of magnetic tape.

Chromium exists in food, air, water and soil, mostly in the Cr(III) form. Cr(III) is comparatively insoluble in water while Cr(VI) is quite soluble and is readily leached from the soil to groundwater or surface water (Pellerin and Booker, 2000 and Gode and Pehlivan, 2005). However, the most severely toxic chromium compounds are chromium oxide and chromium sulphate in trivalent form and chromium trioxide, chromic acid and dichromate as hexavalent chromium (Ramos *et al.*, 1994). Cr(VI) is the toxic form of chromium, released

during many industrial processes including electroplating, leather tanning and pigment manufacture (Faisal and Hasnain, 2004 and Richard and Bourg, 1991). These industries release undesirable Cr(VI) in water and are major anthropogenic source of Cr(VI) in water. More than 1,70,000 tones of chromium wastes are discharged annually in environment as a result of industrial and manufacturing activities (Abassi *et al.*, 1998). Merian (1991) has compiled the global sources of chromium in the environment. These are:

Source	Emission%
1. Volcanic emission	<1%
2. Biological cycle	
a) Extraction from soil by plants	15%
b) Weathering of rocks and soil	15%
3. Man made emissions	
a) From general ore and metal production	3%
b) From coal burning and other combustion process	7%
c) From metal use	60%

The major anthropogenic sources release 10^6 tonnes/annum of chromium in the form of fly ash, industrial effluents, particulates, dust and fumes into air, soil, water and biological systems (Abassi *et al.*, 1998). Of its two oxidation states, Cr(III) and Cr(VI), the hexavalent form is considered to be a group 'A' human carcinogen because of its mutagenic and carcinogenic properties (Murthi and Viswanathan, 1991 and Bai and Abraham, 2001). Cr(VI) is highly soluble and is easily taken up by the cells (Cervants *et al.*, 2001; Sarangi and Krishnan, 2008). Inside the cells it is reduced partially to highly unstable Cr(V) radical, which leads to the formation of reactive oxygen species and the oxidative stress thus generated is the cause of carcinogenicity (Gadd, 1986; Ackerley *et al.*, 2006 and Yun *et al.*,

2001). Cr(III) plays a vital role in insulin metabolism as the glucose tolerance factor (GTF)(Anderson, 1997). Supplementation of Cr(III) has improved the glucose tolerance in diabetes, malnourished children and elder people. The lethal dose-50 (LD-50) value for Cr(III) is about 10mg/kg of body weight (Kothandaraman & Swaminathan, 1997).

Cr(VI) causes liver and kidney damage, internal hemorrhage, dermatitis, respiratory damage and lung cancer. Long term exposure to the respiratory tract and skin can produce perforated and ulcerated nasal septa, inflammation of nasal passage, frequent nasal bleeds and skin ulcers (Harie *et al.*, 1993). It also damages DNA through interference with DNA-polymerase enzyme and free radical formation (Dakiky *et al.*, 2002; Athar and Vohora, 1995). While Cr(VI) is found to be toxic due to its capability to inhibit respiration by inactivating enzymes involved in the respiratory chain. Chromium (VI) is taken up via sulphate or thiosulphate transporter and oxidizes biological molecules resulting in toxicity.

Zinc is one of the most common element in the earth crust and the fourth most widely used metal, following iron, aluminum and copper. It is found in air, soil and water and is an essential element of human diet. The U.S. Recommended Dietary Allowance (U.S.RDA) for zinc is 5-15 milligrams a day for humans. Not enough zinc in one's diet can result in a loss of appetite, a decreased sense of taste and smell, slow wound healing and skin sores, or a damaged immune system. Harmful health effects generally begin at levels from 10 to 15 times the U.S. Recommended Dietary Allowance(in the 100 to 250 mg/day range). World Health Organisation (WHO) recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg/l .

Zinc has many commercial uses. Mostly zinc is used in steel galvanizing process. Other uses include the automotives, construction, electrical and machinery industries. It is used in dry cell batteries and mixed with other metals to make alloys like brass and bronze. Zinc compounds are widely used in the industries to make paint, rubber, dye, wood preservatives and ointments. Zinc may be found in wastewater discharges from acid mine drainage, galvanizing

plants, as a leachate from galvanized structures and natural ores and from municipal wastewater treatment plant discharges (Norton *et al.*, 2004).

Zinc is an essential element and its participation in several metabolic processes has been well documented; nevertheless, a potential gastrointestinal toxicity occurs because of an over accumulation of this metal in the human body (Walsh *et al.*, 1994; Ruiz *et al.*, 2008). Consuming large amounts of zinc, even for a short time, can cause stomach cramps, nausea and vomiting. For longer periods, it can cause anemia, pancreatic damage and lower levels of high density lipoprotein cholesterol. Breathing large amount of zinc (as dust or fumes) can cause a specific short-term disease called metal fume fever. This is believed to be an immune response affecting the lungs and body temperature. Zn-sterates have been found to be possible cause of pneumoitis. Zn salts, particularly chlorides produce dermatitis upon contact with skin. Symptoms of zinc toxicity include vomiting, dehydration, stomach pain, nausea, lethargy, dizziness and muscle incoordination. Zinc ions also have a great affinity towards replacing iron in red cells and plasma proteins and may cause anemia (Abdel- Halim *et al.*, 2003).

Many international and national agencies have set up tolerance limits for these heavy metals. The National Academy of Sciences (U.S.) considers an adequate yet safe intake of chromium to be 0.05 to 0.20 mg/day by an average human (Harie *et al.*, 1993). The limited values given by WHO are as under (Jamode *et al.*, 2003):

Chromium	0.1 mg/l in drinking water
Zinc	5-15 mg/l in drinking water

The Indian standards are as under (Sarkar and Gupta, 2003; Jamode *et al.*, 2003):

IS: 10500-1991	0.05 mg/l of Chromium in drinking water
IS: 10500-1991	5.0 mg/l of Zinc in drinking water

According to environment (protection) law, 1986 (Government of India), for most of the industries including electroplating industry which discharge wastewater to inland surface water, the limit for discharge of hexavalent chromium is 0.1 mg/l where as the limit is 2.0 mg/l for the industries which discharge their wastewater in public sewerage system. The discharge limit is set to a stringent 1.0 mg/l in case of the industries which discharge their wastewater in marine coastal area.

The minimum national standards (MINAS) are the industry specific effluent standards, which have been evolved at the national level. These standards have been laid down by CPCB. According to MINAS standards for electroplating industries are:

Chromium(VI)	0.1 mg/l
Zinc	5.0 mg/l

The electroplating industry has been playing a momentous role in the development and growth of numerous metal manufacturing and other engineering industries since the early part of 20th century. The electroplating industry occupies a place of prominence in the Indian economy on account of its massive potential for employment, growth and exports. For decades, the electroplating sector was reserved for small scale sector in India. This was done primarily to promote employment. Most of the electroplating industries lack technical and financial resources to introduce modern technology. As a result, the electroplating industry, by and large uses obsolete and inefficient technologies for resource utilization and waste treatment.

The electroplating industry is highly water intensive. A large amount of wastewater is produced which contain a high amount of heavy metals. The volume and characteristics of electroplating wastewaters vary widely from industry to industry, depending on the operating practices and water conservation measures adopted in the industry. The disposal of untreated wastewater from electroplating industries into municipal sewers, in many cases, has caused the

contamination of a water course. It has, on the other hand, posed a problem of disposal of sludge from municipal sewage treatment plants owing to the accumulation of toxic metals in the sludge. Electroplating wastewaters are highly corrosive due to the presence of acids. They attack metal and concrete structures, especially the concrete sewers, in which the wastewaters are discharged. Further, the acid hydrolyze the soaps present in sewage, liberating fatty acids, which may form floating scum, cause the floating objects to stick together and clog the sewers.

The removal and recovery of chromium and zinc from the effluent is one such aspect which can help in the cost reduction of sources. Process economies of these industries do not allow these industries for such high cost methods like solvent extraction, evaporation, distillation, electrochemical treatment, reverse osmosis, electro dialysis, ultra filtration, ion exchange, chemical precipitation, especially when processing unit is small.

Wastewater discharge standards for electroplating industry according to CPCB:

Parameters	Concentration not to exceed, mg/l (Except for pH and temperature)
pH	6.0 to 9.0
Temperature	should not exceed 5° C above ambient temperature of receiving body
Oil & Grease	10
Suspended solids	100
Cyanides	0.2
Ammonical nitrogen (as N)	50
Total residual chlorine (as Cl ₂)	1.0
Cadmium (as Cd)	2.0
Nickel (Ni)	3.0

Zinc (Zn)	5.0
Chromium as Cr(VI)	0.1
	Total 2.0
Copper (as Cu)	3.0
Lead (as Pb)	0.1
Iron (as Fe)	3.0
Total metal	10.0

Preventive measures:

1. Volume reduction of wastewater
2. Strength reduction

Curative measures:

- Physical
- Biological
- Chemical
- Combination of above

Among the various conventional techniques applied for the heavy metal removal from wastewater are reduction and precipitation, filtration, adsorption, solvent extraction, evaporation, distillation, electrochemical treatment, reverse osmosis, electro dialysis, ultra filtration, ion exchange, chemical precipitation and phytoremediation (Atkinson *et al.*, 1998; Xiang –Liang *et al.*, 2005). There are some drawbacks with each of these methods. These mainly include high capital and operating cost in the form of chemicals and other expensive instruments. There are also some operational problems, which are encountered during effluent treatment like scaling, fouling and further processing of effluent, imperfect separation. These conventional methods are often ineffective or highly expensive when the initial heavy metal concentrations are in the range of 1-100 ppm and when the discharge concentration required are less than 1 ppm (Shumate *et al.*, 1978; Sharma and Forster, 1993; Tunali *et al.*, 2005). Activated carbon which

is frequently used for the adsorption of pollutants is costly both to use and to regenerate.

The currently practiced technologies for removal of heavy metals from industrial effluents appear to be inadequate and expensive. The major disadvantage with conventional treatment technologies is the production of sludge. As a result, an aquatic problem is changed into solid disposal problem. Therefore, amongst the chemical adsorbents only ion exchange resins were considered as the option for remediation with least ecological problem. However, chemical resins are expensive and the increasing demand of eco-friendly technologies has led to the search of low cost alternatives which can be considered as single use materials. Out of these recent methods, adsorption is preferred by many industries because it is cheap, highly effective and easy to operate (Metcalf and Eddy, 1995). The increasing demand of eco-friendly technologies has led to the search of low cost alternatives that could be considered as single use materials and perform well over the shortcomings of conventional methods. The different shortcomings of the conventional methods are:

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. The disadvantage of this method is that it is very expensive and energy intensive.

Electrodialysis: In this process, the ionic components (heavy metals) are separated through the use of semi-permeable ion selective membranes. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards the 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.

Ultrafiltration: 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 sludge.

Ion-exchange: In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The disadvantages include high cost and partial removal of certain ions. It requires recharging of resin beads.

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.

Phytoremediation: Phytoremediation is the use of certain plants to clean up soil, sediment and water contaminated with metals. The disadvantages include that it takes a long time for removal of metals, generation of toxic sludge or other waste products and the regeneration of the plant for further bioaccumulation is difficult.

These methods have several disadvantages such as unpredictable metal ion removal, high amount of reagents required and the generation of toxic sludge which is often difficult to dewater and also require extreme caution in their disposal. These disadvantages can become pronounced at low metal concentrations in contaminated groundwater, mine tailings effluent and other industrial wastewaters. There is a need for innovative treatment technologies for the removal of heavy metal ions from wastewater which do not bound with shortcomings of these conventional methods.

ADSORPTION: The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent and the material concentrated or adsorbed at the surface of that phase is the adsorbate. Adsorption is thus different from absorption; a process in which material transferred from one phase to another interpenetrates the second phase to form a 'solution'. The term sorption is

a general expression encompassing both processes. Adsorption at a surface or interface is largely due to result of binding forces between the individual atoms, ions or molecules of an adsorbate and the surface, all of these forces having their origin in electric interaction. There are four types of adsorption:

1. Exchange adsorption or ion exchange: It involves electrostatic attachment of ionic species.
2. Physical adsorption: It involves Vander Waals forces
3. Chemical adsorption: It involves reaction between adsorbate and adsorbent.
4. Specific adsorption: It involves attachment of adsorbate molecules on specific functional groups (Slejko, 1985).

The aqueous phase separation of toxic heavy metal ions by biosorption is an emerging field of interest, from both the resource conservation standpoint and the environmental remediation standpoint. Unlike conventional sorptive resins or organic solvents, biosorption employs inexhaustible, inexpensive, and non-hazardous materials that exhibit significant specificity for the target metal contaminants, thus generating low volumes of waste. The application of fly ash (Rai and Kumar, 1999), sawdust (Khatti and Singh, 1999), sheep and goat hair (Sarvanane *et al.*, 2002 and Balasubramanian *et al.*, 1998) are some of the few examples. The search for alternative and innovative wastewater treatment techniques has focused attention on the use of biological material such as algae, fungi, yeast and bacteria for the metal removal and recovery during recent years (Akhtar and Iqbal, 2004). Microbial biomass can passively bind large amount of metals, a phenomenon commonly referred to as biosorption (Tsezos *et al.*, 1997), thus providing a cost-effective solution for industrial wastewater management.

Biosorption is possible both by living and non-living biomass; however, bioaccumulation is mediated only by living biomass (Garnham *et al.*, 1992). Further, bioaccumulation is a growth dependent process and it is difficult to

define a variety of effluents in contrast to biosorption, which is growth independent. Thus, microbial biomass can be used and exploited more effectively as biosorbents rather than accumulation. Biosorbents are attractive since naturally occurring biomass(s) or spent biomass(s) can be effectively utilized. Besides this, biosorption offers an advantage of low operating cost, minimizes the volume of chemical and/ or biological sludge to be disposed, is highly efficient in dilute effluents and has no nutrient requirements (Gupta *et al.*, 2000). These advantages have served as potential incentives for promoting biosorption as a viable cleanup technology for heavy metal(s) pollution.

Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (Fourest and Roux, 1994). The biosorption process involves a solid phase (sorber or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorber for the sorbate species, the latter is attracted and bound to the biosorbent surface by different mechanisms. The process continues till equilibrium is established between the amount of solid bound sorbate species and its portion remaining in the solution. The degree of sorber affinity for the sorbate determines its distribution between the solid and liquid phases. Algae, bacteria, fungi and yeasts have proved to be potential metal biosorbents (Volesky and Holan, 1995). The major advantages of biosorption over conventional treatment methods include (Kratovichil *et al.*, 1998; Mungasavalli *et al.*, 2007; Srinath *et al.*, 2002; Norton *et al.*, 2004):

- Low cost
- High efficiency
- Minimization of chemical and biological sludge
- No additional nutrient requirement
- Regeneration of biosorbent
- Possibility of metal recovery.

- Removal of heavy metals from effluent irrespective of toxicity
- Short operation time

These biosorbents possess metal sequestering properties and can decrease the concentration of heavy metal ions in solution from ppm to ppb level. They can effectively sequester dissolved metal ions out of dilute complex solutions with the high efficiency and rapid rate kinetics. Therefore, biosorption is an ideal solution for the treatment of high volume and low concentration complex wastewaters (Volesky *et al.*, 1992 and Veglio and Beolchini, 1997). The uptake of metals by fungi and yeast has generated an interest in using them for removal of toxic metals from wastewater. The potential of fungal biomass in removing metal ions from wastewater was recognized (Zajic and Chiu, 1972; Jilek *et al.*, 1975; Shumate *et al.*, 1978 and Gadd, 1986). Fungi are used in a variety of industrial fermentation process, which could serve as an economical and constant source of supply of biomass for the removal of metal ions. Fungi can also be easily grown in substantial amounts using unsophisticated fermentation techniques and inexpensive growth media (Kapoor *et al.*, 1999). Therefore, biosorption carried out by fungi could serve as an economical means of treating effluents charged with toxic metallic ions (Kapoor and Virraghavan, 1995; Volesky and Holan, 1995).

The bio-recovery of heavy metals can be affected by physico-chemical parameters of the solution such as pH, ion strength and temperature, and by other characteristic of biomass (concentration, presence of organic and inorganic functional groups and pretreatments) (Rincon *et al.*, 2005; Mehta and Gaur, 2001; Romera *et al.*, 2008). Batch studies provide insight into the effectiveness of metal removal by biomass. However, the continuous operation of a reactor is a more efficient mode of operation in comparison to a batch process. Hence, there is a need to perform column studies for an efficient treatment process. Different type of reactors including fluidized bed columns and continuous stirred tank reactors can be used for column studies. However, packed bed sorption has a number of advantages including the possibility of achieving a reasonably high sorption

capacity with very low effluent concentrations. Adsorption takes place from the inlet of the column and proceeds to the exit and a high degree of purification can be achieved in a single process step (Suzuki, 1990).

Kinetics test show the time-concentration profile for sorption. The sorption reaction in itself is inherently an extremely fast one. It is mainly the particle mass transfer which controls the overall sorption kinetics (sorbent particle size, porosity and mixing in the sorption system). Environmental factors such as the solution pH, ionic strength, to a lesser degree temperature etc are likely to affect the sorption performance.

As the biosorption process mainly involves cell surface sequestration, cell wall modification can greatly alter the binding of metal ions. A number of methods have been employed for cell wall modification of microbial cells in order to enhance the metal binding capacity of biomass and to elucidate the mechanism of biosorption. These modifications can be introduced either during the growth of a micro-organism or in the pre-grown biomass. The condition in which micro-organisms grow affects its cell surface phenotype which in turn affects its biosorption potential. Pre-grown biomass could be given several physical and chemical treatments to tailor the metal binding properties of biomass to specific requirements. The physical treatment includes heating/boiling, freezing/thawing, drying and lyophilization. The various chemical treatments used for biomass modification include washing the biomass with detergents, cross-linking with organic solvents and alkali or acid treatment. These pretreatments have been suggested to modify the surface characteristic/ groups either by removing or masking the groups or by exposing the more metal binding sites.

From an overview of microbial biosorbents and biowaste as sorbent candidate, it can be concluded that laboratory trials do show their potential for commercialization since they possess good metal binding capacity. Although freely suspended biomass may have better contact with the adsorbate during the adsorption, the biomass suspension is normally not the practical form for large scale applications in biosorption process. It turned out that it is very difficult to

ensure equal quality of the porous bed packing, because the fungal mycelial pellets are soft structures of intertwining hyphae which easily adhere and form agglomerates or are compressed by the gravity or due to the flow pressure. Therefore, the formation of channels and zones of unexploited biomass within the bed was inevitable.

The microbial biomass is often immobilized to enhance its stability, mechanical strength, reusability and the ease of handling. Essentially, the main requirement of an industrial sorption system is that the sorbent can be utilized as a fixed or expanded bed and it should not cause much pressure drop across the bed. This will necessitate some degree of pretreatment, sizing, pelleting, chemical modification and immobilization. Immobilization of biomass within a suitable matrix can overcome problems by offering ideal size, mechanical strength, rigidity and porous characteristics to the biological material (Trujillo *et al.*, 1995; Kumar *et al.*, 2007; Anisha and Prema, 2008). Therefore, biosorption carried out by immobilized fungal biomass can serve as an economical means of treating effluent charged with toxic metallic ions (Kapoor and Viraraghvan, 1995 and Volesky and Holan, 1995). The biochemical processing with immobilized microbial cells offers a number of unique advantages over traditional fermentation processes with free cells, such as relative ease of cell mass separation from bulk liquid for possible re-use, prevention of washout, reduced risk of contamination and operational stability. These are aimed at obtaining a suitable structure for use in a bed reactor and may enhance metal specific binding sites. Immobilized forms of biosorbents is ideal for use in column applications with the advantages of improved mechanical strength, online matrix isolation in flow analysis, low resistance to fluid flow, self supporting rigidity, excellent durability, easy regeneration of biosorbent material and relatively high local cell density (Yan and Viraraghvan, 2001; Abu Al-Rub *et al.*, 2004; Li *et al.*, 2008; Wang and Cheng, 2007). Many different natural and synthetic polymeric supports such as alginate, agar, silica, carrageenan, polyethylenimine, polyacrylonitril, polysulfone, polyvinyl alcohol and polyacrylamide have been widely used for immobilization of biosorbents (Xiangliang *et al.*, 2005).

Biotechnological exploitation of biosorption technology for removal of heavy metal(s) depends on the efficiency of the regeneration of biosorbent after metal desorption. Therefore, non-destructive recovery by mild and cheap desorbing agents is desirable for regeneration of biomass for use in multiple reuse cycles. The deposited metals are washed out (desorbed) and the biosorbent is regenerated for another cycle. The desorption of metal ions should result in:

- High concentration metal effluent
- Undiminished metal uptake on reuse
- No physico-chemical damage to the biosorbent

The concentration ratio (CR) is used to evaluate the overall concentration effectiveness of the whole sorption-desorption process

$$CR = \frac{\text{eluted metal concentration}}{\text{Feed metal concentration}}$$

Obviously, the higher the CR, the better the overall performance of the sorption process, making the eventual recovery of the metal more feasible with higher eluted concentration.

Dynamic sorption studies are invariably more demanding. The most optimal configuration for continuous flow sorption is the packed bed column which gradually saturated from the feed to the solution exit end. In the sorption column contractor the saturated zone is moving along the column length pushing the transitional dynamic sorption zone ahead of itself. The packed column reactors are simple to design, easy to construct and operate, and are reported to have advantages over suspended growth reactors like continuously stirred tank reactors (CSTRs). Biosorbents are contained within the packing medium in an enclosed vessel and liquid wastes pass upwards. System wherein liquid wastewater flows downward are also available, but they have less biomass concentration. In these systems, biosorbent do not form slime on packing and regular back-washing prevents clogging. This will also prevent high concentration of suspended solids sloughing continuously into the effluent. The treatment rate is

directly proportional to surface area of packing. PCR is 15- 30 times efficient than CSTRs.

Equilibrium sorption data is required to optimize the parameters for effective biosorption and to assess its performance. The conditions of the sorption system, particularly pH, must be carefully controlled at the required values over the entire period of contact until the sorption equilibrium is reached. This may take a few minutes to hours or much longer, depending on the size and type of biosorbent particle. A simple preliminary sorption kinetic test will establish the exposure time necessary for the given sorbent particles to reach the equilibrium state. The performance of the sorbent is usually gauged by its uptake capacity (Q).

For successful application on a large scale any operation needs to be economically viable. The feasibility of a biosorption process depends on such factors as:

- availability of raw material(biomass)
- biosorbent uptake performance
- source of raw biomass
- chemical/physical treatment of biomass
- immobilization of biomass
- the desorption and regeneration process used

Adsorption and desorption studies invariably yield information on the mechanism of metal biosorption: how is the metal bound on the surface of biosorbent. This knowledge is essential for understanding of the biosorption process and it serves as a basis for quantitative stoichiometric considerations which constitute the foundation for mathematical modeling of the process. A number of different metal binding mechanisms has been postulated to be active in biosorption as:

- chemisorption: by ion exchange, complexation, coordination, chelation;
- physical adsorption: microprecipitation.

Mathematical modeling and computer simulation of biosorption process offers an extremely powerful tool for a number of tasks on different levels. It is essential for process design and optimization where the equilibrium and dynamic test information comes together representing a multivariable system which can not be effectively handled without appropriate modeling. The dynamic nature of sorption process applications (columns, flow-through contactors) makes this approach mandatory. When reaction kinetics is combined with mass transfer which is, in turn, dependent on particle and fluid flow properties only a rather sophisticated apparatus can make sense out of the web of variables. The aim of biosorption process modeling is to predict the process performance under different conditions. The modeling of biosorption process guides experimental work, predicts performance and helps in optimizing the process which is essential for designing the continuous flow process. The most effective mode of a sorption process is undoubtedly based on a fixed bed reactor/ contactor configuration. The sorption bed has to be porous to allow the liquid to flow through it with minimum resistance but allowing the maximum mass transfer into the particles as small as practical for a reasonable pressure drop across the bed. Biosorbents have to be hard enough to withstand the application pressures, porous and/or 'transparent' to metal ion sorbate species, featuring high and fast sorption uptake even after repeated regeneration cycles.

In this study, attempts have been made to develop immobilized fungal biosorbent for the removal of heavy metals from electroplating industrial effluent and an attempt has been made to demonstrate this process in laboratory by using a low cost biosorbent prepared from immobilized fungal biomass.

Thus, the present study was carried out with following objectives:

- 1 To develop fungal biosorbent.
- 2 To optimize the parameter for effective sorption by the sorption system.
3. To immobilize the biosorbent for effective biosorption.
- 4 To assess the performance of biosorbent by batch methods.
- 5 To develop the sorption packed column configuration to assess the performance in dynamic flow.
- 6 To regenerate the biosorbent material in multiple reuse cycles.
- 7 To analyze the sorption equilibria using Freundlich and Langmuir isotherms.
- 8 To determine the spontaneous nature of sorption process.
- 9 To develop kinetic modeling of the sorption process.
- 10 To compare the sorption capacity of the biosorbent with conventional biosorbents.
- 11 To find out functional groups responsible for the process of biosorption.