Chapter-6
Summary

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Increasing pollution due to heavy metals, which are toxic and non-biodegradable in nature, has necessitated more stringent environmental legislation for removal of metals from wastewater. Chromium (VI), which is a carcinogenic form of the metal, is present in the effluent of leather tanning, textile industry, electroplating and metal finishing industries. Zinc is used in steel galvanizing and zinc plating process. Other uses include the automotive, 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 is found in wastewater discharges from acid mine drainage, galvanizing plants, as a leachate from galvanized structures and natural ores, and from municipal wastewater discharges. 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, Cr(VI) and Zn(II) standards for electroplating industry are:

Chrmium (VI)	0.1 mg/l
Zinc (II)	5.0 mg/l

Various conventional methods available for removal of metals from wastewater like chemical precipitation, ion-exchange, memberane separation, oxidation-reduction etc are cost intensive and have other drawbacks like production of toxic sludge in bulk, reduced efficiency at low metal ion concentration in solution. Bioremediation has emerged in the recent years as an alternative technology which is easy to operate, involving little production of toxic sludge and hence an eco-friendly technology.

Different groups of micro-organism including bacteria, algae, fungi and yeast has been used for bioremediation of waste waters. Larger biomass production, low nutrition requirements and non-toxic nature of non-pathogenic fungi provide them an edge over other micro-organisms. Biosorption is possible both by living and non-living biomass; however, bioaccumulation is mediated only by living biomass. Further bioaccumulation is a growth dependent process

viz. it determined the availability of the metal ion in soluble form for biosorption; and it dictated the overall surface charge of the biosorbent material, which in turn influenced the metal uptake behaviour. When the adsorbent dose was increased, there was less increase in adsorption capacity of biosorbent for the utilization of solvent and as a result specific adsorption decreased significantly with increase in mass of adsorbent per unit volume. This was due to the fact that total metal uptake depended on the number of available binding sites where as the specific metal uptake was the amount of metal adsorbed by per unit weight of the biosorbent which decreased due to screening effect. No appreciable increase in removal of Cr(VI) and Zn(II) was observed after the optimum time period. This was due to attainment of equilibrium at particular dose, pH, temperature and time. It was also observed that after certain time, the rate of removal was not as high as it was in initial time periods.

Biosorption got slow down in later stages because initially a large number of vacant surface sites were available for biosorption and after sometime the remaining vacant sites were difficult to occupy due to repulsive force between the solute molecules of the solid and bulk phase. Rate constants for metal biosorption process were significantly higher for non-immobilized biosorbents. The slow rate of Chromium and zinc adsorption for immobilized biosorbents was probably due to slow pore diffusion of the metal ions into the bulk of biosorbent. Upto the concentration of 100 mg/l, these biosorbents were found to be very efficient in metal removal. The immobilized fungus performed better than non-immobilized fungus. At very low metal ion concentrations, the ratio of the sorptive surface area to the total metal ions available was high and nearly all metal ions in solution were adsorbed. This was due to the fact that at low concentrations of metal ions in solution, surface coverage was small and hence almost all the available metal ions were removed. However, at higher concentrations, all sites available on the biosorbent surface got occupied. The equilibrium of biosorption of heavy metals was modeled using adsorption isotherms viz. Langmuir and Freundlich models and the adsorption data was found to fit well with these models. The biosorption process of metal ions

adsorbed onto the biosorbents until all the binding sites were occupied. The breakthrough curves increased sharply and reached quickly to the concentration of the influent after the breakthrough point, which implied the affinity of the biomass to Cr(VI) and Zn(II) was very strong.

FTIR spectra provided a qualitative and preliminary analysis of the chemical functional groups present on the cell wall of the biomass which provided information on the nature of the possible cell-metal interactions in metal biosorption by different biomass. The IR spectra of biosorbent before and after metal uptake were recorded to obtain information on the nature of chemical interaction between metal and the biosorbent in the 4000-400 cm^{-1} range of the IR spectrum. In the presence of metal, the biomass showed some changes in the IR spectrum pattern such as band disappearance after saturation of active sites, bands shifting and bands elongation. The results indicated that the chemical interactions such as ion-exchange and physical adsorption between the hydrogen atoms of carboxyl (-COOH), hydroxyl (-OH) and amine (-NH$_2$) groups of biomass and the metal ions were mainly involved in the biosorption of Cr(VI) and Zn(II) ions onto biosorbent surface. Pretreatment of biomass produced additional binding sites via denaturation of proteins on the cell wall structure. The changes in the functional groups and the surface properties of fungal biosorbents before and after pretreatment were confirmed by the FTIR spectra as shown by a change in functional groups. FTIR spectra of native and pretreated fungus confirmed the bisorbents heterogeneity and evidenced the presence of different characteristic peaks in agreement with presence of amino, carboxylic, hydroxyl and carbonyl groups etc. These advantages served as potential incentives for promoting biosorption as a viable cleanup technology for heavy metal remediation.