ABSTRACT

The presence of heavy metals in waters is a severe public health concern, and due to detrimental effect of them on man and environment, their removal from contaminated water is deemed important to the protection of environmental health. The treatment and disposal of heavy metal bearing wastes presents a unique challenge to the environmental engineers. Unlike many organic wastes, heavy metals cannot be degraded biologically to harmless products. Several methods are used to remove metals from wastewaters. Chemical precipitation, coagulation with alum or iron salts, membrane filtration, reverse osmosis, ion-exchange and adsorption are some of the most commonly used processes. Each has its merits and limitations in application.

Biosorption, the process in which microorganisms (dead, alive or inactivated) or their derivatives are directed to remove and recover metals from the aqueous solutions, has been known for a few decades but has emerged as a promising alternative technology in the last decade. Though there are several report dealing with the potential of laboratory grown microorganisms (algae, bacteria and fungi), fungal byproducts of industrial fermentation, marine algae and activated sludge for heavy metal uptake, little exploration work has been carried out on the possibility of utilizing locally growing macro fungi (fruit bodies). These are not only widely available but also appear to possess properties suitable for continuous flow operation. Hence an extensive investigation to utilize the fruit bodies of locally available macro fungi as biosorbents for metal sequestration from aqueous phase is essential.

Four species of commonly available and locally growing mushrooms were selected for this investigation. These were collected from the local mushroom cultivators, sun dried and grinded to a size range of 710-500 μm. The experiments reported in this thesis were conducted in four phases- preliminary screening of the fungal species, mechanism studies employing selected biosorbent, batch studies and column studies. The preliminary screening of fungal species were carried out on the basis of quantitative determination of maximum metal [Cd(II)] uptake potential (Q_{max}) using Langmuir isotherm. The maximum metal uptake varied from 0.059 mmol/g for *pleurotus sajor-caju* to 0.082 mmol/g for *Volvariella volvacea*. Since the latter exhibited maximum metal uptake compared to other species, *Volvariella volvacea* was selected for further studies.

To investigate the effect of chemical treatment on physical properties and metal uptake capacities, the biosorbent *V. volvacea* was subjected to pretreatment using a number of chemicals like methanol and chloroform, cold alkali and hot alkali sequentially to obtain derivatives mainly devoid of lipids, proteins etc. The biosorbent was also subjected to formaldehyde treatment both in presence of H_2SO_4 and HNO_3. The resultant derivatives were compared based upon physico-chemical properties desirable for a potential biosorbent (thermal stability, physical strength, leaching characteristics, chemical stability, head loss, filterability etc.) in addition to their metal uptake capacity. The results indicated that the biosorbent *V. volvacea* does not require any elaborate chemical treatment to behave as a good and potential biosorbent thus eliminating the cost of pretreatment. Further investigation was then carried out with *V. volvacea* in its native form without any chemical treatment.

The derivatives resulted after sequential elution of cellular components were subjected to spectroscopic studies (Infrared spectra). The results revealed that cadmium was coordinated to the structural proteins and polysaccharides of the cell wall. Energy Dispersion X-Ray Analysis (EDAX) indicated release of calcium ions into the aqueous medium from the biosorbent during cadmium uptake pointing to the fact that most of the uptake was due to ion exchange. This was further substantiated when release of both calcium and magnesium ions were observed during isotherm studies. It was also observed that at low initial cadmium concentration in the solution ion exchange was the predominant mechanism whereas at high cadmium concentration role of other mechanism in addition to ion exchange was evident.

In batch studies, the effects of different factors like pH, biosorbent concentration, ionic strength, calcium and magnesium, chlorides and anionic ligands on the performance of the biosorbent were investigated. Adsorption kinetics and equilibrium isotherm studies were also carried out. These studies were carried out by varying one factor at a time. Batch desorption and regeneration studies were conducted with various eluting agents like HCl, EDTA, $CaCl_2$ and distilled water. In column studies, performance of the biosorbent column in removing heavy metals from distilled water and tap water spiked with heavy metals was investigated. Adsorption coefficients were determined from single column study to predict the breakthrough curve of another column. Column desorption studies were carried out with only HCl as a desorption medium. Laboratory experiments on the performance of fruit bodies of macro fungi *V. volvacea*, indicated that it can effectively be used as a biosorbent for the removal of cadmium, lead and copper from water environment.

The kinetics of biosorption can be represented by a first order reversible equation and film diffusion was appeared to be the rate limiting step in the biosorption as indicated by both kinetics and interruption tests.The equilibrium partitioning of heavy metals onto the biosorbent can be described by Langmuir and Freundlich isotherms. Biosorption of cadmium, lead and copper was found to be pH dependent and higher metal removal efficiencies were observed near neutral pH ranges. Both calcium and magnesium inhibit the uptake of heavy metals marginally in the observed ranges. Presence of chloride ions did not influence the metal removal significantly and ionic strength of the solution beyond 10^{-2}M as $NaNO_3$ reduced both cadmium and lead uptake. Metal uptake was affected by strong anionic ligands like EDTA however, other anionic ligands have little effect on the metal removal efficiency.

Desorption and regeneration studies in both batch and packed bed continuous flow reactors explored the possibility of reuse of the biosorbent. After desorption, reactivation with dilute alkali could successfully retained the full capacity of the biosorbent. Spent bed was desorbed with 0.01N HCl and regenerated by treating with 0.01N NaOH before reuse. The adsorption coefficients determined with logitech method using single column could be used to successfully predict the breakthrougn of another column. The performance of a continuous flow reactors employing *V. volvacea* with cadmium, lead and copper spiked with tap water showed its efficiency in removing mixed metals. The adsorption capacity of the biosorbent *V. volvacea* as obtained from column studies was found to be superior to the adsorption capacities of several other adsorbents reported in literature.