CHAPTER 8

SUMMARY AND CONCLUSION

Biosorption of heavy metals is one of the most promising technologies involved in the removal of toxic metals from industrial waste streams and natural water. It is a potential alternative to conventional process for the removal of metals. If the biomass employed is a waste material, then adsorption represents a cheap alternative to conventional process, due to the use of low cost sorbing materials. In addition, Biological approaches on other hand, offer the potential for the highly selective removal of toxic metals coupled with considerable operational flexibility. Many such processes utilizes micro organism that have key role in the sorption of toxic metals. This mechanism is based on the metal binding capacities of various biological materials. The advantages of biosorption lie in both the good performance in metal removal and cost effectiveness, making use of fungi and raw materials of fermentation and agricultural processes.

The chrome tannery effluent sample was collected from the State Industries Promotion Corporation of Tamil Nadu Limited Industrial Complex, Ranipet, Vellore District, Tamil Nadu, India. The collected samples were serially diluted and used for the isolation of metal tolerant fungi that have the ability to adsorb heavy metal chromium. Three fungal colonies were isolated and identified based on morphological characteristics and by molecular characterization and found to belong to the same genus but different species. The isolated colonies were identified by the phylogenetic analysis as A. oryzae,
A. jegita and A. niger. Then these fungal samples were mass cultured, dried and subjected for the process of pretreatment for the removal of chromium (VI).

The growth and chromium ion consumption of A. oryzae, A. jegita and A. niger cultivated on 0, 25, 50, 75 and 100 mg/L initial chromium concentrations were studied. It was found that the maximum biomass production was found to be 6.15, 7.12 and 5.8 g/L for A. oryzae, A. jegita and A. niger respectively in the absence of chromium ions. When the initial chromium concentration in the solution increases the biomass concentration starts to decrease to the inhibition by the metal ion. The uptake of yield of chromium at different IMC for A. oryzae, A. jegita and A. niger were compared. The increase in lag period with increasing metal level in the medium indicates that metal accumulation is mainly dependent on metabolic activity. The metal uptake was moderately rapid at the lower initial chromium concentration. The specific uptake of chromium was increased with increasing chromium concentration upto 75 mg/L for all Aspergillus species.

The dry biomass of A. oryzae, A. jegita and A. niger were subjected to various chemical modifications. The biomass were subjected to various pretreatment such as acid treatment, alkali treatment, acid doping, wet sterilization, dry sterilization, carbonization and immobilization. The results of the pretreatment clearly shows maximum removal of Cr (VI) was obtained as 90.6, 91.2 and 92.5% using nitric acid doped chemically modified fungal biomass A. oryzae, A. jegita and A. niger respectively followed by dry sterilized biomass. The percentage removal of the dry sterilized biomass were 90.1, 90.8 and 92% for dry biomass of A. oryzae, A. jegita, and A. niger respectively. The percentage removal of nitric acid doped biomass and dry sterilized biomass was found to be similar and hence the biomass obtained by the process of drying sterilization were chosen for further biosorption experiments since it was found to be economical.
The biosorption of hexavalent chromium was investigated for the optimization of the parameters such as contact time, initial metal ion concentration, pH, biosorbent dosages was studied using *A. oryzae*, *A.jegita* and *A. niger*. The biosorption experiments were carried out in batch mode operation. The residual chromium concentration in solution was analyzed spectrophotometrically by DPC method and then verified using AAS. The maximum percentage removal of chromium was found to be 90.1, 90.8 and 92% for the biosorbents *A. oryzae*, *A.jegita* and *A. niger* respectively at 25 mg/L initial chromium concentration, with 1g biosorbent dosage, pH 2.0 at 150 rpm agitation speed in room temperature. The equilibrium time for the biosorption of chromium on to *A. oryzae* and *A.jegita* were 240 min and for *A. niger* the equilibrium was reached at 300 min.

In order to recycle the fungal biomass the metal adsorbed *A. oryzae*, *A.jegita* and *A. niger* were subjected to desorption studies and the values of desorption were estimated based on the concentration of chromium in NaOH, Hcl, EDTA and distilled water. The Cr (VI) metal was found to desorb effectively using 0.1 M NaOH and percentage desorption was found to be 96.1, 96.3 and 97.12% using *A. oryzae*, *A.jegita* and *A. niger* respectively in the first cycle. The desorbed *A. oryzae*, *A.jegita* and *A. niger* were again subjected to Cr (VI) adsorption and the metal removal was slightly lesser than the first cycle and was found out to be 88.2, 89.2 and 91.4% using *A. oryzae*, *A.jegita* and *A. niger* respectively. The percentage of desorption decreases slightly as the number of cycle increases but the results clearly shows that desorption was effective using NaOH and EDTA. The percentage of desorption using *A. oryzae*, *A.jegita* and *A. niger* at the end of fifth cycle were 87.32, 88.6 and 90.28% using 0.1M NaOH. The biosorption using desorbed fungus was also found to be efficient and the percentage removal after fifth cycle for *A. oryzae*, *A.jegita* and *A. niger* using 0.1M NaOH treated desorbed biomass were found to be 83.7, 84.11 and 86.2% respectively. Due to the recycling property of the
biosorbent, it can be reused for several cycles until the rigidity of the biomass is suitable for adsorption. Since the biomass is easily biodegradable.

The surface morphology of the adsorbents was clearly understood with the help of SEM for the biosorbents \textit{A. oryzae, A.jegita and A. niger} before and after metal loading. From the SEM images it is evident that the presence of asymmetrical pattern and rough surfaces as it had more cuts and grooves thus made possible the adsorption of chromium ion in different parts of \textit{A. oryzae, A.jegita and A. niger}. The functional group and metal bonding was confirmed with FTIR for chromium adsorbed biosorbent \textit{A. oryzae, A.jegita and A. niger}. The FTIR spectra of biosorbents \textit{A. oryzae, A.jegita and A. niger} before metal loading were compared with metal loaded biosorbent and the peak shifts due to biosorption were studied. In all the samples, the absorption bands were observed at wave numbers for the unloled biosorbents \textit{A. oryzae, A.jegita and A. niger} are between 418 cm$^{-1}$ and 3421 cm$^{-1}$ and for metal loaded \textit{A. oryzae, A.jegita and A. niger} the peaks are found at wave numbers between 420 cm$^{-1}$ and 3728 cm$^{-1}$. Band shifts were observed for the signals at 3000 cm$^{-1}$ and variation at 1500 cm$^{-1}$ (indicates variable C=C stretch). These changes observed in the spectrum indicated the possible involvement in chromium biosorption proves that functional group on the surface of the biomass.

Biosorption equilibrium is important to find the efficacy of the biosorption process. Several equilibrium models were investigated and the equilibrium constants were evaluated. The order of best fit is based on the correlation coefficient (R$^2$) for \textit{Aspergillus oryzae} was found to be Freundlich(0.9901)>Redlich Peterson(0.9836)>Harkins Jura(0.9609) > Temkin(0.9233) > Langmuir (0.8955), for \textit{Aspergillus jegita} was found to be Freundlich(0.9992)>Redlich Peterson (0.9681)>Temkin (0.9386) > Harkins Jura(0.8898)> Langmuir (0.8545) and for \textit{Aspergillus niger} was found to be
Freundlich(0.9988) > Redlich Peterson(0.9985) > Langmuir (0.9851) > Temkin(0.9803) > Harkins Jura(0.9072).

Kinetic models are employed to test the experimental data. Time dependent experimental data were analyzed for First order, Second order, Power Function and Elovich kinetic models and the constants are calculated. The order of best fit for the equilibrium modeling was carried out for the experimental data. The order of best fit of kinetic modeling for A. oryzae was found to be Elovich model > Power function model > First order kinetics > Second order kinetics, for A. jegita was found to be Elovich model > First order > Power function model > Second order kinetics and for A. niger it was found to be Elovich model > Second order kinetics > First order kinetics > Power function kinetics. In all the cases Elovich kinetics fits well proves that the active site of the biosorbent is heterogeneous and proves that the adsorption was mainly due to chemisorption.

Due to heavy metal pollution discharge from the industries to solve the problem practically, these biosorption experiments were carried out with actual effluent using biosorbents A. oryzae, A. jegita and A. niger. The results showed that biosorbents A. oryzae, A. jegita and A. niger had potential in removing chromium(VI) and the percentage removal of chromium from chrome tannery effluent and the removal percentage was found to be 86.5%, 87.45% and 89.07% respectively. The physico-chemical analysis of the treated effluent showed that the removal of chromium from chrome tannery effluent is a feasible, low cost, economical process and eco friendly process.