CHAPTER 6

SUMMARY AND CONCLUSIONS

6.1 SUMMARY

The removal of heavy metals from the aquatic environment is one of the important issues in many industrialized countries. The commonly used treatment methods to remove heavy metal ions from wastewaters include chemical precipitation, ion exchange, adsorption and membrane processes. Biosorption, the removal of heavy metals by dead biomass, has gained credibility during recent years, as it offers a technically feasible and economical approach. Several biological materials have been investigated for heavy metals removal, including bacteria, algae and fungi.

The present study has examined the biosorption of heavy metals from industrial wastewaters by using algal biomass of *Chlorella, Volvox* and *Zygnema* as well as with fungal biomass *Trichoderma*. The purpose of selecting these biomasses for studying biosorption was to assess the possibility of utilizing waste biomass for heavy metal removal.

Batch experiments were conducted for determining the effect of contact time, sorbent dosage, pH, temperature, agitation speed, particle size of the sorbent and influence of initial metal ion Concentration. Distinctive adsorption equilibria and kinetic models are of extensive use in explaining the biosorption of heavy metals, denoting the need to highlight and summarize their essential issues. In particular, Langmuir and Freundlich models are the most common isotherms. In this study, four isotherm models namely Langmuir, Freundlich, Tempkin and Dubinin- Radushkevich isotherm models were applied for correlating biosorption experimental data. In kinetic modeling, the pseudo-first order, pseudo second order, intraparticle diffusion and Elovich equations are considered as the models for fitting the biosorption kinetic data.
Exploitation of biosorption technology for removal of heavy metals depends on the efficiency of regeneration of biosorbents after metal desorption. Desorption studies were carried out to determine the desorbing nature of the biosorbents and also to analyze the regenerative capacities of the biosorbents.

FTIR analysis has been frequently used to detect vibrational frequency changes in biosorbents. It provides excellent information on the nature of the bonds present in the adsorbent and allows identification of the different functional groups on the cell surface. The FTIR spectrums of the algal and fungal biosorbents before and after metal biosorption were analysed. It can be seen that IR spectra indicated the presence of ionisable functional groups. This gives an indication that these materials can be used as adsorbents for heavy metal removal.

Characterization of surface morphology is often of vital importance in understanding the physical and chemical behaviour of the material. In order to understand the morphology of the biosorbents SEM analyses of the biosorbent samples before and after metal adsorption were carried out. The comparison of SEM pictures between the raw and metal loaded biosorbents showed that the particle has undergone remarkable change after adsorption in all the four biosorbents.

Essentially the main requirement of an industrial sorption system is that the sorbent can be utilized as a column system. Column experiments were conducted for various depths and flow rates for the four biosorbents *Chlorella, Volvox, zygnema* and *Trichoderma* and break through curves were plotted. From the break though curves, it was found that the adsorption capacity of *Chlorella* was more than the other sorbents. The breakthrough data was modeled using the linearized Thomas and Yoon-Nelson models. The neural network models were developed for the other biosorbents *Chlorella, Volvox, Zygnema* and *Trichoderma* using Neuro solutions 6.0 and SPSS package. The performance of the network was assessed by evaluating the observed and simulated results.
6.2 CONCLUSIONS

Lab scale investigations were carried out using the biosorbents *Chlorella, Volvox, Zygnema* and *Trichoderma* for the removal of heavy metals namely chromium, zinc and nickel from industrial wastewater and the following conclusions were drawn from the present studies.

6.2.1 Chromium (VI)

- The sorption efficiency value for chromium followed the sequence: *Chlorella > Volvox > Zygnema > Trichoderma*. One of the reasons why green algae chlorella show high sorption efficiency could be that the surface area is comparatively larger which in turn provides more number of adsorption sites.

- It was observed that the Freundlich isotherm showed good fit to the experimental equilibrium adsorption data than the Langmuir, Tempkin and Dubinin-Radishkevich isotherm equation for Cr (VI) sorption according to the values of $R^2$. Hence, biosorption of Cr(VI) ion on the algae biomass is a multilayer sorption process.

- On evaluating the biosorption kinetics of Cr(VI) ions it was found that the biosorption kinetics fits second order model better than the other models.

6.2.2 Zinc (II)

The sorption efficiency value for zinc followed the sequence: *Chlorella > Volvox > Zygnema > Trichoderma*. Freundlich isotherm showed good fit to the experimental equilibrium adsorption data in comparison with Langmuir, Tempkin and Dubinin-Radishkevich isotherm equations for Zn (II) sorption. The pseudo second order model proves suitable to describe the adsorption kinetic data in the present study. Zinc biosorption was influenced by the pH values, as expected for the ion-exchange mechanism involving mostly carboxyl groups. Higher values of pH resulted in higher quantity of metal adsorbed onto the biomass. Desorption of zinc
loaded onto the biomass was complete using a hydrochloric acid solution. As the results suggest, biosorption onto nonliving *Chlorella* showed a good potential to be an interesting alternative method for zinc removal from industrial wastewaters.

### 6.2.3 Nickel (II)

The sorption efficiency value for chromium followed the sequence: *Chlorella* > *Volvox* > *Trichoderma* > *Zygnema*. The results clearly demonstrated that the algae *Chlorella* can be used as a biosorbent as they are cost effective and highly effective in the removal of Ni(II) ions from aqueous solutions. The biosorption process of Ni(II) metal ion onto the biosorbent was found to be dependent on various experimental factors like initial pH, initial biomass dosage, initial metal ion concentration and contact time. It was also concluded from the results that the adsorption kinetic and equilibrium data satisfactorily match with the pseudo second order kinetic model and the Freundlich isotherm models respectively. The interactions between the metal ions and functional groups present on the surface of the biomass cell wall were confirmed by FT-IR and SEM analysis. Of the four biosorbents, the maximum biosorption capacity with good rate constant and correlation coefficient was obtained for *Chlorella*. The proposed biosorption system was successfully applied to real industrial effluent containing Ni(II) ions.

Column experiments were carried out using the various biosorbents for the removal of heavy metals from industrial wastewater and the following conclusions were drawn from the present studies. Biosorption capacity strongly depended on flow rate and bed depth. It was observed that, the maximum removal occurred at highest bed depth. In contrast to bed depth results, the column performed well at lowest flow rate. Earlier breakthrough time appeared for highest flow rate, resulting in low uptake and least percentage removal. This fact can be explained by the phenomenon that with the increase of bed depth the length of bed through which the influent passes also increases, thus the amount of adsorbate used also increases which results in the increase in breakthrough time. Column adsorption data fitted
well with Thomas and Yoon Nelson models with high $R^2$ values and indicated that external and internal diffusions are not the limiting step for biosorption process.

The data generated from the column experiments were used to train the neural network and the following conclusions were drawn.

- A multivariable feed forward back propagation was designed to determine the relationship between process control variables. Parameters such as volume, depth and flow rate were chosen as input variables. $C_e$ was considered as the dependent output parameter.
- Neural network was trained with 290 data sets of V, D and R and $C_e$. After convergence, the remaining 145 test data sets of input variables V, D and R were presented to the trained network. The performance of the neural network was assessed by evaluating the scatter between the observed and simulated results. The Neural network outputs were very close to the experimental values.
- Neural network approach is highly adaptive and efficient in investigating the relationship among different variables.

6.3 SCOPE FOR FUTURE STUDY

1. This study can be extended for analysis of bi-metal and tri-metal solutions in order to determine the effect of co-ions present in the wastewater.

2. The study can be carried out with immobilized biosorbents since in column mode; free microbial cells possess poor mechanical strength and little rigidity. Immobilization matrices such as sodium alginate, calcium alginate, polyacrylamide and silica can be used.

3. The same study can be extended for improving the sorption efficiency by other pretreatment methods like washing with detergents, organic solvents and alkali or acid treatment.

4. The study can be further extended focusing on the regeneration of sorbents using other desorbing agents such as EDTA, NaOH and NH$_4$OH.