CHAPTER 6

SUMMARY AND CONCLUSION

6.1 SALIENT OUTCOMES

The liquid waste generated from leather processing are treated or managed through various technological innovations to meet the environmental challenges. Significant technological advancements are being made in the end-of-pipe treatment methods to achieve higher efficiency in meeting the standards in a cost-effective manner. The effectiveness of low cost biosorbents for removal of toxic pollutants like chromium, dye and phenol has been established in this study. The main conclusions drawn from this study are:

Effective and efficient removal of chromium using protonated Sargassum wightii, Turbinaria ornata and Bacillus subtilis biosorbent has been established. The pre-treatment of the biosorbent resulted in improved uptake of chromium. Uptake of chromium by the protonated biosorbent was optimum at a pH of 3.5-3.8 for duration of 6 h. Chromium uptakes of 35 and 28 mg/g of protonated seaweed have been obtained at an initial chromium concentration of 1000 mg/L. Similarly, 25 mg of chromium per gram of protonated B. subtilis biomass has been obtained at an initial chromium concentration of 150 mg/L. The biosorption of chromium by protonated seaweed followed Langmuir isotherm whereas biosorption of chromium by B. subtilis biomass followed Freundlich isotherm. IR studies substantiate the complexation of chromium with the carboxyl groups present in the cell wall of the biosorbent. Flame photometry and EDAX studies reveal a possibility of
ion-exchange mechanism. Desorption of chromium loaded biosorbent resulted in 47, 52 and 55% removal of chromium using 4 N sulphuric acid from S. wightii, T. ornata and B. subtilis biomass, respectively.

Potential of calcium alginate beads to remove anionic and cationic dyes from aqueous solution has been elucidated. The adsorption of dyes followed Langmuir isotherm and found to be dependent on temperature. Maximum adsorption capacity of 27.5, 25, 12.5 and 57.70 mg/g has been achieved at an initial concentration of 300 mg/L of acid brown, direct blue, acid orange and basic black dye, respectively employing 4 g/L of calcium alginate, at a pH of 4.0. Thermodynamic parameters have been evaluated, which indicated a spontaneous exothermic adsorption process for anionic dyes and an endothermic adsorption process for cationic dyes. Desorption of dye loaded alginate beads resulted in 56, 81, 92 and 96% removal of acid brown, direct blue, acid orange and basic black dye, respectively.

Biosorptive removal of cationic yellow and cationic blue dye by green seaweed C. scalpelliformis has also been demonstrated. The amount of dye uptake decreased with increase in temperature indicating that the dye biosorption is an exothermic process. At 30°C, a maximum uptake of 27 and 33 mg of cationic yellow and cationic blue dye, respectively per gram of green seaweed has been observed. The sorption data followed pseudo second order kinetics. Equilibrium data fitted well to Freundlich isotherm equation confirming the heterogeneous sorption process of cationic dyes onto seaweed. The dye uptake process was found to be controlled by external mass transfer at earlier stages and by intraparticle diffusion at later stages. Boyd plot confirmed the external mass transfer as the slowest step involved in the sorption process. The average effective diffusion coefficient was found to be
$2.47 \times 10^{-4}$ and $1.652 \times 10^{-5}$ cm$^2$/s for cationic yellow and cationic blue dye, respectively. Thermodynamic parameters showed that the process is exothermic and spontaneous.

Phenol and phenolic syntan have been successfully removed form aqueous solution using protonated Caulerpa scalpelliformis seaweed. The amount of phenol adsorbed was found to be dependent on pH and a maximum uptake of about 87% was observed at a pH of 6.0. The equilibrium data fitted very well with the Freundlich isotherm model. The average effective diffusion coefficient was found to be $1.44 \times 10^{-9}$ cm$^2$/s. Thermodynamic parameter showed that the process is exothermic and spontaneous. The negative value of entropy $\Delta S^o$ showed decreased randomness at the solid-liquid interface during the sorption of phenol onto protonated green seaweed.

Two abundantly available seaweed Sargassum longifolium and Hypnea valentiae have been employed for the preparation of activated carbon containing high surface area. ZnCl$_2$ has been used as an activating agent. The best conditions for the production of high surface area activated carbon are; 30% ZnCl$_2$, 2 h carbonization time and 800°C carbonization temperature. At this optimal condition, the BET surface area of 802 and 783 m$^2$/g and iodine number of 1041 and 961 mg/g have been obtained for ZSLC-800 and ZHVC-800, respectively. A comparison of the kinetic models of the overall adsorption rate showed that the pseudo second-order rate model best describes the adsorption of phenol by activated carbon. Thomas model for different flow rate and BDST model for different column bed heights have been employed. The model constants belonging to each model have been determined by linear regression techniques and are proposed for the use in column design. To sum up, the easy availability and suitability makes seaweed a potential and low cost natural material for the production of activated carbon.
Optimized experimental conditions have been employed for the treatment of commercial tannery wastewater. Protonated S. wightii seaweed has been employed for the treatment of commercial wastewater from a chrome tanning sectional stream. The chromium concentration has been reduced from 750 mg/L to stipulated norms of less than 2 mg/L after five stages of treatment. Calcium alginate beads have been used for the treatment of commercial wastewater containing anionic blue dye. Seven stages of treatment resulted in complete removal of colour. Similarly, protonated C. scalpelliformis has been employed for the treatment of sectional wastewater from top-dyeing process employing cationic blue dye. The complete colour removal was obtained in two stages of treatment. The chromium loaded seaweed was successfully employed for the manufacture of basic chromium sulphate. The developed product has been employed for tanning of goatskins. Studies reveal that the quality of the wet blue leathers is on par with the leathers tanned with commercial BCS. Shrinkage temperature of the leathers is comparable and is above 105°C at an offer of 1.25% Cr₂O₃. Chromium exhaustion is about 74%. Performance of the crust leathers is comparable to that of conventional tanned leathers.

In summary, the study presents the potential application of low cost natural adsorbents for the removal of chromium, dyes and phenol from wastewater and provides a holistic solution to the pollution problem.

6.2 FUTURE SCOPE OF WORK

Although some attempts have been made at the commercialization of biosorption for wastewater treatment, the progress is very modest considering that there has been more than a decade of fundamental research. The important features required for the successful application of biosorption technology to real situations include, but are not limited to:

- Screening and selection of the most promising biomass, with sufficiently high biosorption capacity and selectivity
• Improving the selectivity and uptake via chemical and/or genetic modification methods
• Examining the mechanical strength of biomass and if insufficient for reuse, improving rigidity by proper immobilization or other chemical methods

The increasing demand for more effective remedial technologies results in a huge window of opportunity for biosorption whose competitive advantage warrants its future success. The enormous potential of application for biosorption and its strong economic and technical advantages open considerable market opportunities that can actually be quantified through a responsible market analysis. The development of biosorption process requires further investigation in the direction of modeling, regeneration and immobilization of biosorbents. Scaling up of this technology and commercialization through partnerships could be the future scope of this study.