CHAPTER SIX

SUMMARY AND RECOMMENDATIONS

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6.1 Summary

Heavy metal extraction from industrial effluents has significant economic and environmental advantages. Conventional treatment methods become less effective when the concentration of metal falls in the range of parts per million. Alternative methods based on biological systems involving the use of immobilised biomass on suitably constructed bioreactors are being developed (Darnall, 1991; Stoll and Duncan, 1997). The biomass of algae, fungi and bacteria has been employed for the removal and recovery of toxic metals and also metals of commercial value (Corder and Reeves, 1994; Friss and Myers-Keith, 1986; Kuyucak and Volesky, 1988a).

To be of practical use, biosorbents must be able to resist abrasion, withstand pressure and remain easily permeable to the metallic species to be sequestered. Immobilising the biomass into a desirable particulate or granular form is one approach to improving its physical characteristics.

In the present study, preliminary investigation was conducted on copper biosorption by the nonliving biomass of a brown alga, *Sargassum baccularia.* An immobilisation technique has been developed to entrap the algal biomass in polyvinyl alcohol polymeric matrix in order to provide mechanical strength for the biomass to be packed into a column for continuous flow operation.

The experiments conducted in this work were designed to simulate conditions commonly encountered in actual industrial effluents. The results obtained may help to identify the factors affecting metal biosorption process and be useful in designing wastewater treatment systems for the removal of heavy metals employing algal biomass as metal biosorbents.

Proper engineering design of process equipment requires a good understanding of the process kinetics. Kinetics of copper biosorption by the native form of *S. baccularia* as well as immobilised *S. baccularia* beads was studied in batch experiments. Results obtained indicate that the kinetics of copper biosorption by the native biomass was relatively fast, achieving equilibrium within one hour of contact with copper-bearing solution. However, the immobilised biomass gel beads needed a longer contact time to attain equilibrium compared to the native biomass due to the diffusivity of copper ions in the pores of the beads.

In addition to kinetic studies, equilibrium studies of the biosorption process were also conducted. Equilibrium isotherms were employed as a method of characterising the biosorption equilibria of copper on the algal biomass. Equilibrium data obtained using batch experiments were found to correspond well to the Langmuir model when the native biomass was used as the biosorbent.

There are many advantages of conducting an equilibrium study. The two most important benefits are a more complete understanding of the algal biomass-metal interaction and the development of a quantitative database which could be of great use in the design of a biosorption process. The effect of initial solution pH on biosorption equilibria was evaluated, as it is a crucial engineering parameter that influences the biosorption of metals. Initial solution pH affects the speciation of the copper ions in solution as well as the chemistry of the functional groups responsible for copper binding on the biomass surface. Results obtained indicate that copper uptake increased with increasing pH values.

A biosorption process comprises two important components: adsorption or metal removal from aqueous solution and desorption or metal recovery from metal-laden biosorbent. Desorption of adsorbed copper from the immobilised biomass was possible using a mineral acid (HCl) and a chelating agent (EDTA). Kinetics of copper desorption by HCl and EDTA was studied in batch experiments to obtain the time required for the desorption process to reach equilibrium.

The reusability of the immobilised algal beads was studied. Multiple cycles of copper adsorption-desorption were carried out in a batch mode. Results showed that the immobilised biomass could be successfully regenerated and reused for five consecutive cycles with some reduction in copper reloading capacity in Cycles 2-5.

Batch experiments using the immobilised biomass beads only provide basic information on the effectiveness of the metal-biosorbent system. Data obtained from batch processes usually are not valid for other flow conditions such as fixed-bed operation. For technical applications, a biosorption process is more likely to be operated in a fixed-bed process configuration which allows continuous operation.

It is therefore of interest to investigate the potential of the immobilised algal biomass for use in a fixed-bed configuration. The reusability of the immobilised biomass was assessed by conducting three cycles of copper loading-desorption with EDTA as the desorbent. The effect of inlet copper concentration and flow rate on the performance of the fixed-bed column was investigated. A simple theoretical fixed-bed model was used to predict the behaviour of the experimental fixed-bed column.

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Interpretation of the experimental results presented in this study led to the following major conclusions:

1. An immobilisation method has been successfully employed to incorporate the biomass of a marine alga, *Sargassum baccularia*, into polyvinyl alcohol matrix.
2. The BET surface area of the beads was 24.1 m^2/g of beads and the average pore diameter was 181.6 Å.
3. Kinetic studies on copper biosorption by the native biomass of *S. baccularia* indicate that approximately one hour was required for the system to reach equilibrium. By contrast, a biosorption system based on the immobilised biomass needed approximately 20 hours to attain equilibrium, indicating the presence of diffusional resistances in the porous beads.
4. The native biomass exhibited a potential to adsorb copper effectively under optimal conditions with a maximum adsorption capacity of 1.66 mmol/g at pH 6.0.
5. Compared to the native biomass, the immobilised biomass beads showed lower maximum adsorption capacities of 0.49 mmol/g and 0.63 mmol/g at pH 3.0 and 6.0, respectively.
6. Hydrochloric acid and EDTA were effective in desorbing copper bound on the immobilised biomass. Desorption kinetic studies showed that the process was relatively fast, reaching equilibrium within four hours of contact with the desorbent.

7. Highly concentrated copper solution was obtained by using HCl at pH 1.0 as the desorbent with a solid-to-liquid ratio (S/L) as high as 11. However, the optimum S/L ratio would have to be kept below 5 in order to achieve more than 90 % desorption efficiency.

8. Recycling of the immobilised biomass was possible for five consecutive cycles of copper adsorption-desorption using HCl and EDTA as the desorbents. However, the copper uptake capacity of the immobilised biomass in Cycles 2-5 was reduced to 52 - 66 % of the original uptake observed in the first cycle.

9. EDTA appears to be a slightly better desorbent compared to HCl with higher copper reloading capacity. The total amounts of copper adsorbed and desorbed were relatively higher for the entire five cycles with EDTA as the desorbent.

10. Laboratory-scale fixed-bed column studies show that there was little change in the performance of the biosorption column packed with the immobilised biomass for three consecutive cycles of copper loading-desorption.

11. Highly concentrated copper solution was obtained when the fixed-bed column was regenerated by using EDTA as the desorbent.

12. Relatively low influent copper concentration and low column flow rate will give satisfactory and high copper uptake efficiency in the fixed-bed column.

13. A simple two parameter fixed-bed model was capable of predicting the behaviour of the fixed-bed column. Although exact quantitative agreement between theoretical predictions and experimental data was not obtained, the model managed to predict the general behaviour of the fixed-bed column under various operating conditions.

6.2 Recommendations for Future Studies

Through the completion of this study, a number of topics which deserve further consideration have been identified. The specific metal binding mechanisms of *S. baccularia* are still not very well defined. More work is also needed to elucidate the functional groups on the surface of the biomass which are responsible for copper biosorption. The effect of the immobilisation method on the behaviour of the biomass was not investigated in a comprehensive manner. More work has to be done in order to enhance the metal uptake capacity and uptake rate of the immobilised biomass.

Although recycling and desorption of the copper-laden biomass was possible a reduction in the copper uptake capacity of the immobilised biomass was observed. This might be due to the adverse effects of the desorbents, HCl and EDTA. Future work should focus on exploring other potential desorbents which can regenerate the immobilised biomass in multiple cycles of adsorption-desorption without affecting the metal uptake capacity of the biomass.

In this work, preliminary studies were conducted using a fixed-bed column packed with the immobilised algal biomass. More work is needed to provide sufficient understanding of the behaviour of the fixed-bed column for process design and scale-up.

All the results presented in this work had been derived from studies involving a single metal. In actual industrial wastewater, many inorganic and organic compounds are often present together with the metals of interest. Future work should investigate the behaviour of the immobilised biomass in biosorption studies involving multi-component solutions.

It appears that the biosorption process can supplement or even substitute conventional metal removal and recovery processes. However, the economics of the biosorption process needs to be evaluated in order to assess its commercial viability.