CHAPTER V

CONCLUSIONS

5.1 Summary, Findings and Contributions

To meet the objective of establishing the physico-chemical characteristics of PSMC biosorbent in relation to its biosorption mechanism, comprehensive studies on advance characterisation of biosorbent were performed. The results not only provide valuable information that elucidate the biosorption mechanisms, but also identify components and functional groups that involved in the biosorption process. An approach using TORCHIA ^{13}C ssNMR method was adopted to investigate and evaluate the biosorbent characteristics and complexation mechanism.

From literature review, there is lack of studies for biosorbent preparation methodology, especially in washing pre-treatment. Extensive laboratory work on optimisation and evaluation of washing pre-treatment were conducted which resulted in the development of a methodology for biosorbent preparation. This study ensures the repeatability and reproducibility of biosorbent and biosorption studies.

Optimisation and evaluation of heavy metal biosorption in synthetic solutions were conducted to determine the optimal operating conditions for heavy metal biosorption. These investigations are important to achieve the objective of heavy metal biosorption in synthetic solutions. In addition, an approach using the half saturation constant concentration in heavy metal biosorption was adopted in order to obtain results within a shorter time and also to minimise the use of biosorbent under controlled conditions.

The objective of biosorbent application study was evaluated through biosorbent performance in the treatment of automobile wastewater and its subsequent recovery of heavy metal from biosorbent. The evaluation of biosorbent performance in treatment of automobile wastewater result infers that the PSMC biosorbent is a potential biosorbent for industrial wastewater. The elution and recovery test conducted provided information regarding the high recovery of the heavy metal and biosorbent.

In order to meet objective of predictive modelling of biosorption, a novel multiple output prediction ANN model was introduced and developed. The constructed three layered ANN structure was tested extensively using the data obtained for reliability. Such approach is vital for plant management and effluent monitoring.

These investigations have resulted in significant contributions to the overall understanding of biosorption process, biosorbent advanced characteristics and biosorption modelling. These contributions include:

i. The major component of PSMC is lignocelluloses with chitin and proteins components. The lignin present in PSMC plays a major role in the biosorption process when compared to cellulose. Carboxyl, hydroxyl and amide are three major functional groups that involve in the heavy metal biosorption.
ii. Advanced characterisation analysis results including TORCHIA ^{13}C ssNMR experimental design indicate Pb(II) biosorption involves ion exchange mechanism through replacement of light metal ions and chemisorptions involve chemicals bondings. Complexation occurs through the formation of lignin syringyl and guaicyl-Pb(II) complexes as well as chitin-Pb(II) complexes. The proposed mechanisms are not merely assumptions but have been ascertained by several observations in advanced characterisation investigations.

iii. The optimised parameters for washing pre-treatment in biosorbent preparation were found to be at 20 g/L of biosorbent concentration, two hours of immersion time and three cycles of washing pre-treatment. This is the only study that has reported on washing pre-treatment in biosorbent preparation. The adopted methodology save time and cost in order to achieve maximum leaching of contaminants from biosorbent.

iv. The developed washing pre-treatment methodology increased 50 % of Ni(II) biosorption efficiency from 28.36 ± 0.09 % to 78.22 ± 0.03 % for NW-PSMC and PSMC respectively. Furthermore, an average of Ni(II) biosorption from five batches of sampling samples was obtained at 47.25 ± 1.18 %. These strongly suggest that the established washing pre-treatment methodology is reliable and consistent as results showed excellent repeatability of Ni(II) biosorption efficiency and reproducibility of biosorbent in batch mode.

v. In biosorption optimisation study, the experimental design using the half saturation constant concentration is one of the significant new approach that has resulted in minimising the operating time and the use of biosorbent. The half saturation constant concentration for Pb(II) was determined at 0.08 g while for both Cu(II) and Ni(II), the half saturation constant concentration was obtained at 0.7 g. The optimal heavy metal biosorption condition for initial pH was found to be at un-adjusted condition of pH 5 – 6 for all heavy metal. Pb(II) biosorption attained equilibrium phase within 90 minutes of contact time whilst both Cu(II) and Ni(II) achieved equilibrium phase were within 10 minutes of contact time. Heavy metal biosorption was an initial heavy metal concentration dependent process. However, temperature did not show any significant effect on the heavy metal biosorption process.

vi. The selectivity order of single heavy metal biosorption is similar to bi-heavy metal and multi-heavy metal biosorption. The PSMC biosorbent has a highest selectivity towards Pb(II) followed by Ni(II) and finally Cu(II). This trend is corresponded to the descending electronegativity order of the heavy metal. These findings can be applied to the application study of biosorbent especially in industrial wastewater containing multi-heavy metal.

vii. The heavy metal biosorption operating conditions in synthetic solutions were evaluated using existing models. Results were found to be in good agreement with Langmuir isotherm which infer a monolayer biosorption system. The q_{max} were 21.10 mg/ g, 3.87 mg/g and 3.03 mg/g for Pb(II), Cu(II) and Ni(II). High Langmuir *b* values indicated PSMC biosorbent is effective in targeted heavy metal biosorption. Experimental data better fitted to pseudo second-order kinetic than pseudo first-order kinetic. This model not only supports the heavy metal biosorption are not uni-molecular reactions but also suggest that chemisorption is the rate limiting factor with several mechanisms possibly occurring simultaneously in the biosorption process. From the thermodynamic model, heavy metal biosorption is a sponteneous exothermic and reversible reaction. These evaluations provided basic and vital information for biosorbent application study.

viii. The heavy metal biosorption in treatment of automobile wastewater was found to be lower than synthetic single heavy metal solutions due to competition of other cations and protons as well as operating conditions of heavy metal biosorption. A high recovery of heavy metal from biosorbent was achieved at 88.20 ± 4.91 – 93.05 ± 1.46 % using 0.1M nitric acid. Meanwhile, the biosorbent recovery was obtained at 91.45 ± 2.38 % - 94.24 ± 1.12 %. The consideration for biosorbent loss during the biosorption-desorption cycle carried out in this study is novel and has never been reported before. The recovery of heavy metal allows the minimisation of hazardous waste. Details of biosorbent application studies are useful in column and large scale pilot investigations.

ix. A novel ANN model structure with multiple output is introduced and successfully developed. The optimised ANN model was found to be at 10 hidden layers, 0.6 learning rate and 0.6 momentum rate. The simulation trained network showed excellent prediction data when compared to experimental testing data with equation $y = 0.9998x$, correlation coefficient of 0.9750, m.s.e of 1.46×10^{-3} and s.s.e of 1.58×10^{-1}. Hence, multiple output prediction play an important role not only in plant operational management but also in effluent quality monitoring.

Generally, these findings provide evidence that method development in biosorbent preparation, characterisation, biosorption process and modelling are significantly well established and evaluated. Therefore, established knowledge can be directly applied to biosorption process to elucidate biosorption mechanisms, provide information for large scale study and predict the water quality of effluent and shutdown of operational plant in order to minimise cost and time to obtain reliable and consistent results.

5.2 Conclusion from This Study

The general conclusions can be drawn as following:

i. Laboratory procedures have been applied to characterise the biosorbent. The advanced characterisation analysis of TORCHIA ^{13}C ssNMR has been introduced to elucidate biosorption mechanism.

ii. Laboratory procedures have been established to optimise and evaluate the washing pre-treatment in biosorbent preparation.

iii. The half saturation constant concentration approach has been adopted to optimise and evaluate the heavy metal biosorption under various operating conditions.

iv. A novel ANN prediction model was introduced and used to simulate the multiple output under various biosorption operating conditions. The model was successfully developed, optimised and validated with experimental data.

v. The PSMC is a potential biosorbent as it is effective, low cost, renewable and minimised waste secondary products. This biosorbent is well fitted towards environmental sustainability and transform bio-waste to wealth concepts which improve environment, for better human health and living quality.

5.3 Recommendation for Future Investigations

It is recommended that the following investigations be conducted in the future:

i. Investigation on optimisation parameters of particle size, agitation rate and cations interferences should be conducted. Such studies will give information that present the overall spectrum of independent parameters in fundamental heavy metal biosorption process.

ii. Investigation on advanced characterisation of biosorbent after Cu(II) and Ni(II) biosorption should be extended to deepen the knowledge of the Cu(II) and Ni(II) biosorption mechanisms. Furthermore, proposed complexation mechanisms also need to be investigated and evaluated by ^{13}C ssNMR experiments in order to confirm the structure of complexes formed.

iii. Regeneration study of biosorbent need to be continued with the aim to understand the performance of biosorbent in terms of reusability as well as to validate the desorption study conducted in this study.

iv. A fixed-bed column study must be considered as outcome will enable the successful application in larger scale studies.

v. A study on cost implications on heavy metal biosorption compared to conventional methods, namely, precipitation and ion exchange resins should be conducted in order to establish the economic viability study.

vi. A modelling study using tools such as Response Surface Methodology (RSM) or SPSS should also be conducted to offer optional tools for heavy metal biosorption modelling.