CHAPTER I

INTRODUCTION

1.1 Background of Study

As one of the persistent pollutants in the environment, heavy metal are hazardous, not biodegardable and bio-accumulate in living organisms. Consequently, heavy metal contamination of water sources warrants serious concern worldwide due to the deleterious effects of heavy metal to both human health and the environment (Duruibe *et al.*, 2007). There are two major source of heavy metal contamination, namely natural and anthropogenic activities. Naturally occurring heavy metal in water may come from algae blooms, volcanic activities, earthquakes, leaching of ore and mineral deposits. On the other hand, anthropogenic activities such as electroplating, metal refining, chemical manufacturing industries and mining play a major role in heavy metal pollution. Of these anthropogenic activities, industries producing effluent is one of the major contributor to heavy metal contamination of water bodies due to improper treatment and management, even though these can be controlled through implementation of regulations and intervened by ISO 14000.

Heavy metal ions are easily introduced into the aquatic environment and redistributed throughout the water body. Ultimately, these heavy metal end up being deposited in or accumulated in sediments leading to consumption by biota. Bioaccumulation of heavy metal in living tissues throughout the food chains, not only poses a serious health hazard to humans, it also threatens the environment (Cuculic *et al.*, 2009). Therefore, treatment of heavy metal contaminated water is pertinent to safeguard human health and the environment.

Currently, treatment of heavy metal for contaminated water can be achieved through various application of physical, chemical and biological treatment technology (Wang and Chen, 2009). A variety of methods has been applied to treat heavy metal from wastewater, namely, membrane filtration technologies, electro-dialysis, ion exchange, oxidation-reduction, chemical precipitation, bioaugmentation and mircobial bioremediation. However, these treatment technologies are, in most instances, not economically feasible when industrial wastewater having less than 100 mg/L heavy metal.

In Malaysia, chemical precipitation is the most popular treatment technology applied in industries owing to the simplicity of the process and the relatively lower cost when compared to more technologically advanced treatment system such as membrane filtration, ion exchange, electro-chemical precipitation. However, chemical precipitation generates a large amount of hazardous chemical waste that incurs high solid waste management cost (Congeevaram *et al*., 2007; Megat Hanafiah *et al*. 2007). On the other hand, ion exchange with commercially available resins, activated carbon or membrane technology is prohibitively costly due to cost for treating large volumes of wastewater with low heavy metal concentration (Chojnacka, 2010).

In view of such shortcomings, an inexpensive and effective treatment system that generates minimal or no secondary waste products would be an ideal system. This has mooted the search of an alternative remediation technology involving the development of biosorption for heavy metal-laden industrial wastewater. Volesky and Holan (1995) defined biosorption as the removal of metal or metalloid species, compounds and particulates from solution by biological material known as biosorbent. Performance of biosorbents such as from bacteria, fungi, algae, industrial waste and agricultural waste, is usually investigated via its efficiency or effectiveness of heavy metal biosorption (Demirbas, 2008; Vijayaraghavan and Yun, 2008). The potential of agricultural waste to be developed as biosorbent has been highlighted by Lesmana (2009) since it is easily available in large quantity and at low cost.

Materials suitable as biosorbents generally contain carboxyl, hydroxyl, ketone and amino functional groups (Mashitah *et al*., 1999). The specificity of heavy metal biosorption process is influenced by biosorbent functional groups. However, there is lack of qualitative data on advanced characterisation on the functional groups to elucidate biosorption mechanism which involves physical and chemical interactions between heavy metal and biosorbent. By obtaining both quantitative and qualitative data on biosorption and using these data together will allow a more practical application of biosorption leading to the improvement in the quality of life and the environment.

1.2 Problem Statement

Rapid industrial development, both locally and globally has increased the amount of effluent containing heavy metal that is being released to the environment. In most wastewaters, the concentration of heavy metal present is much larger than the permissible limits and therefore, requires treatment. Conventional methods for heavy metal treatment include chemical precipitation, ion-exchange, electro-dialysis, membrane filtration and adsorption (Lesmana *et al*., 2009). However, these treatments are ineffective or extremely expensive in most cases, especially when heavy metal ion concentration in aqueous solution is in the range of 1 to 100 mg/L (Nurchi and Villaescusa, 2008). The chemical precipitation treatment method, being the most popular, has a major drawback, for it generates a large amount of hazardous waste sludge which needs further treatment and disposal through solid waste management.

Drastic increase in volume and type of agricultural wastes has become a burgeoning problem in the wake of population growth. According to United Nations Environment Programme (2009) 140 billion metric tons of agricultural waste is generated every year globally. Agricultural wastes take the form of residual stalk, leaves, roots, husk, nut, waste wood and animal waste (Khan *et al*., 2004; Park *et al*., 2010). In general, agricultural waste is carbon rich as it contains high amounts of cellulose, lignin, pectin and tannin. This widely available, renewable and virtually free agricultural waste is an important resource for reuse and recycle in green technology development. Although there is an emerging trend on the utilization of agricultural waste for biofuel and biochar technologies, agricultural waste is still largely under utilized and left to rot or openly burned in the fields, especially in developing countries.

With regards to common practices, Malaysia like other developing countries does not have strong regulatory instruments to control polluting practices. Such practices when unchecked leads to climate change, water and soil contamination, thereby posing risk and hazard to human and ecological health. Agricultural waste management and sustainable heavy metal treatment technology are still major gaps to be filled. There is an obvious lack of awareness in looking for sustainable heavy metal treatment technology. This can be conducted using agricultural waste for treatment and metals recovery. The challenge, therefore, is to generate revenue from the recovered materials and develop a sustainable heavy metal treatment technology.

Biosorption as an emerging treatment technology can be likened to killing two birds with one stone by deploying agricultural waste of *Pleurotus ostreatus* spent mushroom substrate compost (PSMC) as biosorbent to treat heavy metal contamination problem. It can provide a means of sustainable heavy metal treatment technology development by converting agricultural waste into wealth. PSMC is abundant and widely available agricultural waste from mushroom cultivation farms in Malaysia since its monthly production exceeds 100 metric tons. It is mainly made up of rubber tree sawdust and *Pleurotus ostreatus* mycelium. The PSMC combines the biosorption capability of both the lignocellulosic sawdust as well as the fungal biomass of the oyster mushroom (Akmar Zakaria *et al*., 2009; Javaid *et al*., 2011; Qasimullah *et al*., 2011; Tay *et al*., 2011a). Functional groups such as hydroxyl, carboxyl, amide, amine and sulfhydryl serve as active binding sites for heavy metal biosorption process.

Generally, investigations of heavy metal biosorption have focused on the determination of biosorption efficiency or effectiveness, isotherms, kinetics and thermodynamic parameters as well as fourier transformed infrared spectroscopy (FTIR) characterisation

(Dermibas, 2008; Febrianto *et al*., 2009). Another factor that has been a stumbling block for the implementation of biosorbent application is the lack of a vital prediction tool that can assist managers organise and interpret industrial wastewater monitoring data. The lack of a prediction model, especially one with multiple output involving biosorption efficiency and effectiveness as well as prediction of effluent water quality under any operating conditions has to be addressed before biosorption can become an acceptable treatment system.

Therefore, it is necessary to initiate advanced characterisation study of the biosorbent such as ^{13}C solid state nuclear magnetic resonance (^{13}C ssNMR) and X-ray photoelectron spectrometer (XPS) targeted to elucidate the biosorption mechanism by further evaluating the interaction between biosorbent functional groups and heavy metal. Furthermore, study on the development of a multiple output prediction model is needed in order to provide forecast guidelines and help planning for optimal plant operation as well as assure water quality of effluent is under permitted level. In conclusion, biosorption of heavy metal using PSMC biosorbent represents a cost effective and sustainable heavy metal treatment technology development in addition to minimize the solid waste management by transforming bio-waste to wealth.

1.3 Objectives of Study

The goal of this study is focused on evaluating the potential of agricultural waste namely, *Pleurotus ostreatus* mushroom substrate compost (PSMC) as biosorbent for heavy metal treatment. The specific objectives of this study are:

1. To establish the physic-chemical characteristics of PSMC biosorbent in relation to its biosorption mechanism.
2. To optimise and evaluate the biosorption efficiency of Pb(II), Cu(II) and Ni(II) from synthetic heavy metal solutions.
3. To evaluate the potential application of PSMC biosorbent in the treatment of automobile wastewater and its subsequent recovery of heavy metal from biosorbent.
4. To develop an artificial neural network (ANN) model for selected heavy metal biosorption.

1.4 Scope of Work

This project consists of three parts; field work sampling, laboratory based studies and mathematical analysis including modelling. Field activities involve sampling from C & C Mushroom Cultivation Farm Sdn. Bhd., at Lot 6, Kawasan Perindustrian Gerisek, 84700 Muar, Johor and wastewater sampling from Perusahaan Automobil Kedua Sdn. Bhd. (Perodua Manufacturing Sdn. Bhd.) at Lot 1896, Sungai Choh, Mukim Serendah, 48000 Rawang, Selangor, Malaysia. The four phases of laboratory work include preparation of biosorbent, advanced characterisation of biosorbent, optimisation and evaluation of heavy metal biosorption process, evaluation of biosorbent application in automobile wastewater and recovery of heavy metal from biosorbent. Results from laboratory activities are used in the mathematical analysis of Langmuir isotherm, kinetics and thermodynamic model and ANN modelling that predict the biosorption efficiency and water quality of effluent. The scope of work for this study is summarized in a flow chart given in Figure 1.1 while activities that have been conducted to achieve the objectives are shown in Figure 1.2.

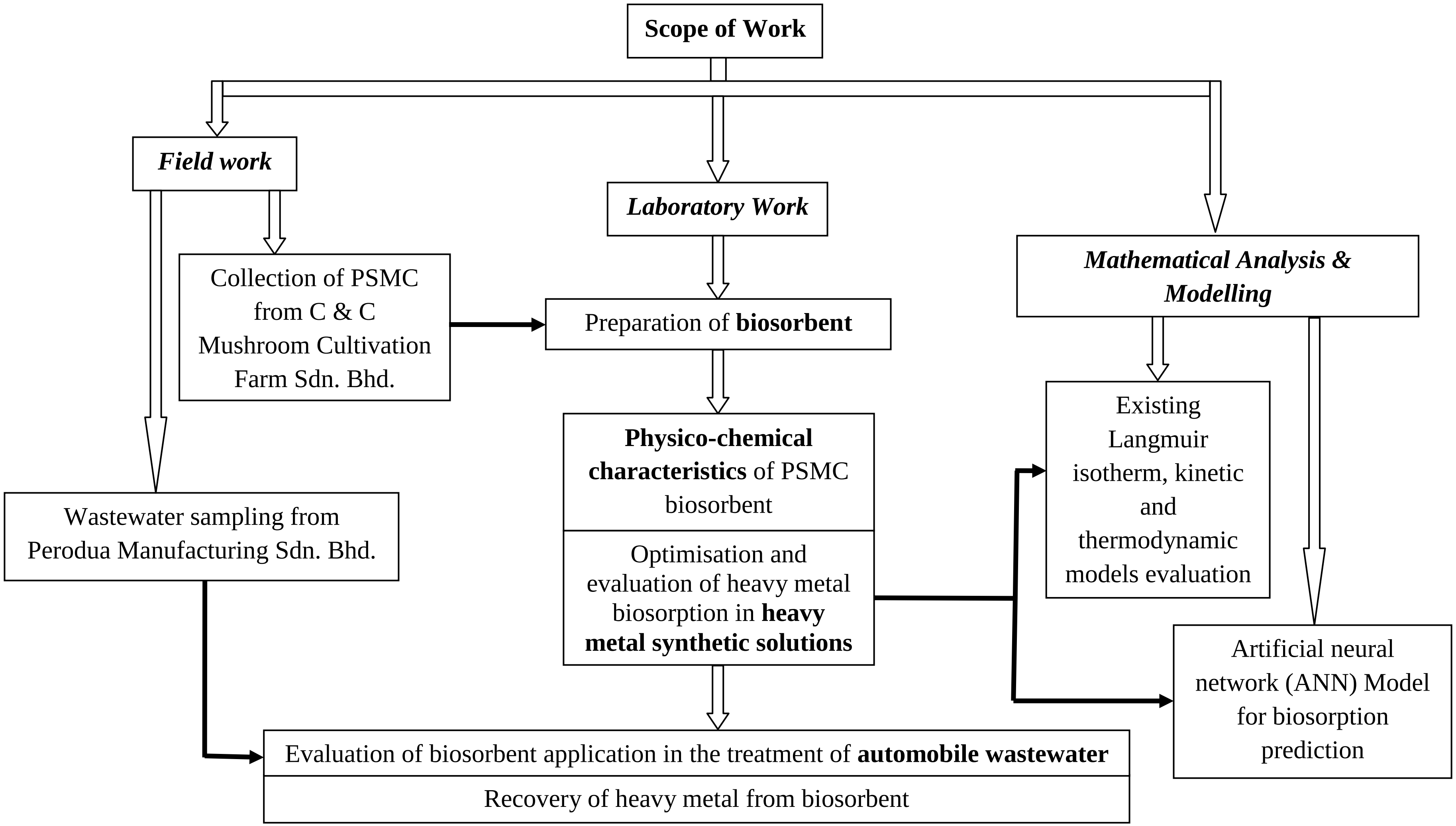

Figure 1.1 Scope of work conducted during this project

OBJECTIVE	ACTIVITY
Objective 1 To establish the physic-chemical characteristics of PSMC biosorbent in relation to its biosorption mechanism.	Preparation of biosorbent • Field work of sampling from farm. • Laboratory work of biosorbent washing pre-treatment. Biosorption mechanism through advanced characterisation • Laboratory work of analysis include BET surface area, CHNSO composition, cellulose and lignin composition, SEM/ EDX, zeta potential, XPS, FTIR and ^{13}C ssNMR.
Objective 2 To optimise and evaluate the biosorption efficiency of Pb(II), Cu(II) and Ni(II) from synthetic heavy metal solutions.	Optimisation study • Laboratory of optimisation parameters of half saturation constant concentration of biosorbent, initial pH, contact time and initial heavy metal concentration for single and multi-heavy metal biosorption. Temperature effects on single heavy metal Existing models evaluation • Mathematical analysis of obtained optimisation study results for Langmuir isotherm, pseudo first-order kinetic, pseudo second-order kinetic and thermodynamic equation.
Objective 3 To evaluate the potential application of PSMC biosorbent in the treatment of industrial wastewater and its subsequent recovery of heavy metal from biosorbent.	Application study • Sampling of industrial wastewater from automobile industry. • Laboratory work of biosorbent application in the treatment of automobile wastewater which evaluate via biosorption performance. • Recovery of heavy metal from biosorbent
Objective 4 To develop an artificial neural network (ANN) model for selected heavy metal biosorption in synthetic heavy metal.	Modelling of ANN • Modelling of selected heavy metal biosorption through ANN with multiple output variables by using obtained results.

Figure 1.2 Objectives and activities for developing the *Pleurotus ostreatus* spent mushroom substrate compost as biosorbent for heavy metal treatment in aqueous solutions.

1.5 Significance of the Study in Malaysia

The outcome of this study contributes to body of knowledge through advanced characterisation study. Advanced characterisation not only focuses on functional groups determination of biosorbent components, but also oxidation states of heavy metal ions. With regards to this, a better understanding on interaction between biosorbent function groups and heavy metal ions is explained in order to elucidate biosorption mechanism. Furthermore, developed biosorption prediction ANN model generates new knowledge in biosorption. Development and application of multiple output ANN model is a useful prediction tool to provide forecast guidelines for optimal biosorption process and estimate water quality of effluent. Thus, ANN modelling also drives to ensure economic saving and sustainability in biosorption process besides knowledge acquaintance.

In the literature review, investigation on biosorbent concentration to be used in experimental design is not discussed and evaluated. This study introduces a new approach of the half saturation constant concentration of biosorbent to evaluate biosorption performance as different types of biosorbent have their own materials characteristics (Tay *et al*., 2011b). Reliable results can be obtained in shorter time and it minimizes the use of biosorbent. Earlier studies have shown that there is lack of standardized guidelines and evaluation of biosorbent preparation. Another method development is washing pre-treatment procedures for biosorbent preparation. It has effectively removed contaminants, thus improves biosorption performance and reproducibility of biosorbent in batch mode. By using minimal amount of water to achieve maximum improvement of the biosorption performance of the biosorbent, it helps conserve valuable resources such as water, time and labour for the production of the biosorbent. Both of these processes improve biosorption performance as well as strengthen the drive to affirm long term economical, environmental and human social living quality aspects.

A product is developed from PSMC, as a novel biosorbent has been initiated by Tay *et al*. (2011b). This PSMC biosorbent generates revenue from the agricultural waste instead of treatment and disposal through solid waste management. The use of PSMC as a viable and potential biosorbent for heavy metal treatment is in line with the concept of transforming bio-waste to wealth. A further perceived benefit is that biosorbent is degradable in the environment as it derives from non-living biological material. It is also a renewable source since excellent recovery of heavy metal from biosorbent can easily attain using dilute acid. Application of PSMC biosorbent does not require necessary chemical input for treating heavy metal contaminated wastewater and it generates minimal waste or secondary product. Hence, this product will promote better sustainability in heavy metal treatment as well as to improve environmental protection and quality of living.

1.6 Limitation of Study

This study was conducted to analyse only one type of spent mushroom substrate compost, namely, PSMC obtained from a mushroom cultivation farm. Hence, spent mushroom substrate compost of others *Pleurotus* species or other mushroom genera were not analysed. The number of heavy metal of interest is restricted to only three as justified by the literature review presented; copper (II), lead (II) and nickel (II). Hence, it is believed that experimental results will offer a focused insight on these heavy metal.

Even though chemical modifications of biosorbent may increase biosorption efficiency and effectiveness, the biosorbent used in this study is with minimum processing for removing contaminants and does not undergo any chemical modification process. The rationale of using unmodified, minimally-treated PSMC is to reduce both the cost and chemicals needed as to be more sustainable and environmental friendly.

Biosorption optimisation parameters were limited to biosorbent concentration, initial pH, initial heavy metal concentration and temperature. In addition, this study is limited to experiments conducted in batch mode. Continuous mode biosorption and scaled up pilot study are not considered as this study focuses on the generation of scientific knowledge on mechanism of biosorption.

A predictive model concept was developed to simulate the observed selected biosorption performance and water quality of effluent. The model's inputs include biosorbent concentration, initial pH, contact time and initial heavy metal concentration. However, this model does not account for the temperature factor as temperature has been found to have little effect heavy metal biosorption. The ANN model does not offer any equation to be presented.

This study is restricted to recovery of heavy metal from biosorbent using dilute nitric acid in order to clarify elution of heavy metal and biodegradability of biosorbent. Regeneration of biosorbent and optimisation on types and concentrations of desorption solutions were not considered. This is because without regeneration study, PSMC potentially still be competitive, especially for pre-treatment or combined treatment of heavy metal contaminated wastewater.

1.7 Concluding Remarks

Wastewater containing heavy metal needs to be well treated before discharge to the receiving environment. The use of biosorbents from agricultural waste have potential to address issues of conventional heavy metal treatment technology. Hence, this study on PSMC as biosorbent, provides the much needed knowledge on the mechanism of biosorption and efficiency of biosorbent. This could influence PSMC to be adopted as a sustainable treatment technology for heavy metal contaminated wastewater.