CHAPTER ONE

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In recent years, there has been a growing consciousness on the need to protect our environment from degradation caused by rapid development and industrialisation. Studies on 116 major rivers in Malaysia revealed that 13 rivers were seriously polluted while 61 rivers were classified as slightly polluted (DOE, 1996). However, the number of rivers seriously polluted increased to 16 while the number of rivers being slightly polluted shot up to 73 in 1998 (DOE). The overall river water quality was on a deteriorating trend.

The manufacturing sector consisting of the metal finishing, rubber-based, food and beverage as well as the paper industries were cited as the main culprits with effluent from the metal finishing industries a difficult problem to be resolved. A large majority of these operators are small and medium industries (SMI) that do not have any form of treatment for their discharges due to financial constraints and poor awareness on the hazards of waste towards the environment. Those with treatment plants are faced with operational constraints and lack of maintenance (ENSEARCH, 1996). Therefore, it is not surprising that concentrations of mercury, lead and zinc were found to exceed standards in 9 out of 50 rivers monitored while lead concentrations alone exceeded standards in 12 rivers (DOE, 1993). Earlier studies conducted by Babji *et al.*, (1986) on tissues of fishes collected from downstream of such industries indicated high level of heavy metal accumulation. Similar studies conducted by Rosnani (1986) on 49 species of fish from the West Coast of Peninsular Malaysia also revealed the state of heavy metal pollution in coastal waters.

When effluent from industries with heavy metal waste are released into the environment without proper treatment, it would result in serious public health disorders. The detrimental effects of many of these heavy metals are well established from mercury poisoning in Minamata Bay and cadmium poisoining (Itai-Itai disease) in Japan in the early 50s to lead poisoning that is linked to the fall of the Roman Empire (Volesky, 1990). Although heavy metal poisoning has yet to be formally recorded in Malaysia, the amount generated in the form of toxic and hazardous waste amounts to a staggering 220 000m^3 per annum (Rosnani, 1986).

Although conventional methods are available for the treatment of metal bearing wastewater such as chemical precipitation and ion exchange, and occasionally evaporation, electrodialysis, membrane processes, carbon adsorption and cementation (solidification and stabilisation), these methods are costly. By-product such as heavy metal sludge from chemical precipitation and highly concentrated wastewater from evaporative process still require final disposal. These will inevitably incur additional costs. Treatment is also ineffective when the metals in solution are in the range of 1 to 100 mg/L of dissolved metal(s) (Volesky, 1990). Hence, such methods are not readily adoptable, particularly by the small and medium scale operators. With the number of environmental policies being drawn up and more stringent governmental regulations being imposed, industries can no longer utilise the cheapest treatment and disposal facilities, which sometimes tend to compromise on the effluent quality.

It is imperative that novel methods for the treatment of heavy metals be explored and researched. According to Yeoh (1987), for such technologies to be readily applied, it must be highly competitive against existing technologies by producing effluents of higher quality and economically viable. Numerous studies on the use of such low cost indigenous materials for removal of heavy metals by adsorption, ion exchange or chelation include sawdust (Srivasta *et al.*, 1986), exhausted coffee grounds (Macchi *et al.*, 1986), coconut husk (Tan, 1986), peat (Kassim and Ahmad, 1986), fungi (Lee *et al.*, 1998) and algae (Tan, 1999, Chu *et al.*, 1997). According to Volesky (1990) such biosorbents are gaining widespread attention from researchers due to its selectivity, efficiency, cheapness and its ability to remove and recover strategic and valuable metals.

According to Volesky (1990), certain types of biomass can retain relatively high quantities of metal ions by "passive" adsorption and/or complexation. This is commonly referred to as *biosorption*. Biosorption, as this passive metal sequestering capability is generally termed, is caused by a number of different physico-chemical mechanisms, depending on a number of external environmental factors as well as on the type of a metal, its ionic form in the solution and on the type of a particular active binding site responsible for sequestering the metal. An important feature of biosorption is that it can be responsible for binding and accumulating metallic species even when the cells are no longer metabolically active, i.e. the biomass is dead. However, the remaining cell debris such as cell walls can exhibit adsorption properties and can be used as potential biosorbents.

The application mode of biosorbent technology is very similar to ion exchange and activated carbon adsorption. The major advantage in the deployment of biosorbent materials are their low anticipated price with good metal uptake capacities. One example is a recent patent by Volesky and Kuyucak (1988) using *Sargassum natans*, a brown marine algae in the recovery of gold in a dried and untreated form. These materials are not only natural, but it could be sourced from the oceans where it is renewable, abundant and can be obtained very economically. The ability to outperform conventional technologies is another advantage. Table 1.1 lists the disadvantages of conventional technologies in treating wastewater laden with heavy metals.

Table 1.1: The drawbacks of some conventional technologies in treating heavy metal wastes

Conventional Technologies	Disadvantages
Chemical Precipitation	Excess sulfide precipitation will result in the formation of noxious H_2S gas and exact amount is difficult to achieve. Precipitating agents such as natural or synthetic polyelectrolytes produce heavy metal sludge that pose a problem for final disposal.
Reverse Osmosis	The choice of membrane is difficult especially when treating multiple metallic species. Fouling of the membrane that may shorten the service life of the membrane.
Ion Exchange	Pretreatment is needed for wastewater with high suspended solids. Dilute waste will cause low metal transfer rate to resin, hence lowering its efficiency.
Electrodialysis	Dilute heavy metal waste have very low electrical conductivity, necessitating a high electrical power input. Accumulation of acidic and basic solutions on membranes causes fouling.

Source: Tan, (1999)

Agricultural wastes in Malaysia are usually disposed by mulching or open burning. Some of these wastes such as oil palm waste end up as animal feedstock. Very few are employed as potential biosorbents. In 1987, Yeoh employed rice husk char (RHC) and rice husk ash (RHA) in his studies to sequester heavy metal. Using Langmuir adsorption isotherm, the maximum uptake for RHC was found to be 2.65 mg/g, 2.42 mg/g and 2.78 mg/g for copper, nickel and zinc. As for RHA, it was found to be 1.54 mg/g, 1.33mg/g and 0.97 mg/g respectively.

Coconut husk fibres were also applied as a potential biosorbent by Tan (1986). A series of batch experiments using copper and lead as model ions showed that the degree of metal removal was dependent on pH, the concentration of the metallic species as well as competing ions.

Hasan *et al.* (2000) and Hashim *et al.* (1999) concentrated their research on biosorbents that are actually important agricultural commodities in Malaysia. The former utilised rubber wood ash while the latter employed fly ash from oil palm (POFA) waste. Both biosorbents were reported to have high metal uptake capacities with a maximum uptake of 0.22 mmol/g for POFA in treating copper while rubber wood ash was reported with a maximum uptake of 0.492 mmol/g at pH 5 at 30^0 C using nickel as the model ion.

Biosorption of metals by pure or even mixed strains of microbial cultures has been recognised for quite some time. Biomass of some pure microbial strains shows promises of very high and sometimes selective uptake of metallic species from dilute metal-bearing solutions (Volesky, 1990).

As an example, *Rhizopus arrhizus*, a fungi has been studied to remove uranium (Tsezos, 1983; Tsezos and Volesky, 1982), thorium (Tsezos and Volesky, 1982), copper (Brady *et al.*, 1999; Brady and Tobin, 1998; Zhou and Kiff, 1991) as well as other heavy metals. Studies revealed that either in its native form or as a dead biomass immobilized onto a support matrix, it remains to be a potent biosorber for a broad range of metallic species (Tobin *et al.*, 1984). Others such as *Fusarium sp.*, *Gibberella sp.*, *Sporoticum sp.*, *Aspergillus sp.* and *Penicillum sp.* were also studied by Lee *et al.*(1998) to remove iron.

Brady and Duncan (1994) also studied yeast biomass such as *Saccharomyces cerevisiae* immobilized onto polyacrylamide to remove copper, cobalt and cadmium ions. Its ability to be regenerated using a chelating agent such as ethylenediaminetetraacetic acid (EDTA) and recycled for further bioaccumulation events with little loss of accumulation capacity were their research results.

According to Kuyucak and Volesky (1990), algae are the most extensively studied microbial biomass for the treatment and recovery of heavy metals as they are the easiest to observe and most conspicuous. Reflecting well the environmental conditions and their changes, algal populations have been observed for a long time as indicators of shifting ecological balances and alterations in natural nutritional conditions as well as toxic effects originating from man's activities. Natural populations of algae can readily respond to and have actually been used to monitor the degree of pollution in the aqueous environment. In this conjunction, the interaction of algae and heavy metals has also often been traditionally examined.

In 1998, Chang and Huang employed a fixed bed column to treat lead, copper and cadmium from contaminated water using calcium alginate immobilized biomass of *Pseudomonas aeruginosa.* Langmuir isotherms for maximum uptake of each metallic

In 1998, Chang and Huang employed a fixed bed column to treat lead, copper and cadmium from contaminated water using calcium alginate immobilized biomass of *Pseudomonas aeruginosa*. Langmuir isotherms for maximum uptake of each metallic species were 1.60, 2.42 and 1.06 mmol/g respectively. While Chang and Huang (1998) used immobilized biomass in their study, Rai and Mallick (1992) compared between two species of microalgae *Anabaena doliolum* and *Chlorella vulgaris* in their native and immobilized form to treat copper and iron with great efficiency. Phang (1997) also noted the efficiency of *Chlorella vulgaris* not only in the bioremediation of agroindustrial waste but also in the treatment of heavy metal waste.

Of late, marine algae have been the focus of numerous biosorption studies due to their excellent metal binding capacity (Holan *et al.*, 1993). The *Sargassum* species, a brown marine macroalgae has been investigated by numerous researchers (Valdman and Leite, 2000; Lee and Volesky, 1999; Schiewer, 1999; Tan, 1999; Yang and Volesky, 1999; Chu *et al.*, 1997; Kratochvil and Volesky, 1997; Kratochvil *et al.*, 1997; Lee and Volesky, 1997; Crist *et al.*, 1988) for its important role in sequestering heavy metals.

This present study focuses on *Sargassum baccularia*, a brown marine macroalgae as a biosorbent. Biomass of *S. baccularia* was immobilized onto PVA and an analytical mathematical model was used in a fixed bed column to predict the adsorption characteristics. Copper was selected as the model ion because it is commonly found in industrial wastewater discharged by small and medium scale electroplating and metal finishing industries.

The present work has been divided into three parts. In the first part, Langmuir and Freundlich adsorption isotherms were used to establish the kinetic behaviour of the system for maximum uptake of copper ions at different pH. Next, an analytical mathematical model was used to evaluate the breakthrough curves of immobilised *S. baccularia* in a laboratory scale fixed bed column. The experiments were categorised into model calibration and model application.

For the final part, multiple cycles of adsorption and desorption studies were carried out to determine the reusability of immobilised *S. baccularia* in a fixed bed reactor. EDTA, a chelating agent was used to strip bound copper ions on the surface of *S. baccularia* because studies by Tan (1999) and Chu *et al.* (1997) established that EDTA is a better desorbing agent than inorganic acids. Previous study by Tan, (1999) focussed only on the reusability of immobilised *S. baccularia* in a batch condition but for practical engineering application, the reusability of *S. baccularia* was tested in a fixed bed reactor.