CHAPTER ONE

INTRODUCTION
CHAPTER ONE

INTRODUCTION

1.1 General Background

With the vision to achieve developed country status in the year 2020, Malaysia has been showing a rapid growth in industrialisation since the 1980s which in turn has generated large volumes of waste including those containing heavy metals. Agricultural runoff, industrial and domestic effluents and acid mine drainage have all contributed greatly to metal loads in the natural water systems. Without proper treatment and disposal methods, heavy metals will be accumulated throughout the food chain. This not only endangers human life but also threatens the ecosystem.

Environmental pollution problems as exemplified by the Minamata disease (mercury poisoning) and Itai-itai disease (cadmium poisoning) in Japan are well-known phenomena that caused serious threat to life and health. It should be borne in mind that environmental destruction in Japan was a very prominent feature from the very beginning of the country's modernisation and industrialisation period (Ui, 1992).
Rapidly industrialising countries like Malaysia should therefore reassess their modernisation orientations so as to control environmental destruction. Life-threatening industrialisation-induced environmental pollution must be avoided especially in the case of uncontrolled discharge of industrial wastewater containing heavy metals. Therefore, effective management policies as well as improved and innovative wastewater treatment processes must be continuously developed for the control and prevention of heavy metal discharge to the environment.

1.2 Heavy Metal Pollution in Malaysia

Currently, the Department of Environment (DOE) controls and prevents water pollution in Malaysia based on the Effluent Discharge Standards stipulated in the various Regulations under the Environmental Quality Act, 1974. Based on the National Water Quality Indices and data collected from 909 river monitoring stations in Malaysia in 1996, 42 rivers were classified as clean, 61 rivers were reported slightly polluted and 13 rivers polluted (DOE, 1996). However, the overall river water quality was generally on a deteriorating trend.

In terms of marine water quality status, no occurrence of lead and copper levels exceeding the Proposed Interim Standard of 0.1 mg/L was recorded in Pahang, Kelantan, Negri Sembilan, Trengganu and Selangor. However, the percentage of
samples exceeding the interim standard for lead and copper ranged from 1.5 to 40% in Johor, Kedah/Perlis, Pulau Pinang, Perak, Sabah and Sarawak (Table 1.1). The overall quality of marine waters was still very much influenced by the degree of discharge of partially treated or untreated industrial wastes and other land-based sources.

<table>
<thead>
<tr>
<th>State</th>
<th>No. of stations</th>
<th>No. of samples</th>
<th>Percent Samples Exceeding Interim Standard (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>Pahang</td>
<td>17</td>
<td>53</td>
<td>0</td>
</tr>
<tr>
<td>Johor</td>
<td>43</td>
<td>86</td>
<td>0.76</td>
</tr>
<tr>
<td>Kedah/Perlis</td>
<td>16</td>
<td>69</td>
<td>0</td>
</tr>
<tr>
<td>Kelantan</td>
<td>12</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>N. Sembilan</td>
<td>10</td>
<td>21</td>
<td>0</td>
</tr>
<tr>
<td>Pulau Pinang</td>
<td>25</td>
<td>152</td>
<td>2.5</td>
</tr>
<tr>
<td>Perak</td>
<td>14</td>
<td>29</td>
<td>0</td>
</tr>
<tr>
<td>Sabah</td>
<td>32</td>
<td>87</td>
<td>0</td>
</tr>
<tr>
<td>Sarawak</td>
<td>11</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td>Trengganu</td>
<td>16</td>
<td>32</td>
<td>0</td>
</tr>
<tr>
<td>Selangor</td>
<td>6</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Marine Interim Standard (mg/L)</td>
<td>0.1</td>
<td>0.001</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Source: Department of Environment (1996)
Throughout 1996, industries like metal finishing and electroplating, food and beverage, textile, rubber-based, cement, vehicle assembly, paper as well as leather experienced difficulties in complying with the requirements of the Environmental Quality (Sewage and Industrial Effluent) Regulations with only less than 85% compliance. Metal finishing and electroplating topped the list with only 66% found to have complied with the Regulations.

Among the main reasons for non-compliance were inefficient operation of effluent treatment plants as a result of an increase in production and absence of effluent treatment plants especially for the small and medium-sized industries and slow response to treatment plant upset.

It was also reported that 632,521.31 MT/year of scheduled wastes were generated in 1996 (DOE, 1996). Heavy metal sludges contributed 10.56% (66,794.25 MT/year) of the total scheduled waste while acids (heavy metals) and alkalis (heavy metals) contributed 316.26 MT/year (0.05%) and 25.3 MT/year (0.004%), respectively.

When heavy metal-bearing waste streams are insufficiently treated before being discharged, they find their way into the environment and subsequently into the food chain. For many of the industries, inappropriate disposal methods include the use of domestic sewage systems for inadequately treated waste discharges, the use
of surface drains and other water bodies for effluent discharge and both on and off-site surface disposal of sludges and toxic wastes. As a result, there is an urgent need for the development of cost-effective treatment systems that can effectively and efficiently remove toxic metals from industrial wastewater.

1.3 Conventional Treatment Methods for Heavy Metal Removal

1.3.1 General Background

The main health concerns with heavy metals arise primarily because they may adversely affect human health for prolonged exposure periods. Substances that are cumulative poisons and those that are carcinogenic are of particular concern. Therefore, methods for heavy metal removal are continuously being developed and new technologies that are more practical and economically feasible are being explored by researchers.

Conventional heavy metal removal techniques that are well established and widely employed include precipitation, ion exchange, reverse osmosis, electrodialysis and solvent extraction.
1.3.2 Precipitation

Chemical precipitation is the most popular technique for inorganic heavy metals removal. It can be conducted either batch wise or continuously. Lime, caustic soda and sodium carbonate are among the most widely used chemicals. This process includes the following steps: pH adjustment, flocculation and sedimentation. Settled solids are dewatered and stabilised for disposal.

Alternatively, heavy metals can be precipitated from wastewater with sulfide. However, one of the major drawbacks for sulfide precipitation is that excess sulfide in solution tends to react with water to form noxious hydrogen sulfide gas. Moreover, adding precisely the required amount of sulfide is difficult to achieve, not to mention that metal sulfide sludges oxidise to sulfate when exposed to air and the metal ions tend to resolubilise.

Natural and synthetic polyelectrolytes can also be used as precipitating agents. Polygalacturonic acid, alginic acid and gelatins are among the natural polyelectrolytes being studied while polymethacrylic acid and polyethyleneimmine fall into the synthetic polyelectrolytes group.

Precipitated solids in this method are removed in a properly designed clarification system. However, effluent is usually filtered to ensure maximum removal of solids.
By applying this method, the problem of disposing the metal-laden sludges still remains. Metals may be recovered from the sludges before final disposal by a variety of techniques but recovery is usually not economical.

1.3.3 Reverse Osmosis

Heavy metal removal by reverse osmosis can be done by applying a pressure greater than the osmotic pressure of the solution and forcing the water to flow through the membrane whilst retaining the metal ions.

In the treatment of wastewater, reverse osmosis may be used by itself or may supplement other methods. This technology is usually employed for the recovery of precious or common metals in the metal finishing industry.

In principle, this is a simple technique but the development of suitable membranes is much more difficult. A membrane must possess selectivity for water over the metal ions and must have sufficiently high permeability to enable a reasonable flow rate of water across it without applying excessive high pressures.

Other operational constraints of this technology are caused by fouling of the membrane and the phenomenon of concentration polarisation, which is caused by ion built-up, may shorten the service life of the membrane.
The use of high pressures and the need for sophisticated process equipment to adequately support the membrane give rise to high capital costs. Frequent membrane replacement and the associated high maintenance costs are additional factors which hinder the application of reverse osmosis to remove heavy metals from industrial wastewater.

1.3.4 Ion-exchange

Ion-exchange is one of the most effective techniques for removing heavy metals from wastewater. It is employed extensively for metal finishing bath purification, polishing effluents after primary treatment and recovering of precious metals.

In this process, the ion-exchange column is packed with resins containing bound anions; the cations present (usually hydrogen ions) being free so that they are exchanged with the metal ions in the effluent. The resin contains bound cations and free hydroxyl ions, so that water is the net product from the process.

Once the resin is saturated with the metal ions removed from the effluent, it is regenerated or eluted by using sulfuric or hydrochloric acid. The resin is then treated with sodium hydroxide and washed with water before reuse.
Although this technique is widely used, it still faces some operational constraints. When the waste streams contain suspended solids, the suspended solids must be removed from the influent to prevent blockages and fouling. Dilute waste will cause low metal transfer rate to the resin surface and require large beds with high superficial velocities for efficient ion exchange.

Other than that, certain type of resins tend to deteriorate with use under oxidising conditions. The spent regenerate solution, smaller in volume and more concentrated than original waste streams, might create a disposal problem.

1.3.5 Electrodiagnosis

Electrodiagnosis is another technique which utilises membranes. In this case the metal ions move through the membranes by application of an electromagnetic force (emf). The treatment unit consists of a number of chambers made up of alternate cation-anion membrane located between two electrodes. When dilute solution is fed through the units and an emf applied, the cations migrate towards the anode. Since the membrane only allows the transfer of one type of ions, one side of the membrane becomes more concentrated with metal ions while the other becomes more dilute.
There are a number of intrinsic disadvantages by applying this technique. Dilute solutions, particularly those produced in the unit, have very low electrical conductivity thus necessitating high electrical power input to produce acceptable ionic transfer rates across the membrane. Consequently, accumulation of acidic and basic solutions on opposite sides of the membrane will happen and precipitates may be formed which will foul the membrane. The membrane might lose its ion selective properties too.

Furthermore, electrodialysis involves high capital and operating costs even though the value of recovered metals may help to offset the costs in a small amount.

1.3.6 Solvent Extraction

In this technique, an immiscible solvent is used to extract metals from the wastewater streams. A variety of solvents have been used, mainly for extracting copper and most of these are chelating compounds.

Normally, the organic solvents employed are extremely expensive. In order to make solvent extraction economically viable, solvent loss must be kept to a minimum. Moreover, many of the complexing agents commonly used in solvent extraction are deadly to fish even at low concentrations.
1.4 Biologically Based Treatment Technologies

Conventional treatment technologies described in Section 1.3 may be ineffective or expensive or both, especially when dealing with metals that are dissolved in large volumes of solution at relatively low concentrations of 1-100 mg/L (Volesky, 1990). Therefore, alternative metal removal or recovery techniques are being considered.

There has been ample evidence of passive metal uptake observed with certain types of microbial biomass (Foster, 1976; Muraleedharan et al., 1991; Soderlng et al., 1988). This in turn has attracted the attention of many researchers in exploiting the potential for heavy metal removal or recovery by employing the microbial biomass. Algae, fungi and bacteria are the major biomass families being studied which can be used in bioremediation to economically and efficiently remove metals from effluents, especially at low concentrations.

The mechanism of metal uptake in these biological systems comprises two stages. The first is a passive, rapid and reversible reaction known as 'physical adsorption' or 'biosorption' to the surface of the cell wall. The second step, which is metabolically active, involves uptake of heavy metals into cells and is termed 'chemisorption' or 'bioaccumulation' (Aksu and Kutsal, 1990).
Normally, metabolism-independent biosorption is reversible and leads to non-destructive desorption whereas metabolism-dependent intracellular accumulation is largely irreversible and necessitates destructive recovery. Therefore, an important consideration in biologically based methods of metal accumulation is the ease of metal recovery for reclamation or reuse. Non-destructive recovery is desired for regeneration of the biomass for reuse in subsequent metal uptake.

1.5 Objectives and Scope of Research

The main objective of this study is to investigate the feasibility of using immobilised biomass of *Sargassum baccularia*, a marine alga, to remove and recover copper from aqueous solutions. Copper is selected as the model metal because it is commonly found in industrial wastewater discharged by various industries, especially the electroplating industry.

The present study comprises three main research components. The first part of this work focuses on developing a suitable immobilisation technique to entrap the algal biomass in a polyvinyl alcohol polymeric matrix. Copper uptake kinetics by both the native and immobilised biomass is investigated to obtain the time taken for the copper-alga system to attain equilibrium. In addition, biosorption equilibrium studies are conducted to generate equilibrium isotherms as a function of solution pH.
The second part of this work focuses on desorption of bound copper and reuse of the immobilised algal biomass in batch stirred-tank experiments. Recovery of the bound copper and simultaneous regeneration of the biomass for reuse are important aspects of a biosorption process. A chelating agent, ethylenediaminetetraacetic acid (EDTA), and a mineral acid, hydrochloric acid (HCl), are used as desorbents to recover adsorbed copper from the immobilised biomass. Kinetic studies of the desorption process are carried out. In addition, other process parameters such as the concentration of the desorbent and the ratio of copper-laden biomass to volume of desorbent are optimised. The adsorption-desorption process is carried out for five consecutive cycles to assess the effect of the desorbents on the reusability of the immobilised biomass.

The last part of this work investigates the removal and recovery of copper from the immobilised algal biomass in a fixed-bed process configuration. Continuous fixed-bed biosorption of metals can be easily scaled up for commercial applications. Three cycles of copper loading and elution are conducted to assess the performance of the fixed-bed system packed with the immobilised biomass. A theoretical fixed-bed model is fitted to the experimental breakthrough curves to estimate the model's parameters. The model is then used to predict the performance of the fixed-bed biosorption process.