Chapter One

CHAPTER ONE

INTRODUCTION

Heavy metals in the environment are a cause for concern. Soils, ground waters and surface waters contaminated with these metals pose a danger. This is because heavy metals can enter the ecosystem at different levels of the food chain. In the process, bioaccumulation and biomagnification of the heavy metals occur. This is ultimately a hazard to man.

Ingestion of heavy metals can cause a variety of diseases. These include damage to the kidneys, liver, bone structure, the central nervous system, blindness and even death. A case in point was the indiscriminate discharge of wastewaters containing cadmium and mercury into the waterways in Japan that resulted in the outbreak of the Minamata and Itai-itai diseases (Laws, 1993).

It is important therefore that the reduction, storage, treatment and disposal of waste waters containing heavy metals must be given priority if we are to prevent similar outbreaks. Innovative and improved methods of wastewater treatment to remove these metals is one way.

1.1 Heavy metals and their toxicity

Heavy metals are those elements whose compounds form positive ions when in solution and whose oxides form hydroxides rather than acids with water. Broadly speaking, heavy metals include all metals of the Periodic Table except those in Groups I and II (Volesky, 1990).

Even at low concentrations in the environment, heavy metals can be toxic to life. Table 1.1 classifies elements according to their toxicity and availability in the environment (Wood, 1974).

Table 1.1 Classification of elements according to toxicity and availability.

Non-critical	Toxic but rare	Very toxic and accessible
Na C F	Ti Ga Hf La	Be As Au
K P Li	Zr Os W Rh	Se Hg Ni
Mg Fe Rb	Nb Ir Ta Ru	Tl **Cu** Pd
Ca S Sr	Re Ba	Zn Ag Sb
H Cl Al		Cd Bi Pt
O Br Si		Co Te **Pb**
N		Sn

The two elements (metals) that are relevant to the present study are copper and lead. It can be noted that these metals belong to the group that is both toxic and accessible.

1.1.1 Copper and its toxicity

Copper is a transition metal belonging to Group IB in the Periodic Table. Its atomic number and relative atomic mass are 29 and 63.6, respectively. Being a transition metal, it has a number of properties which include spectral, magnetic, complexing capacity and oxidation states. In its natural state, it commonly occurs as sulphides and is commonly found in organic-rich sediments because it forms chelate complexes (Venugopal and Luckey, 1978). Pollution of waters by copper is usually due to industrial waste from the mining, smelting, electroplating, tanning and anti-fouling paints industries. Copper is also present in some insecticides and fungicides.

Copper poisoning occurs most frequently after overexposure to insecticides, inhalation from agricultural sprays or their residues in food and suicidal or accidental ingestion of copper containing solutions. Although most of the copper ingested is excreted by the body, chronic poisoning may occur if exposure occurs over prolonged periods. Such chronic exposure can cause Wilson's disease. The disease is characterised by the deposition of copper occurring in the brain, skin, liver, pancrease and even the heart (Venugopal and Luckey, 1978).

1.1.2 Lead and its toxicity

The common industries that deal with lead are the battery manufacturing, motor vehicle repairs, cable making and metal grinding industries. Lead poisoning results from ingestion of lead-containing materials such as paint or water which has stood in lead pipes. Poisoning can also occur from inhalation of fumes from burning storage batteries or solder (Poskaner, 1978). Absorption is usually slow and prolonged exposure is required to develop any adverse effects. Most of the absorbed lead is stored in the bones, blood or brain. Gastro-intestinal symptoms are common. Lead colic (painters'cramps) is characterised by severe abdominal pain. Damage to the brain can occur and in children it is known to cause convulsions, mental retardation and even death (Poskaner, 1978).

1.2 Heavy metal pollution in Malaysia

Heavy metal pollution in Malaysia is largely due to industrial wastewaters flowing into the river systems. The Department of Environment has an ongoing river water quality monitoring programme. Thirty six rivers monitored for lead by the DOE exceeded the Proposed Interim National Water Quality Standard of 0.01mg/l Class III. For copper twenty four rivers monitored exceeded the standard of 0.01mg/l Class III (DOE, 1996).

1.3 The metal finishing industry in Malaysia

A major source of heavy metal pollution in Malaysia is the metal finishing industry. In 1997 (DOE, 1997), only 69% of the metal finishing and electroplating industries had complied with the Sewage and Industrial Effluent Regulations 1979 (Appendix I). Inefficient operation or absence of effluent treatment plants (DOE, 1997) are among the main reasons why the metal finishing and other industries have not complied with the Environmental Quality (Sewage and Industrial Effluents) Regulations 1979.

In the metal finishing industry, metal parts are plated to make them more functional, lasting and decorative so as to enhance their value. The processes involved are firstly, degreasing, cleaning, pickling (acid removal of surface oxides) of the parts and then electroplating, electroless plating, etching and conversion (Higgins, 1989). The waste streams from these activities contain acids and bases, toxic heavy metals, solvents and oils. These are listed in Table 1.2 below.

Table 1.2 Metal finishing operations & typical wastes generated.

Operation	Wastes
Degreasing	Solvents, oils
Cleaning	Alkali metals, chelates, solvents
Pickling	Acids, metals, chromates
Metal plating	Acids, metals, cyanide
Etching	Metals, acids, chelates
Conversion coating	Chromates, phosphates, metals

Source: Higgins (1989)

High concentrations of a range of toxic heavy metals are present in the waste from the metal finishing industry. Some of the heavy metal constituents commonly found are summarised in Table 1.3.

Table 1.3 Heavy metals commonly found in metal finishing wastes.

Type of process	Common constituents
Acid pickling	Cd, Cu, Fe, Ni, Zn
Alkaline pickling and cleaning	Al, Zn
Acid and alkaline plating	Cd, Cu, Sn, Ni, Zn
Chromic acid-based bath	Al, Cd, Cr, Zn
Phosphoric acid-based bath	Fe, Mn, Zn
Metal polishing	Al, Cu, Fe, Ni
Cyanide solution	Cd, Cu, Zn, etc

Source: Pickett (1978)

The metal finishing industry is a sector within the small and medium scale industry of Malaysia. According to Rosnani (1986), the small and medium scale industry (and this includes the metal finishing industry) appeared to be responsible for indiscriminate disposal of toxic waste. This situation still prevails. The reasons are because firstly, these industries have a small capital outlay to start with. The construction of waste treatment plants is costly for them. Secondly, these industries are located in urban areas or illegally developed on Government land. Space becomes a problem. Lastly they lack technical and managerial expertise. For many, the disposal of untreated waste illicitly into surface drains and domestic sewage systems is the norm.

The centralised toxic waste treatment plant at Bukit Nenas, Negri Sembilan receives industrial wastes for treatment and disposal at its secure landfill at a stipulated cost. Many of the small and medium-scale industries such as the metal finishing industry however are unable to afford the cost of this treatment and consequently store their waste on-site or at temporary storage sites off-site, either partially treated or fully treated. To some extent, the Environmental Quality (Scheduled Wastes) Regulations (Government of Malaysia, 1989) has brought the management and disposal of these toxic wastes under control. Medium to large scale plants have installed treatment facilities while the number of waste generators that have complied with the notification requirement as mandated under Regulation 3 of the Environmental Quality (Scheduled Wastes) Regulations, 1989, increased from 2252 in 1996 to 3103 in 1997 (DOE, 1997).

1.4 Waste treatment technologies for heavy metals

Chemical precipitation

Unlike organic pollutants, heavy metals are difficult to detoxify and cannot be degraded. The most common method employed to treat heavy metal waste is chemical precipitation. This is done by adding lime or caustic soda to produce metal hydroxide precipitates. Alternatively, sulphide compounds may be added to form metal sulphide precipitates. After de-watering, the metal laden sludge is collected and disposed off in a landfill.

The main disadvantage of this method is in the separation of solids and the disposal of the sludge. It has been shown that metal hydroxide sludges collected in clarifiers contain up to 3.4% solids (Schwoyer and Luttinger, 1972). To mitigate this problem anionic polyelectrolytes, alum and ferric chloride have been used as sludge conditioners and flocculating agents. The sludge produced has to be ultimately disposed in a landfill. This is not a good environmental practice because there is always the possibility that the heavy metals from the heavy metal sludge (classified as a hazardous waste) may leach out and pose a threat to the environment.

Furthermore, chemical precipitation is suitable only for wastewaters containing high concentrations (parts per thousand or higher) of metal pollutants. With dilute wastewaters (in the range of ten parts per million or less), chemical precipitation is ineffective and costly.

Ion-exchange

In this method, the ion exchange resins are used to remove and concentrate the heavy metals. These resins are polymeric beads that contain functional groups that act as binding sites. Depending on the resin type the appropriate heavy metal may be removed. Electrowinning is then used to remove the metal ions from the wastewater by plating the metal onto cathodes of an electrochemical cell. The advantage of this method is that the heavy metals are recovered and may be reused. Although the ion-exchange/electrotrowinning treatment method is `environment friendly', it is very expensive. The method has also limited value and is not cost-effective where the wastewater contain low concentrations of metal ions.

Activated carbon

Activated carbon adsorption using acidic powdered carbons have been shown to be an effective method of removal especially for metals such as mercury, lead, copper and chromium (Huang and Blakenship, 1984; Bowers and Huang, 1981). However its greatest disadvantage is cost. Since most of such waste effluents come from small and medium-scale industries, this poses a special problem.

Reverse osmosis

Another alternative treatment technology that has been applied for the treatment of plating wastewaters is the reverse osmosis process. It is a process in which water is separated from dissolved salts in solution by filtering through a semipermeable membrane, at a pressure greater than the osmotic pressure caused by the dissolved salts in the wastewater. The process has been used for the removal of cadmium, copper, nickel, and chromium at pressures of 200 to 300 lb/in^2 or 1378 to 2067 kPa (Eckenfelder, 1989). The concentrated stream is returned to the plating bath and the treated water is reused by returning to the next to last rinse tank. The primary limitation of reverse osmosis in the treatment of industrial wastewaters is its high cost. A very high quality feed is required for the efficient operation of the reverse osmosis unit because membrane elements can be fouled by colloidal matter in the feed stream. Pre-treatment of a secondary effluent is usually necessary and iron and manganese removal is sometimes necessary to decrease scaling potential. Regular cleaning of the membrane elements (about once a month) is necessary to restore the membrane flux (Metcalf & Eddy, 1991). This technology may therefore not be a viable cost-effective option for the small and medium scale industries.

Despite having undergone conventional treatment, wastewaters may still not satisfy the discharge requirements. The heavy metal content in the wastewater may be too low for further conventional treatment while being too high for wastewater discharge standards. Because of their limitations and the poor cost-effectiveness of the above methods, there is a need to develop alternative methods that are cheaper, efficient and environment friendly. Biosorption has been identified as one of the most promising new technologies for the removal of heavy metals from industrial wastewaters.

1.5 Biosorption

The ability of biological materials, both living and non-living, to passively bind (adsorb) metal species dissolved in solution onto the cell surface is commonly known as biosorption.

The biosorption process can reversibly bind metal ions to the surface of non-living microbial biomass because the dead organisms are unaffected by the toxic nature of the metal ions. It is therefore an effective treatment technology to remove and recover heavy metals from industrial wastewater.

A variety of biological materials have been used by researchers to study biosorption. These include bacteria, fungi, algae (Volesky,1987), oil palm waste (Hashim *et al.*, 1996), banana piths, naturally occurring chitins and deacetylated chitosan from shrimp shells (Sandford, 1989).

1.6 Objectives and scope of research

The main thrust of this research was to focus on the uptake of copper and lead by the non-living biomass of *Sargassum baccularia* (Mertens) C. Agardh. Specifically, the objectives of this study were as follows:-

- To review the existing literature on biosorption by algae.
- To investigate the uptake of copper and lead separately, as two single component systems, by the alga *S. baccularia.*
- To investigate the uptake of copper and lead when both are present together and the nature of their interaction in the binary system.

This study was embarked upon to add continuity to the work done by Samuel (1996) who had obtained promising results with the locally obtained brown alga *S. baccularia*. It was recognised that there could be great potential in the use of locally available *S. baccularia* as an effective biosorbent to treat heavy metal bearing wastewater. Not only is this brown alga a cheap source of biomass but it is found abundantly along the coasts of Peninsular Malaysia. Furthermore, there is a need to develop cost-effective, efficient and environmentally responsible technologies for the metal finishing industries in Malaysia. As was mentioned earlier, they are an industry group with limited financial resources.

The experiments in this study were carried out as a batch reaction system. Copper and lead were selected as they commonly occur in high levels in industrial waste streams. As mentioned earlier in Section 1.2, they are commonly present in Malaysian rivers.

The study comprises two main areas - single and binary component studies presented in Chapter Three. Each area focused on a different aspect of biosorption by the biomass of *S. baccularia*. Experiments 1 and 2 dealt with biosorption equilibrium studies for copper and lead respectively in a single component system. Experiments 3 and 4 dealt with copper and lead biosorption in a binary system. Here the selectivity of the biomass towards one metal in the presence of another was of primary interest. It was expected that there may be competition between the metals for the binding sites which would in turn affect their individual affinities towards the biomass.