CHAPTER ONE

INTRODUCTION

1.1 Sources and Characteristics of Industrial Waste

Both individuals and industries produce liquid and solids wastes. The liquid portion, wastewater, is essentially water supply after it has been fouled by use. From the standpoint of sources of generation, wastewater may be defined as a combination of the liquid of water-carried wastes removed from residences, institutions and commercial and industrial establishments together with such groundwater, surface water, and storm water as may be present. The ultimate goal in wastewater management is the protection of the environment commensurate with economic, social, political and health concerns.

With increasing density of population and industrial expansion, the need for treatment and disposal of waste has grown. Therefore, most unit operations and processes used for wastewater treatment are constantly undergoing continual and intensive investigation from the standpoint of implementation and application. As a result, many modifications and new operations and processes have been developed and implemented; more need to be made to meet increasingly stringent requirements for environmental enhancement of water. In addition to the developments taking place with conventional treatment methods, alternative treatment systems and technologies are also being developed and introduced.

Industrial waste treatment may be required for a variety of reasons depending on the location of the industrial plant, the regulations governing the discharge of effluents, and the availability and economics of process water.

The volume and strength of industrial wastes are usually defined in terms of units of production. The volumes are highly variable in quantity and quality, depending principally on the product produced. Since very little water is consumed in industrial processing, large volumes are often returned as waste. These wastes may include toxic metals, chemicals, organic materials, biological contaminants and radioactive materials. The design of treatment processes for these wastes is a highly specialised operation.

1.2 Heavy Metal Pollution

Heavy metal pollution is extremely pernicious because these metals are environmentally persistent and toxic. Unlike most organic pollutants, heavy metals are generally refractory and cannot be degraded or readily detoxified biologically.

According to Rosnani (1986), there are a number of toxic heavy metals whose growing levels in the environment are of concern. They are present in the discharges of a variety of industrial effluents and are causing localised toxicity problems or at least environmental imbalances in the regions of their discharge points. The Water Quality Monitoring Programme of the Department of Environment (DOE) in 1992 confirmed that heavy metal pollution in rivers was due to industrial activities (DOE, 1993). Over the years significant levels of heavy metals have been observed in the tissues of aquatic organisms e.g. fishes found especially at the downstream of heavy industry discharge points (Babji *et al*., 1986).

In general, mining, ore processing, smelting, and metal winning operations are associated with effluents containing metallic elements, as are metal-processing operations and industrial activities that utilise metals as catalysts or metal compounds as pigments, reagents and also as biostatic or biocidic agents. Among the heavy metal waste producers, the metal finishing industry was found to be the major producer of such waste. About 25% or 94,000 m^3/year of hazardous waste generated in Peninsular Malaysia were produced by the metal finishing industry (Dames and Moore, 1988).

1.3 Adverse Effects of Heavy Metal Pollution

Pollution from man-made sources can easily create local conditions of elevated metal presence which could lead to disastrous effects on animals and humans. Actually, man's exploitation of the world's mineral resources and his technological activities tend to unearth, dislodge, and disperse chemical elements in a manner which could be labelled as a tertiary mobility of metallic elements which have recently been brought into the environment in unprecedented quantities and concentrations and at extreme rates. Many metallic elements play an essential role in the function of living organisms; they constitute a nutritional requirement and fulfil a physiological role. However, overabundance of the essential trace elements and particularly their substitution by nonessential ones (such as the case may be for cadmium, nickel or silver) can cause toxicity symptoms or death. For example, significant numbers of people in Bulgaria and other countries have been exposed to the hazards of excess metals in the municipal water supplies. The metals (Zn, Cu, Pb, Cd, etc.) have a harmful effect on human physiology and other biological systems when they are found above the tolerance levels (Ong, 1996).

Two metallic species which are of concern from the pollution and toxicity point of view are copper and zinc. Copper is one of the most common industrial metals. Zinc is also used very extensively in industry, mainly in galvanising and manufacturing brass and other alloys. Zinc production in the world is estimated at approximately 7 million tons/year. There are numerous industrial activities involving these two very common metals and as a result there are correspondingly numerous sources of industrial effluents discharging both copper and zinc into the environment. Large smelting operations invariably affect a larger area with their discharges over a period of many years. Absorption of excess copper by man results in "Wilson's disease" in which excess copper is deposited in the brain, skin, liver, pancreas, and myocardium. Zinc is perhaps the least toxic of all the heavy metals and it is actually an essential element for the living cell. However, all elements are eventually toxic if present and absorbed in excess and zinc is no exception. The toxicology of zinc and its effect on the environment are still being broadly studied.

1.4 Existing Treatment Technologies

Due to the increasing value of some metals, as well as due to the greater awareness of the ecological effects of toxic metals released into the environment, there has been considerable interest recently in the development of treatment technology for the removal and recovery of heavy metals from waste streams. Many treatment processes can be used for removing metals from aqueous solutions including chemical precipitation, chemical oxidation or reduction, ion exchange, electrochemical treatment, membrane filtration and evaporation recovery. However, most of these processes may be ineffective or extremely expensive, especially when the metals are in solutions containing in the order of 1 to 100 mg/L of dissolved metal(s). As a result, safe and effective disposal of metal-containing wastewater remains a challenging task for many industries due in part to the fact that cost-effective treatment alternatives are not readily available.

1.4.1 Chemical Precipitation

Chemical precipitation is the treatment process most often employed to remove heavy metals from industrial waste streams. This method is used by a vast majority of the electroplating facilities in Malaysia. The precipitation process is governed by the law of mass action which affects the equilibrium that exists between crystals of a metal salt compound in the solid state and its ions in solution.

The conventional practice of converting dissolved metal ions into hydroxide sludge through the chemical precipitation method was thought to be a means of eliminating any environmental hazard the metals might pose. In fact, although the volume of the sludge is much smaller than that of the wastewater, a solid waste stream is generated that requires further controls to ensure that the disposal of the metal sludge is environmentally acceptable. About 15% of the total hazardous waste generated in Malaysia were in the form of heavy metal sludge (DOE, 1989).

In addition, chemical precipitation is inefficient in producing effluent with low metal concentrations to meet the discharge standards at reasonable cost (Volesky, 1990; Darnall, 1991). Also, the presence of aqueous organic ligands in wastewater can hinder metal hydroxide precipitation, which may result in residual metal concentrations that may no longer meet the increasingly stringent effluent discharge standards (Luo *et al.*, 1992; Peters and Ku, 1987).

1.4.2 Evaporation

This process consists of evaporating water from metal-bearing solutions such as electroplating rinse water to drive off the water as vapour and thus concentrate the solution for recovery, reuse or waste minimisation. Evaporative recovery and reuse are appropriate for almost all process rinse water systems, with the exception of those which chemically deteriorate with use. In evaporative recovery, all non-volatile constituents of the wastewater are retained in the concentrated product. This process uses high energy and therefore it is only cost effective in concentrating rinse water that is to be returned to the electroplating process (Higgins, 1989). In practice, this has been a major disadvantage of evaporative recovery, since the built-up of impurities can result in defective plating practices such as discoloration.

1.4.3 Membrane Processes

Among the methods that have recently reached commercial status are the pressure driven membrane systems. These are known as reverse osmosis and ultrafiltration. Osmosis and reverse osmosis depend on the presence of a barrier or membrane that is selective so that the solvent of a solution can pass through the membrane while other components of the solution or the solutes cannot. Such a membrane is described as semi-permeable. The osmotic pressure is the pressure required to stop the flow of solvent through a semi-permeable membrane separating two solutions of different concentrations. To separate water from dissolved solids by reverse osmosis the applied pressure must be greater than the osmotic pressure. The important applications of reverse osmosis are desalination of seawater and brackish water, the recovery of plating rinse water and the removal of nitrates from groundwater (Higgins, 1989). However, this process is unsuitable for treating small volumes of wastewater due to high capital and operating costs.

1.4.4 Electrowinning

Electrowinning is a process which is based on electrolysis principle to remove metal ions from wastewater by plating the metal onto the cathode of an electrochemical cell. The metal is then scrapped off from the cathode. The process is usually used for gold and silver recovery but it is often not cost effective for removing less precious metals (Davis and Sandy, 1992). In addition, the process is not effective in removing metals from wastewater containing low levels of metal ions.

1.4.5 Ion Exchange

Ion exchange is a method used to concentrate metals from aqueous solutions. The key to using ion exchange for waste treatment is to remove only the toxic ions while allowing most of the non toxic ions to remain. Ion exchange has proven successful in selectively removing many of the pollutants encountered in metal-bearing wastes. Proper application of the process requires selecting the appropriate resin and regeneration sequence and usually some pre-treatment of the wastewater before ion exchange.

The major disadvantage of this process is the high costs of the ion exchange resins. It requires large volume of resin for treating wastewater containing high concentrations of metal ions and later on requires large amount of regenerant to regenerate the resin back to normal position.

1.4.6 Biological Treatment Systems

In general, biological processing is the most efficient way of removing organic matter from municipal wastewater. These living systems rely on mixed microbial cultures to decompose and to remove colloidal and dissolved organic substances from solution. Collection and removal of heavy metals from industrially generated metal-containing wastewater by micro-organisms also have been practised to a certain degree using biological systems where live microbial sludge or biofilms fulfil the role of metal sorbents. However, it may not be practical to attempt to use raw biomass in a metal sorption process. Biosorbent material, or for short, biosorbent, is basically produced from the raw biomass which possesses high metal uptake ability. When dead and no longer metabolically active, such biomass actually represents a biosorbent material. Recent development of potent biosorbent material indicates that such biosorbents may be able to compete with commercial ion exchange resins in heavy metal removal (Ong, 1996).

1.5 Objectives and Scope of Research

The overall objective of this project is to develop cost-effective adsorption technology for the treatment of metal-bearing wastewater. Towards this end, the scope of work focuses on the use of indigenous materials which are inexpensive and readily available as adsorbent. Two such materials, palm oil fuel ash and activated carbon derived from coconut shells, were investigated in detail for their ability to remove zinc and copper from aqueous solutions.

Adsorption is a versatile separation process for removing ionic contaminants (e.g. heavy metals) from wastewater. It is a non-destructive process and allows for recycling of the metals. Application of the adsorption process in a wastewater treatment and recycle system will significantly reduce water consumption and the volume of wastewater discharged, thus reducing water use and sewer fees and the size and cost of the pollution control system.

In general, adsorption processes can concentrate heavy metals in a dilute wastewater into a concentrated metal solution which is more amenable to metal recovery. With proper adsorption material, the system or process can provide an effective and economical solution to pollution control requirements.

In recent years, the feasibility of using agricultural waste materials as adsorbent to remove heavy metals from aqueous solutions has been the subject of numerous studies. Most of these studies focused on the adsorption aspect, e.g. optimising the experimental conditions to maximise the removal of metal ions. By contrast, desorption or elution of adsorbed metal ions from the adsorbent has not been investigated adequately. Desorption studies are an integral part of an adsorption process because an effective desorption step allows the production of a concentrated metal solution and at the same time permits the regeneration of the adsorbent for reuse, resulting in significant cost savings. The cost of the adsorbent usually dominates the overall economics of an adsorption process.

The major aim of this research is therefore to investigate the desorption of zinc and copper from two indigenous adsorbents, namely palm oil fuel ash (POFA) and activated carbon derived from coconut shells. The specific objectives are as follows:

- To investigate the suitability of a mineral acid (nitric acid) as regenerant in the desorption of zinc and copper;
- To optimise the experimental conditions for desorption;
- To study the kinetics of desorption; and
- To investigate the reusability of the two adsorbents in multiple cycles of adsorption and desorption.