

## Chapter 1: Introduction

### 1.1 INTRODUCTION

Heavy metal pollution in the environment has received attention due to the greater understanding of their toxicological importance in the ecosystem, agriculture and human health. The most important feature that distinguishes heavy metals from other toxic pollutants is that they cannot be degraded or readily detoxified biologically and have a tendency to accumulate in living material. The heavy metals discharged in the wastewaters can be toxic to aquatic life and render natural waters unsuitable for human consumption. Therefore, the elimination of heavy metals from wastewater is important for public health. Electroplating industries, in practice, release a relatively small amount of wastewater to the environment in comparison to other industries but the wastewaters are highly toxic in nature. Industrial wastewaters generated in the metal finishing and electroplating industries typically contain toxic heavy metals such as copper, cadmium, nickel, lead, zinc, chromium, etc. The plating operation consists of several stages such as cleaning, pickling, plating, rinsing plating, etching which produces a significant amount of wastewater. The metals and chemicals are present in the wastewater in soluble ionic form and most of them are extremely toxic. Tables 1.1 and 1.2 list the typical characteristics of the wastewaters and raw materials used in the metal finishing processes respectively. According to the 'Industrial pollution guideline' of ESCAP, the effects of pollution due to electroplating wastewater can be broadly classified into the following groups :

- a) Pollution of ground water and surface waters
- b) Toxicity to fish and other aquatic life
- c) Effects on biological sewage treatment processes
- d) Effects on sewers

### **1.1.1 Pollution of ground and surface waters**

Ground and surface waters could be contaminated from the untreated waste water. If untreated electroplating wastewater is discharged onto land, it may cause ground water contamination with toxic metals and may render it unfit for drinking purposes. The leaching of metals to ground water normally takes place through the soil. On moving downwards from the soil surface to the aquifer, a number of purification processes take place. When the soil permeability is low, the percolating flow can penetrate deep into the underlying soil where sorption processes retard metal migration. This results in the ground water contamination. The concentration of the toxic metals in surface waters receiving the effluents would depend solely on the dilution.

### **1.1.2 Toxicity to fish and other aquatic life**

The transport and dispersal of heavy metals from anthropogenic sources to aquatic ecosystems cause an environmental contamination problem. As the concentration of the heavy metal increases in the aquatic environment, it can be accumulated by aquatic organisms. The toxicity of the polluted water depends on the physical and elemental parameters like pH, temperature, hardness and oxygen content. Among all types of chemicals and metals used in the electroplating processes, hexavalent chromium and cyanide are considered to be

Table 1 : Typical electroplating wastewater

No.	Type of Plating	m <sup>3</sup> /d	pH	SS	Concentration (mg/l)									
					Cd	Cr <sup>6+</sup>	CN	Pb	Cr <sup>3+</sup>	Cu	Ni	Sn	Zn	Fe
1.	Ni,Cr, Cu	27.8	7.5	1,840	-	-	-	-	-	-	4.2	-	0.9	2.9
2.	Ni,Cr, Zn, Brass	1.6	6.5	-	-	-	23.0	-	-	21.0	-	-	-	-
3.	Ni,Cr, Zn, Au, Brass	1.5	5.7	130	-	0.0	7.8	-	0.1	-	0.8	-	6.5	-
4.	Ni,Cr, Zn, Cd, Brass	3.7	5.9	160	-	0.0	43.0	1.1	-	-	11.0	0.0	34.0	21.0
5.	Ni,Cr, Cu	3	6.8	110	-	3.7	-	-	3.7	2.6	0.3	0.0	17.0	45.0
6.	Ni,Cr, Zn	48	7.1	-	-	-	3.6	-	-	-1.2	-	-	-	-
7.	Ni,Cr, Zn	22.2	10.2	50	-	-	19.0	0.0	-	0.0	3.8	0.0	54.0	-
8.	Ni,Cr, Zn	3.7	5.2	450	-	0.0	-	0.0	1.0	0.1	0.2	0.0	54.0	-
9.	Ni,Cr, Zn	4.1	8.5	3	-	-	-	0.0	-	0.0	0.1	-	0.0	0.0
10.	Ni,Cr, Zn	1.8	5.7	80	0.0	11.0	0.0	-	0.2	1.9	159.0	0.0	7.3	0.8
11.	Ni,Cr, Zn, Sn, Ag	3.5	3.1	120	-	-	7.8	0.0	-	0.7	1.8	0.0	75.0	21.0
12.	Ni,Cr, Zn, Cu, Brass	0.9	6.4	-	-	-	66.0	-	-	-	-	-	-	-
13.	Ni,Cr, Zn, Sn, Ag	1.3	5.6	330	0.0	-	24.0	0.0	-	4.7	6.2	0.0	18.0	0.0
14.	Ni,Cr, Cu	4	5.9	50	-	-	-	0.2	-	0.0	27.0	-	0.4	7.8
15.	Ni,Cr	3.5	2.8	10	-	0.0	-	0.0	24.0	0.0	57.0	0.0	0.1	7.1
16.	Zn, Bright, Tin	4.3	7.5	800	-	-	76.0	0.0	-	0.0	-	0.0	85.0	12.0
17.	Ni,Cr, Cu	3.9	3.8	660	-	0.0	-	0.2	28.0	224.0	0.3	0.0	3.0	10.3
18.	Ni,Cr, Zn, Brass	11.2	6.6	10	-	0.0	20.0	-	0.2	0.1	0.1	0.0	1.3	-
19.	Ni,Cr, Zn, Cu, Sn	1.5	6.2	670	-	0.0	-	-	4.2	0.3	0.1	0.0	16.0	9.8
20.	Ni,Cr, Zn, Sn, Brass	3.1	9.6	24	-	0.0	24.0	0.1	0.1	0.0	0.1	0.0	0.2	0.7
21.	Ni,Cr, Zn	1.3	4.7	410	-	5.4	46.0	0.2	48.0	0.4	20.0	-	54.0	61.0
22.	Ni,Cr, Zn	2.3	2.2	140	-	0.0	20.0	-	6.2	0.4	6.7	-	6.1	244.0

Source : Rakmi, A.R. (1996)

**Table 2 : Chemicals used in electroplating**

Process	Raw materials
1. Pretreatment	Soda ash, Caustic Soda flake, hydrochloric
2. Nickel Plating	Nickel chloride, nickel sulphate, boric acid, brightener, sulphuric acid, nickel anode, nickel square, nickel carbonate, nickel crown, Nickstar New 35
3. Brass Plating	Copper sulphate, Tosa emery powder 120, nitric acid, brass salt, brass anode, ammonium chloride, caustic soda, detergent, lead bar, cleaner, lacquer, hydrochloric acid.
4. Chrome Plating	Chromic acid, Chrome anode, Chrome salt, sulphuric acid, catalyst.
5. Copper Plating	Copper sulphate, Copper anode, Caustic soda/flake, soap powder/wetting agent, Copper cyanide, chromic acid, sulphuric acid, sodium cyanide, brightener, metabisulphate, hydrogen per oxide
6. Zinc Plating	Zinc oxide, zinc brite AP, zinc purifier No.1, zinc anode, sodium cyanide, Asahi Zinkel Z-60R, zinc powder, nitric acid, sodium hydroxide, lacquer stripper.
7. Silver Plating	Potassium silver cyanide, silver anode, caustic soda, silver cyanide, nitric acid, hydrochloric acid, degreaser, brightener.
8. Tin Plating	Stannous sulphate, tin anode, hydrochloric acid, detergent, degreaser.
9. Painting	Ion phosphate, paint, tinner, derusting acids.
10. Anodising	Dyestaff, caustic soda, hydrochloric acid, sulfuric acid, nickel square, oxalic acid, phosphoric acid, sodium nitrate, glucomate, coloring agent, aluminium extruded
11. Graveling	Photopolymer, alkaline.
12. Galvanizing	Sodium orthosilicate, lime, hydrochloric acid, sulfuric acid, nickel square, oxalic acid, phosphoric acid, sodium nitrate, glucomate, coloring agent, aluminium extruded.
13. Copper coating	Copper sulphate, ammonium chloride, stannous sulphate, lime, electroalkaline cleaner, high carbon steel, low carbon steel.
14. Engraving	Nitric acid, sulphuric acid, Newfine sal, ferric chloride, N-butanol, polychloroethylene, alcohol, hydrochloric acid

Source : Rakmi, A.R.(1996)

highly toxic to aquatic life. The uptake of heavy metals by aquatic organisms take place by three processes:

- i) from the water by respiration (mercury only)
- ii) absorption of water from the body surface,
- iii) ingestion of food.

Among these mechanisms, the uptake of metals from the ingestion of food is the most important route of bioaccumulation. The toxicity of various chemicals such as are found in plating wastes (Burford,1953) is shown in Table 1.3.

Table 1.3: Toxicity of plating wastes constituents to aquatic life

Substances	Concentration (mg/l)	Test Organism	Effect
Chromic acid	0.3 (as Cr)	Daphnia Magna*	Toxic
Hydrochloric acid	60 (as HCl)	Daphnia Magna*	Toxic
Nitric acid	107 (as HNO <sub>3</sub> )	Daphnia Magna*	Toxic
Sulphuric acid	83 (as H <sub>2</sub> SO <sub>4</sub> )	Daphnia Magna*	Toxic
Strong acid	To pH 5.0	Fish	Toxic
Cadmium chloride	0.01 (as Cd)	Gold fish	Kills in 8-18 hrs
Cadmium sulphate	513 (as Cd)	Minnows	Kills in 3 hrs
Copper sulphate	0.04 (as Cu)	Daphnia Magna*	Toxic
Copper sulphate	0.8 (as Cu)	Goldfish	Kills in 24 hrs
Sodium chromate	0.1 (as Cr)	Daphnia Magna*	Toxic
Potassium dichromate	36 (as Cr)	Goldfish	No effect in 108 hrs.
Potassium dichromate	180 (as Cr)	Goldfish	Kills in 3 days
Chromate(ion)	20 (as Cr)	Trout and Minnows	Kills in 8 days
Chromate(ion)	50 (as Cr)	Sunfish, bluegills	Not toxic in a month
Chromate(ion)	0.01 (as Cr)	Micro-flora	Toxic
Ferric chloride	24 (as Fe)	Goldfish	Kills in 1-15 hrs.
Ferrous sulphate	37 (as Fe)	Goldfish	No effect in 100 hrs
Ferrous sulphate	368 (as Fe)	Goldfish	Kills in 2-10 hrs.

\* Daphnia Magna is a representative fish food organism commonly found in streams.

### **1.1.3 Effects on Sewers**

Electroplating wastes are highly corrosive in nature due to the presence of acids. Concrete structures, especially the concrete sewers in which the wastewaters are discharged, can be easily corroded by the plating wastewaters. Alkaline wastes are also corrosive but they are not as detrimental as acid wastes to most of the construction materials.

### **1.1.4 Effects on Sewage Tr atment**

Electroplating wastes have a deleterious effect on biological sewage treatment processes due to the presence of acids, alkalis and toxic metallic ions such Cr(VI), Cu(II), Zn(II) and Ni(II). compounds which inhibit or kill the microorganisms that take part in the purification of sewage. Although presence of small concentrations of the heavy metals in sewage may not affect its biological purification, most of these metals are precipitated during the process and get accumulated in sludge, rendering it unfit use as manure. It has been found that hexavalent chromium and nickel ions even at small concentrations (1 to 10 mg/L) affect nitrification and the general performance of the sewage treatment plant. Sodium and potassium cyanides also inhibit nitrification initially but have no effect after a few days. Higher concentrations of copper, iron, nickel, and cyanide affect gas production in anaerobic sludge digestion.

### 1.1.5 Industrial Wastewater and Heavy Metal Pollution

The term 'heavy metals' are important in both biological and industrial activities which can be defined as metallic elements of a density greater than  $6\text{g/cm}^3$  (Davies, 1980). Some heavy metals which are essential for the growth of plants and animals are shown in the Table 1.4. The heavy metals pose a threat to the environment when their concentration is elevated above normal levels by human activity.

Table 1.4: Essential heavy metals for the growth of plants and animals.

Element	Density ( $\text{g/cm}^3$ )	Mean content in crystal rock (ppm)	Essential (plant/animal)	Known pollutant	Very toxic and relatively available
Ag	10.5	0.07		P	√
Au	19.3	0.05			√
Bi	9.8	0.17		P	√
Cd	8.7	0.2		P	√
Cr	7.2	100	E	P	
Co	8.9	25	E	P	√
Cu	8.9	55	E	P	√
Fe	7.9	$6 \times 10^4$	E	P	
Hg	13.6	0.08		P	√
La	6.2	25			
Mn	7.4	950	E		
Pb	11.3	13		P	√
Mo	10.2	1.5	E	P	
Ni	8.9	75	E	P	√
Pt	21.5	0.05			
Tl	11.9	0.45		P	√
Th	11.5	9.6		P	
Sn	7.3	2		P	√
U	19.1	2.7		P	√
V	6.1	135	E		
W	19.3	1.5	E	P	
Zn	7.1	70	E	P	√
Zr	6.5	165			

Source : Davies (1980)

The release of metal contaminants to the environment seems to be an unavoidable concomitant of metal extraction, production and use. In South East Asian countries, especially in Malaysia the metal plating industries are growing rapidly in conjunction with metal manufacturing and other engineering

industries. According to a survey of the Department of Environment of Malaysia(1985), approximately 220,000 m<sup>3</sup> toxic and hazardous wastewaters are generated in Peninsular Malaysia per annum. About 43% of the total amount (which contain toxic heavy metals and other chemicals) is contributed to the metal finishing industries. The strict environmental regulations related to heavy metal discharges make it necessary to develop schemes for the removal of heavy metals from wastewaters.

### **1.1.6 Techniques of Treatment**

Many methods have been proposed for the removal of heavy metals. Chemical precipitation, alum or iron coagulation, membrane filtration, ion exchange and adsorption are some of the most commonly practiced process (Patterson,1975). Safe and effective disposal of heavy metal containing wastewater is always a challenging task for the industries due to the fact that the cost-effective treatment alternatives are not readily available.

#### ***1.1.6.1 Chemical Precipitation***

Chemical precipitation is a unit process, usually involved in wastewater treatment in which the physical state of the dissolved and suspended solids in water are altered by chemicals to facilitate their removal through sedimentation. In order to remove metal ions from industrial effluents, the hydroxide precipitation process is commonly employed which turns metal ions into hydroxide precipitates. As hydrolysis of the metal ions occurs, the size and surface charge of the ionic species increase. When the colloid surface becomes charged, a charged double layer surrounding the colloid is formed. The existence of these double layers around colloids inhibits the close approach of colloids to each other (Weber *et al.*,1972). Thus the colloids or hydrated metal



ions may form a stable suspension. In order to precipitate metal ions as salts out of wastewater, the hydrated metal ion must be destabilized. Factors influencing destabilization mechanisms include type and dosage of coagulant, pH, chemical composition of wastewater and mixing conditions (Clark *et al.*, 1993). The sludge produced in this process is sparingly soluble in water and its volume depends on the pH and concentration of metal ions in the wastewater. Generally, this process yields a high volume of sludge which is dewatered and stabilized prior to disposal. Since the water from the sludge dewatering process contains a high concentration of dissolved salts, it cannot be reused and it is expensive to deionize the water (Darnall, 1991).

#### **1.1.6.2 Ion Exchange**

Ion exchange is considered to be a stoichiometric process; that is, every ion removed from the solution by electrostatic attraction to the charged surface is replaced by an equivalent amount of a similarly charged ionic species displaced from the interfacial region. The whole process is conceptualized as the reversible exchange of electrolyte counter ions in the diffuse layer near a charged surfaces or in a separate phase, as for Donnan equilibria (Weber *et al.*, 1972).

Ion exchange resins are made in the form of very small spheres or beads, so that when packed in a columns, they present an enormous surface area to the effluent and each bead has on its surface thousands of functional groups (Robert, 1991).

The two main processes involved in sorption of an ion on a charged solid in an aqueous system are:

- 1) Nonspecific electrostatic attraction to the charged surface
- 2) Chemical bonding at discrete sites on the surface.

In this process, it requires a large volume of resin to treat a high concentration of metal ion solution, and divalent ions which are frequently present in wastewater might compete with heavy metals for the binding sites of the resin (Darnall, 1991). Ion exchange resins can be regenerated and used over and over again. Cationic resins are regenerated by mineral acids but a high concentration of salt residue is produced in the regeneration process (Higgins, 1989).

#### ***1.1.6.3 Evaporation***

Although metallic compounds can be separated effectively from the wastewater by this old technique, it is highly energy intensive. It will therefore be cost effective only in concentrating rinse water that is to be recycled to the main process.

#### ***1.1.6.4 Membrane Process***

The most important use of the membrane-filtration technique is in the desalination of sea water. It can also be used to remove heavy metals from contaminated wastewater. In this, water is separated from dissolved metal ions by forcing the water through a semipermeable membrane. The transport mechanism is primarily diffusion, rather than sieving action as in microfiltration and ultrafiltration. Membrane separation units like reverse osmosis process can remove particles as small as  $10^{-3}$  to  $10^{-4}$   $\mu\text{m}$ , which include ionic materials and dissolved salts. This process is suitable for treating large volume of wastewater but is not economical for the treatment of small volume of wastewater.

### **1.1.6.5 Adsorption**

Adsorption, in general, is the process of collecting soluble substances that are in solution on a suitable interface. Adsorption at a surface or interface is largely the result of binding forces between the individual atoms, ions or molecules of an adsorbate and the surface, all of these forces having their origin in electromagnetic interaction (Weber and VanVliet, 1980). The process can occur between any two phases, such as liquid-liquid or liquid-solid interfaces. The material being concentrated or adsorbed is the adsorbate, and the adsorbing phase is termed as adsorbent. Since adsorption is a surface phenomenon, all adsorbents are characterized by surface area. The quantity of adsorbate that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate and the temperature. Generally, the amount of material adsorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called an adsorption isotherm.

Among all adsorbents, activated carbon is the most widely used because of its capability to adsorb a broad range of different types of adsorbates. Activated carbon is most widely used for the removal of organic contaminants and is most effective when the organic solutes have a high molecular weight and low water solubility, polarity and degree of ionization. However, in studies in the field of metallurgy, many researchers have indicated that the carbon adsorption of metallic compounds can be successfully achieved for certain aqueous waste streams.

Huang and Blankenship (1984) suggested that activated carbon adsorption appears to be a particularly competitive and effective process for the removal of heavy metals at trace quantities.

## 1.2 RESEARCH OBJECTIVES

In the first phase of this experiment, the use of wood ash as adsorbent for the removal metal from water was investigated. Nickel compounds, which are commonly found in the industrial effluents were used in this study. The methods developed for the removal of various metals in the treatment of wastewater are reduction, precipitation, ions exchange and adsorption onto activated carbon etc. However, in developing countries, none of these methods have achieved economic viability (Pandey *et al.*, 1985). In recent years, attention has been focused on the use of low cost, naturally occurring and abundantly available biosorbents. Materials such as Chinese peat (Zhipei *et al.*, 1984), surplus activated sludge (Venkobachar,1990) and waste slurry generated from a fertilizer plant (Srivastava *et al.*, 1989) have all been tried as low cost adsorbent. Recently, coconut-husk fiber, palm pressed leaves (Tan *et al.*,1993), compost, leaf mould, sawdust, sugarcane bagasse, sugar-beet pulp and maize cob (Sharma *et al.*,1994a;b;c) have been studied. The present work examines the use of wood ash for treating wastewater in a batch process.

The present work has the objectives:

- 1) The effects of various functional parameter like pH, temperature, contact time, concentration of metal ion, and dosage of adsorber on metal uptake by wood ash.
- 2) Investigation of the rate constant of metal uptake by the Lagergren equation.
- 3) Determination of optimum time and temperature of adsorption for equilibrium studies.
- 4) Characterization of adsorption behavior by using Langmuir and Freundlich isotherm models.
- 5) Examination of the performance of wood ash in the presence of various coincidental anions and cations as a chelating agent.

The main focus of this study was to find the optimum condition and adsorbability of metal ions from the wastewater in a batch system.

The second phase of this study covered the recovery of heavy metals from effluents containing Ni salts. This technology is very important not only from the view point of environmental protection but also for the recovery of valuable materials.

In this work, investigations on the efficiency and feasibility of the reverse osmosis process (thin film composite membrane) to concentrate heavy metals (i.e., nickel) and to reclaim high quality process water, were carried out.

The objectives of this study were to establish following.

- 1) The relationship between permeate flow rate and transmembrane pressure drop (TMP) for different feed concentrations.
- 2) The effect of TMP on concentration of heavy metals in the permeate.