1. INTRODUCTION

1.1. The Emergence of Environmental Problems

For centuries water has been protected by natural mechanisms of self purification which have acted without any disturbances to the environment. Pollutants excreted by some organisms were degraded by others. As a result, a dynamic equilibrium between the particular components of nature has been preserved and local ecological disturbances, which occur periodically, have never exceeded the ability of natural purification processes to control them. Natural processes have long been disturbed by man through time in the creation of artificial environments in his search for material comfort.

The industrial developments of the present century have forced advanced communities to take an ever-increasing interest in the environment against pollution and this has become a statutory obligation in modern times throughout the globe. The present concern for the environment has spawned numerous government agencies that have issued regulations concerning the materials that can be legally discharged into the air and water in the effluent from manufacturing establishments. While there has been considerable success in reversing this trend, one road block to greater progress often has been the lack of necessary technology to remove reliably and economically the pollutants which are the cause of degradation of receiving waters. Such immense environmental challenges can only be met through the marshaling of the talents of the best environmental engineers and scientists around the world and through the design and application of cost-effective solutions[1].

Industrial wastes are the liquid discharges from an establishment that prepares any material or article for market. The fast progress in industrialization in both the developed and developing countries requires urgent measures in order to prevent further damage to the environment by polluted surface and ground water.

Industrial wastes are very complex and although in many cases common methods and processes of treatment may be used, a complete knowledge of the limitations and advantages of the different recognized methods is required so as to select the most suitable method for a given problem.

1.2. The Wastes Treatment Technologies

Wastes treatment technologies can be classified as chemical, biological and physical processes. Although these operations and processes occur in a variety of combinations in treatment systems, the principles involved are the same[2,3].

Treatment methods in which the application of physical forces predominate are known as physical unit operations. Screening, mixing, flocculation, sedimentation, flotation, filtration, and gas transfer are typical unit operations.

Treatment methods in which the removal or conversion of contaminants is brought about by the addition of chemicals or by other chemical reactions are known as chemical unit processes. Precipitation, adsorption, and disinfecting are the most common examples used in wastewater treatment. In chemical precipitation methods, treatment is accomplished by producing a chemical precipitate that will settle, and the polluting constituents are removed by precipitation and occlusion.

Treatment methods in which the removal of contaminants is brought about by biological activity are known as biological unit processes. Biological treatment is used primarily to remove the biodegradable organic substances (colloidal or dissolved) in wastewater. Basically, these substances are converted into gases that can escape to the atmosphere and into biological cell tissue that can be removed by settling. Biological treatment is also used to remove nutrients (nitrogen and phosphorus) in wastewater.

It is noted that unit operations and processes are grouped together to provide various levels of treatment. Historically, the term "preliminary" and or "primary" refer to physical unit operations; "secondary" refer to chemical and biological unit processes;

and “advanced” or “tertiary” refer to combinations of all three. A more rational approach is first to establish the level of treatment required before the effluent can be reused or discharged into the environment. The required unit operations and processes necessary to achieve that requirement can then be grouped together on the basis of fundamental considerations.

1.3. Wastes Problem in Malaysia

In Malaysia, with the accelerating tempo of industrialization, the generation of toxic waste is becoming increasingly significant and warrants serious attention. Toxic and hazardous waste are always referred to waste which by virtue of its property or behavior could, or is likely to, present a significant health risk to persons or the environment, by reason of its chemical, biological or physical properties. Each year, more than a million tons of different types of industrial wastes are generated. A portion of these wastes are capable of seriously polluting the environment and causing considerable damage.

As part of the nation's effort to protect the environment from pollution, legislation has been introduced by the Malaysian government which prescribes legal limits for toxic materials. For such laws to be enforced, methods must be available, both for treating the effluent to meet wastewater pretreatment standards and for monitoring the effluent to ensure that the legal limits are not exceeded.

In accordance to section 3(1) of Environmental Quality Act which has been implemented since 1974, the Director General of Environment is responsible for all activities relating to the discharge of wastes into the environment to control the quality of water, and the limit of various toxic organic and inorganic materials that can be discharged in to our water stream[4,5], but the laws have either been loosely framed or inadequately or improperly enforced, so that no concerted effort has been exerted and no great amount of work done. Illegal wastes disposal still often happen and appear in local news media.

According to the DOE director-general Datuk Dr. Abu Bakar Jaafar[6,7], from a study conducted by Dames and Moore, metal finishing and electronic industries were the main pollutants contributor. In 1994, a total of 145 registered electroplating firms cited nationwide, and 212,472 tones of toxic waste was generated by such industries[6,7]. The various sources of wastes generation include foundry, metal finishing, packaging and printing, etching, car workshops and battery producers. The DOE survey showed that only 63% of the 54 surveyed firms were able to comply with the department's discharge standards. This does not include small backyard operators and their number may be double that of the registered firms. Most of the factories that failed to comply cited reasons related to technological problems and lack of space to install treatment plants. Some of them could not afford to treat their waste to meet the DOE's standards. Since 1991, only seven metal finishing factories had been charged in courts for failure to meet DOE emission standards, but each was fined amounts that were much less than the costs of installation of the treatment plants needed[6,7,8,9].

1.4. Effluent From Metal Finishing Industries

The metal finishing industry broadly covers electroplating, electroforming, chemical coloring, surface treatment with phosphates or chromates, anodizing, painting, and lacquering. The base metals involved may be copper; ferrous alloys, including stainless steels; and alloys of copper, zinc, aluminium, magnesium, and lead. Non-metallic base materials (such as plastics, etc.) may also be electroplated. Acid and alkalies, both concentrated and diluted, are used in the preparation of the base surfaces for the various finishes. The plating baths may be acid or alkaline and are almost without exception water solutions of salts of the metals to be deposited. Therefore, the effluents from a plating establishment may include any combination of the metals and anions shown in Table 1[9]. The waste from any one plant would never contain all of the constituents listed in Table 1[10] and, ordinarily, ingredients contributing to B.O.D. are low.

These electroplating effluents normally contain appreciable quantities of various toxic materials:- acids or alkalis, heavy metals such as nickel, chromium, copper and zinc, and two specific types of salts which are considered to be particularly toxic, namely chromates and cyanides. The contamination of our environment by heavy metals is a constant and disturbing problem. Heavy metals are among the least understood of contaminants. Most heavy metals are toxic to some degree to all life-forms. In right quantities some are essential to life, which we require only in minute (trace) amounts and very toxic indeed at higher concentrations. In humans, toxic heavy metals poisoning can lead to severe nervous system disorders and can cause death. Even trace amounts of heavy metals within an organism's environment are potentially dangerous, because heavy metals do not decompose over time (as do most organic pollutants) and often accumulate within the organism throughout its lifetime. This accumulative effect is accentuated in succeeding species along each food chain[11].

TABLE 1.-[a]Possible Constituents in Electroplating Waste[10]

Metals	Anions
Ammonium	OH^-
Sodium	SO_4^{2-}
Potassium	
Calcium	PO_4^{3-} (or complex)
Magnesium	NO_3^-
Aluminum	NO_2^-
Zinc	Cl^-
Cadmium	F^-
Nickel	S^{2-}
Cobalt	
Iron	BF_4^-
Chromium	CrO_4^{2-}
Lead	CN^- (free or complex)
Tin	CNO^-
Copper	CO_3^{2-}
[b]Silver	SiO_2 (or SiO_4)
[b]Gold	[c]R_xCOO^-
[b]Indium	$R_xSO_3^-$
[b]Platinum group	SO_3^{2-} (or equiv. source of SO_2)

[a] Paint waste, solvents, and lubricants may also be present.

[b] These high-cost metals are usually removed by recovery methods.

[c] Such as formates, acetates, citrates, and tartrates, as well as higher fatty acid salts.

However, plating wastes may vary greatly, as compared to most plant wastes, since any combination of these constituents may be present and in widely different amounts. Because of this, an analysis of the proper handling and treatment of each plant's waste on an individual basis is essential. Also, the cost of the installation and its operation may vary widely.

Analytical variability must also be considered when examining waste water for specific components such as heavy metals, TOC, and BOD, which may contribute to toxicity. These variations in analysis of effluents constituents and toxicity must be considered when evaluating potential treatment alternative.

1.5. The Treatment Technologies Of Inorganic Heavy Metal Wastes

The classical inorganic toxicants are the cationic metals and metalloids, derived from a wide variety of industrial activities. Commonly included in this group are: cadmium (II), chromium (VI, III), copper (I, II), lead (II), mercury (I, II), nickel (II), zinc (II). In some instances, the oxidation state will be a major determinant of how a particular technology performs, and oxidation state modification may be an integral aspect of the treatment technology. The classical example is the oxidation of ferrous to ferric ions, preparatory to ferric hydroxide precipitation. It is serendipitous that higher pH here favors both the kinetics of the ferrous ion oxidation process and the precipitation of the oxidized product. In other instances, process control may require multi-staging. One example is hexavalent chromium reduction to trivalent chromium at acidic pH, followed by chromic hydroxide precipitation at alkaline pH[12,13,14] .

Metals are present in wastewaters from a broad spectrum of industries, Table 2[15] provides perspective on the range of metals and typical metals levels observed. Conventional technologies are normally targeted for the typical metals concentrations. A great variety of treatment technologies are reported in use for control of cationic metal toxicants. The common technologies are: precipitation-hydroxide/oxide, carbonate, sulfide co-precipitation, ion-exchange, membrane procession, electrolytic recovery, and evaporative recovery. The others are solvent extraction, reverse osmosis, and foam flotation methods[2,15,16,17,18].

Table 2. Metal Concentrations in Industrial Wastewaters.[11,15]

	Concentration mg/l		
Metal	Low	"Typical"	High
Arsenic	0.5	10	1,000
Cadmium	1.0	25	5.000
Chromium	1.0	50	50,000
Copper	1.0	25	7,500
Iron	5.0	50	5,000
Lead	0.5	10	900
Mercury	0.005	1.0	2,000
Nickel	5.0	50	900
Zinc	5.0	50	3,000

Table 3 summarises the technologies used among fifty-three electroplating facilities evaluated in one study[15]. Precipitation and co-precipitation, accounts for 60 - 80 percent of the treatment systems described, with the rest fairly evenly distributed among the other technologies listed[11].

Table 3. Treatment Processes Utilized at Fifty-three Electroplating Facilities.[11,15]

Treatment	Cu	Ni	Cr	Zn
Precipitation				
Batch	4	5	8	4
Continuous	21	22	18	11
Integrated	5	5	12	3
Ion exchange	2	3	3	0
Evaporation	2	1	3	7
Electrolysis	2	0	2	2
Reverse osmosis	2	3	2	0
No treatment	2	3	2	1
Plants having specific metal waste	40	42	50	28

The simplest system for dealing with the effluent would be merely to use sufficient rinse water to dilute the processed effluents to a level at which they may be discharged without being harmful. However, water supplies have become much more expensive and water has even become a scarce commodity in some countries[19].

1.6. Ion Exchange Method

Ion exchange describes the physical-chemical process by which ions are transferred from a liquid phase to a solid phase and vice versa.[11] Ions held by electrostatic forces to charged functional groups on the surfaces of a solid are exchanged for ions of like charge in a solution in which the solid is being contacted.

Ion exchange technology is well established, particularly for water softening. Ion exchange is applied for discharge or for direct recovery. Examples include recovery of chromate in plating rinsewater. Advantages and disadvantages of the ion exchange process were discussed in Refs. 11, 20.

Three major areas of application of ion exchange in the metal finishing industry have been demonstrated[21]: Wastewater purification and recycle; end-of-pipe pollution control; and chemical recovery.

In the first area of application, mixed rinse solutions are deionized to permit reuse of the treated water which will significantly reduce water consumption and volume of wastewater discharge, thus reducing water use and sewer fees, as well as the size and cost of the pollution control system.

The ion exchange process can be applied as a means of directly treating wastewater to remove heavy metals. In this approach, wastewater pretreatment entails pH adjustment, to ensure that pH is within the operating range of the resin, and filtration, to remove suspended solids that would foul the resin bed.

The ion exchange process can concentrate the heavy metals in a dilute wastewater into a concentrated metal solution that is more amenable to metal recovery. The purified rinse water is also recycled.

1.7. Membrane Procession Methods

Membrane processes involve physical separation phenomena (e.g., ultrafiltration) or physico-chemical phenomena (e.g., reverse osmosis, electrodialysis). Reverse osmosis is widely applied for pollution control and product recovery[11,15], while electrodialysis is more directly applicable for freshwater production from saline or brackish water supplies. There is a growing application of reverse osmosis for wastewater concentration and recovery of plating chemicals, such as treatment of zinc or nickel-plating solutions[11,15], since reverse osmosis is suited for handling the near-neutral nickel solutions, and the economics are favorable for recovery and reuse of expensive nickel chemical. In comparison studies of reverse osmosis systems in nickel wastewater treatment, the relative efficiency of recovery (percent nickel rejection) was found to be dependent upon both membrane type and module used[17,22].

1.8. Electrochemical Methods

1.8.1. Electrolytic Processes

Electrolytic processes are used for the removal and reclamation of heavy metals from concentrated wastewater, and the more dilute polishing streams. Destruction of cyanides and the treatment of chrome wastes have been the subjects of much research[23-31] and have been used in industrial water treatment plants[2,15,32]. The electrochemical treatment of plating effluents have some advantages compared to conventional chemical treatment methods.

At the cathode, the reactions may include the reduction of a metal ion to the metal itself

$$M^{2+} + 2e^- \rightarrow M \qquad (1)$$

or, in aqueous media, the reduction of the hydrogen ion or water to hydrogen gas

$$2H_3O^+ + 2e^- \rightarrow H_2\uparrow + 2H_2O \qquad (2)$$

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^- \qquad (3)$$

At the anode, the corresponding oxidations take place and oxygen and hydrogen ions are formed:

$$6H_2O \rightarrow 4H_3O^+ + O_2 + 4e^- \qquad (4)$$

For an aqueous solution containing several species at various concentrations, the potentials of the various possible electrode reactions may be so close that several reactions could take place at a single electrode. Thus, in practical situations it is common to speak of the efficiency of an electrode reaction.

In all electrolytic processes, anodes are prone to attack and become oxidized that they are passivated and difficult to maintain a high-performance electrode surface. Therefore, anode consumption and replacement should be considered among the economic factors in evaluating the system.

Dimensional and characteristics (such as overvoltage for hydrogen evolution) changes in the cathode due to metal deposition could take place and cathode efficiency may thus fall. An inefficient cathode (favor the hydrogen evolution) could be developing a region of higher pH than the pH of the bulk. This might cause precipitation of species in solution. Organic films or slimes could also deposit.

The most common, and difficult to control form of electrode deterioration is that generally referred to as "fouling", in electrochemical treatment methods. Due to a coating of insoluble salts, oxides, organic materials, or biological films accumulated at the electrode surface, a high resistance is interposed to the desired electrolytic potential. Also, variations in feed may be enough to push the chemistry at an electrode surface from a nominally nonfouling condition to a fouling one.[11]

1.8.2 Electrodialysis processes

Electrodialysis[33] is used to concentrate or separate ionic species in an aqueous solution. The aqueous solution is passed through alternately placed anionic and cationic permeable membranes with an electric potential applied across the membranes. The electric potential provides the force to enable ion migration. Therefore, there are two hydraulic circuits, one which is ion-depleted while the other is ion-concentrated.

1.8.3 Electroflotation processes

The electroflotation[34-36] process (also known as electroflocculation) can be used as a method of removing heavy metal by forming metal hydroxide and then separating this dilute suspensions or colloid into slurries and liquid. It is a variation of the classical flotation technique using electrolytically generated gas bubbles as separating agents. This method consists essentially of the removal of sludge from the electrolyte by its flotation by finely dispersed bubbles of hydrogen and oxygen which are formed as a result of the electrolysis of the aqueous part of the liquid being cleaned. In addition, the hydroxide generated at cathode can react with heavy metal in solution and cause formation of metal hydroxide colloidal particles. The hydrogen and oxygen bubbles formed through reactions (2), (3), (4) in section 1.8.1 pass through the electrolyte, attach to the suspended particles (sludges), and raise them to the surface of the solution, where the particles appear as foam. Removal of this foam completes the electroflotation cleaning of the electrolyte.

1.9. The Precipitation Treatment Methods

Precipitation treatment is the most widespread technology applied for inorganic toxicants control. Its application is especially prevalent for the control of metals. At first, industrial wastewater treatment was perceived as a very simplistic hydroxide formation process, and theoretical models of the technology derived from nominal metal hydrolysis equilibria concepts. However, over the past two decades, research and development on metals speciation, solubility, and solid phase characteristics have yielded significant advances in our understanding of precipitation.

The treatment results observed[28,37] are influenced less by simple solubility aspects than by other phenomena. Further, recent studies[2,24,27,38] have clearly demonstrated that for a number of important metals, the kinetics of precipitate formation (and sometimes transformation) have a significant effect in the performance of the technology.[11]

The factors influencing precipitation treatment efficiency are: formation kinetics; co-precipitants formed; treatment pH; salt formed; complexing agents; suspended solids removal efficiency. Table (4)[39-42] lists the solubility products for hydroxides of metals commonly found in industrial effluents.

Table 4. pKs value at 25 °C for metal hydroxide[39-42]

Hydroxide	pKs
AgOH	7.7
$Cu(OH)_2$	19.2
$Zn(OH)_2$	16.35
$Ni(OH)_2$	15
$Co(OH)_2$	15
$Fe(OH)_2$	14.7
$Fe(OH)_3$	37.4
$Mn(OH)_2$	14.2
$Cd(OH)_2$	14.0
$Mg(OH)_2$	11
$Ca(OH)_2$	5.4
$Al(OH)_3$	32
$Cr(OH)_3$	32
$Sn(OH)_2$	26.26

$pK_s = -\log K_s$, where $K_s = [M^{z+}] \times [OH^-]^Z$

From the solubility product, it is possible to estimate the pH value at which precipitation will begin to occur for a given concentration of the metal ion. Fig. 1[42] shows the solubilities of metal ions at various pH values, if other factors (such as complexation, foreign ions) are not taken into account. The slopes of the lines in Fig. 1 correspond to the valencies of the metal ions. Table (5)[42] is given the pH value at which the solubility is 10 ppm and 1 ppm. In more concentrated solutions, it is necessary to consider ionic activities and ionic strengths[43].

Fig.1. log(solubility) versus pH and pOH.[42]

c =solution metal ions concentration

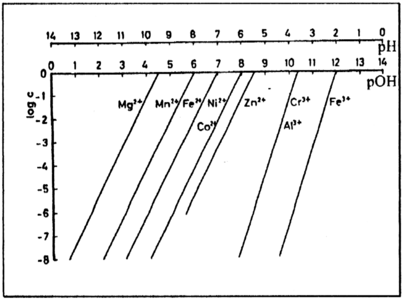

Table 5. The pH value indicates where the solubility is ≤ 10 ppm and ≤ 1 ppm[42]

	pH	
Metal ion	solubility: ≤ 10 ppm	≤ 1 ppm
Mg^{2+}	11.5	12.0
Mn^{2+}	10.1	10.6
Fe^{2+}	8.9	9.4
Ni^{2+}	7.8	8.3
Co^{2+}	7.8	8.3
Zn^{2+}	7.2	7.7
Cr^{3+}	5.1	5.4
Cu^{2+}	6.3	6.8
Al^{3+}	5.0	5.3
Fe^{3+}	3.2	3.5

Modern Treatment technology attempts to utilize the results of recent studies[24,43-47] and improved knowledge of metals chemistry to select control measures aimed at improved solids settling and handling, reduced solubility, kinetic control protocols, and selective metals precipitation geared toward metals recovery for reuse. Further, there is increased recognition that optimal conditions to achieve such objectives are derived from process liquid segregation and management.

Another significant advance in the understanding and application of "precipitation" technology involves the adsorptive phenomenon which is often termed adsorptive co-precipitation. One ion is adsorbed into another (bulk) solid, which is either preformed and added into the treatment reactor, or formed in-situ. This technology lies in two key aspects. First, the process behaves in an essentially isothermal fashion. Thus, increased adsorptive removal can be achieved as the concentration of the bulk solid is increased. This advantage is offset by the increasing volume of sludge formed, as the bulk adsorbing solid often constitutes the solids derived from the process. Nevertheless, residual unabsorbed ion levels far below those achievable by normal precipitation are possible.[11,48] The second aspect is the ability to manipulate the bulk solid surface charge and soluble adsorbing ion speciation in order to enhance or selectively suppress adsorption of certain species.

1.10. The Precipitation Mechanism[11,49]

Formation of a precipitate is a physical and chemical phenomenon. The study of precipitation should not be limited to kinetic measurements alone without more detailed knowledge of the chemistry of the precipitation reaction.[50,51] Precipitation starts within supersaturated solutions and it proceeds through several steps such as: nucleation, crystal growth, and several aging processes such as Ostwald ripening, recrystallization, and agglomeration.[52]

A wide spectrum of solid phases can initially form, depending upon thermodynamic and kinetic factors, as well as the matrix of ions present. The morphology of the particles, such as, their size, shape, and uniformity, is greatly influenced by the conditions of precipitation. For example, the concentration of reacting components, pH, temperature, mode of mixing, and time of aging[53] are important factors.

Precipitation is not possible unless the solution is supersaturated. Completeness of precipitation of a desired species is determined by the equilibrium solubility of that substance under the conditions prevailing at the time of precipitation.[54]

For a sparingly soluble salt M_vX_v, this may be discussed in terms of the equilibrium

$$\text{(solid) } M_{\nu_M}X_{\nu_x} = \nu_M M^{z+} + \nu_x X^{z-} \text{ (solution)} \quad K_{sp} = a_M{}^{\nu_M} \,.\, a_x{}^{\nu_x} \qquad (5)$$

where the ion activity product (IAP) of the solution = $a_M{}^{\nu_M} \,.\, a_x{}^{\nu_x}$, and K_{sp} is the solubility activity product of the precipitate.

The state of saturation of a solution with respect to a solid is defined as.[23]

$IAP > K_{sp}$ (supersaturated) (6)

$IAP = K_{sp}$ (saturated, equilibrium) (7)

$IAP < K_{sp}$ (undersaturated) (8)

Although precipitate formation is predicted as thermodynamically favorable at or above saturation values (i.e., $IAP > K_{sp}$), precipitation will generally not occur until a significant degree of supersaturation is reached.

The solubility products resulting from thermodynamic studies cover a range of values. Differences of a few orders of magnitude are not uncommon and there are various reasons for such discrepancies. The composition and properties, that is, the reactivity of the solids, vary for different modifications of the same compound or for different active forms of the same modification. In addition, species influencing the solubility equilibrium, such as complexes, are sometimes overlooked.[55] The structural units of the solid hydroxide are rarely present in solution as simple ions, but rather usually form a larger variety of complexes and polynuclear ions.[56]

Theoretical equilibrium speciation in a precipitation system is usually represented by solubility diagrams which are appropriate under certain conditions. Factors that modify or invalidate the diagram include changes in ionic strength, temperature or pressure; the presence of common ion or complexing agents, and insufficient reaction time to achieve equilibrium[57]. Precipitation reactions occur according to different schemes at different [base]-to- [metal] ratios and different precipitation products are often formed.

In analytical separations, it is well-known that foreign ions take part in several phenomena that affect the composition and purity of the precipitates: adsorption, postprecipitation, occlusion, co-precipitation.[58] Gradual addition of alkali to metal salt solutions generally results at first in precipitation of basic salts. A series of studies of hydrolysis precipitation of aluminum(III) solutions showed that the time course of the process is different in the presence of sulfate than it is in the presence of other anions such as nitrate or chloride.[59]. The electrometric studies of Britton[60] on the precipitation of copper hydroxide demonstrated the formation of basic salts of copper(II) when NaOH was slowly added to a solution containing cupric ions. If an agent or ligand is available which can react with the cation of the precipitate, the solubility of a compound can be markedly enhanced.

The solubility of a precipitate in an aqueous solution containing a common ion is lower than it is in pure water, provided no complex ions are formed in appreciable concentrations. This phenomenon is known as the common ion effect.[54]

Temperature affects both the equilibrium position of the precipitation reaction and the reaction rate. In general, the solubility increases with increasing temperature, with a few notable exceptions.[11,61] The fact that the solubility products of most salts increase steadily with temperature is consistent with the observation that the dissociation of most crystals into hydrated ions requires considerable energy, and thus the dissolution process is endothermic[11].

The hydroxide precipitate releases water adsorbed on the surface when standing in the mother liquor, leading to a decrease in its volume. Simultaneously, the crystal lattice of the hydroxide becomes more regular and primary species tend to grow. Possible chemical or structural changes in the precipitate must be considered, if the properties of the solid phase are measured long after formation.[23]

The process of precipitate formation involves a unique internal system that regulates the particle size distribution through the level of driving force, supersaturation. The supersaturation level determines the rates of nucleation and growth, which in turn determine the dynamic particle size distribution at any given time.[62]

Nucleation and particle growth comprise the physical reaction in which a precipitate is formed. Nucleation proceeds through the formation within a supersaturated solution of the smallest particles of a precipitate that are capable of spontaneous growth. Particle growth consists of the deposition of ions from the solution upon surfaces of solid particles that have already been nucleated.[11]

Nucleation controls the number, size, structure, and morphology of the precipitated crystals. Nucleation determines the surface area on which precipitation can take place and therefore it establishes the tempo of the precipitation.[63]

In the formation of nuclei in solution there are a number of additional complicating factors such as diffusion, solvation of solute ions and desolvation on precipitating, surface adsorption, and double layer formation.[64] All these factors can affect the nucleation mechanism through the level of activation energy involved in the process.

Particle size distribution and therefore nucleation and particle growth rates are generally influenced by several parameters such as residence time, agitation, impurity concentrations, and temperature.

Aging is a process accompanied by a decrease in the specific surface area of the precipitate, growth of the mean particle size, a decrease in the number of crystals, and a decrease in the precipitate volume.

Aging of the precipitate can take place through:

(1) Recrystallization of the primary particles through transformation of needles, thin plates, or dendrites into a more compact shape.

(2) Transformation of crystal from a metastable modification into a stable modification. The non-structural (adsorbed in the lattice), and structural (chemically bonded to the metal) water contents in metal hydroxide precipitates are decreased during aging as a result of lattice reorganization and growth of the particles. The practical consequences of the aging phenomena are especially evident in the separation of the solid phase. For example, the specific filtration resistance of the suspension decreases, increasing the filtration efficiency.[50,51] Chemical changes can also take place during aging.[50,51] Therefore, by adjusting aging time, improvement of filtration properties of the suspension, or limitation of chemical changes can be achieved.

(3) Ostwald ripening is the growth of large particles at the expense of small ones. The small crystals will find the solution undersaturated and therefore dissolve, whereas the large particles find it supersaturated and grow. This theory showed that solution cannot be in equilibrium with a precipitate consisting of particles of two or more sizes.[65]

1.11. Co-precipitation[11,49]

Co-precipitation and adsorption are related since both involve heterogeneous equilibrium reactions. Adsorption is one of the principle mechanisms of co-precipitation.[66] Co-precipitation is a process in which a solid is precipitated from a solution containing other ions. These ions are incorporated into the solid by adsorption on the surface of the growing particles, physical entrapment in the pore spaces, or substitution in the crystal lattice.[11,67]. Adsorption is a process in which the solid species is added to a solution containing other ions, called adsorbates. In this case the adsorbates are removed by adsorption onto the solid's surface. In this system, solid state diffusion is the only mechanism by which a species can reach the interior of non-porous particles.[66]

The type of adsorbent present also governs the extent of the removal process. One solid (adsorbent) used to perform this treatment is ferric oxide. For example, iron co-precipitation with cadmium has yielded a residual cadmium concentration of 3 μg/l.[11,15]

Many parameters would affect the removal of adsorbates from solution, this including, pH, the equilibrium concentration of the cation in solution, and the presence of other interacting ions. In addition, the properties of the solid adsorbent are important. These include type of solid formed, surface area available, age, and surface charge. Each variable affects the extent of removal by either co-precipitation or adsorption.

In general, hydrous oxide surface active species (S) can be classified as: (1) a neutral one, SOH°, (2) a negatively charged one (from the loss of a proton), SO^{-} and (3) a positively charged one (from proton gain), SOH_2^{+}. It is the exchange of protons to and from the oxide surface which generates specific site types available for adsorption. The equilibrium reactions are given by[10]:

$$SOH_2^+ = SOH^\circ + H^+ \qquad K_{s1}^{\ app} \qquad (9)$$

$$SOH^\circ = SO^- + H^+ \qquad K_{s2}^{\ app} \qquad (10)$$

where $K_{s1}^{\ app}$, and $K_{s2}^{\ app}$ are the apparent equilibrium constants because they include electrostatic effects and hence are functions of the extent of surface ionization.

Under ideal conditions, protons are released from the particle surface, and the dissociated proton is transported through the interfacial potential gradient to the bulk solution. Protons at the surface, H_s^+, are distinguished from protons in solution, H^+, by the electrical potential difference, ψ, between the regions. By assuming a Boltzmann distribution (Gouy Chapman theory), the H_s^+ activity can be calculated as

$$a(H_s^+)= a(H^+) \exp(-F\psi_o/RT) \qquad (11)$$

where R and T are the ideal gas constant and absolute temperature, respectively, F is Faraday's constant (96,500 C/mol), and ψ_o is the potential.[68]

Assuming the activity coefficients for the surface species are equal, equations (9), (10), and (11) can be combined as

$$K_1^{\ int} = \{SOH^\circ\}\ \{H_s^+\}/\{=SOH_2^+\} = K_{s1}^{\ app} \exp(-F\psi_o/RT) \qquad (12)$$

$$K_2^{\ int} = \{SO^-\}\ \{H_s^+\}/\{=SOH^\circ\} = K_{s2}^{\ app} \exp(-F\psi_o/RT) \qquad (13)$$

where "int" represents the intrinsic equilibrium constants, which correspond to chemical interactions only. The surface charge, σ_0 (C/m^2), resulting from reactions (12) and (13) is computed as

$$\sigma_0 = F/AS\,[\{SOH_2^+\} - \{SO^-\}] = F\,[\Gamma_H - \Gamma_{OH}] \qquad (14)$$

where Γ_H and Γ_{OH} are the adsorption densities (mol/m^2) of H^+ and OH^- ions, A is the specific surface area of the particle (m^2), and S is the concentration of particles (g/l). The pH at which Γ_H and Γ_{OH} are equal is known as the point of zero net proton charge (PZNPC).[69] The PZNPC is the point of zero charge, pH_{pzc} in the absence of specifically adsorbing cations and anions . The surface is negatively charged when the pH exceeds the pH_{pzc} and is positively charged at $pH < pH_{pzc}$ [67] In the presence of specifically adsorbing cations and anions, the pH_{pzc} is shifted. The PZNPC shifts to a lower pH by adsorbing cations and the pH_{pzc} shifts to a higher pH. The opposite occurs during anion adsorption. The PZNPC and PZC are equal only when H^+ is the adsorbing species.[69]

Dzombak and Morel[69] found that the fundamental concept upon which all equilibrium models are based is that adsorption takes place at defined coordination sites. Mass law expressions with electrostatic correction factors describe adsorption reactions. These reactions form a major component of co-precipitation.[11,66]

Several possible mechanisms for enhanced removal by co-precipitation to account for the additional uptake not explained by adsorption theory[11] have been proposed:

(1) There is a degree of adsorbate ion entrapment in the forming precipitate. Meites[70] has cited occlusion into the amorphous lattice as a secondary removal mechanism during co-precipitation.

(2) Because the ions are present throughout the entire precipitation process, they might be able to react with a greater number of higher energy surface hydroxyl groups. This concept was proposed by Leckie et al.,[66] who suggested that the surface is composed of

high-energy sites that readily bind adsorbates. As the surface ages, these sites decrease in number, leaving less "active", sites having lower energies.

(3) A fraction of the adsorbate ligands were precipitated. This mechanism can be ruled out if the concentrations of the secondary ions added are well below their saturation concentrations.

Farley et al.[71] noted that localized precipitation at the particle surface resulted in enhanced metal removal. This occurred when the concentration of adsorbate exceeded the solubility product, and the adsorption isotherm rises sharply.[11,71]

1.12. The Other Treatment Technologies

Evaporative recovery is among the numerous other technologies referenced in the technical literature and has somewhat wide usage. The high capital and operating costs of evaporative recovery system are such that their application is generally only warranted where an enriched feed stream is available, and the market value of the recovered metal is significant. Tables 6, 7, 8[11,15] compare the performances of the different treatment technologies described in table 3, for copper, nickel and chromium. As demonstrated by the results, all technologies, when properly applied and operated, are capable of achieving good effluent quality.

Table 6. Copper effluent data from fifty three plant survey[11,15]

Treatment Process	Plants	Cu(mg/l)
Precipitation		
Batch	4	0.08-1.47
Continuous	21	0.03-3.7
Integrated	5	0.16
Ion exchange	2	1.0-2.0
Evaporation	2	0.08-0.53
Electrolysis	2	0.2
Reverse osmosis	2	0.29-0.3
Media effluent		0.2

Table 7. Nickel effluent data from fifty three plant survey[11,15]

Treatment Process	Plants	Ni(mg/l)
Precipitation		
Batch	5	0.25-0.48
Continuous	22	0.06-7.0
Integrated	5	0.0002-2.0
Ion exchange	3	1.0-5.0
Evaporation	1	1.5
Electrolysis		
Reverse osmosis	3	0.00-2.5
Media effluent		0.5

Table 8. Chromium effluent data from fifty three plant survey[11,15]

Treatment Process	Plants	Cr(VI)(mg/l)	Cr(mg/l)
Precipitation			
Batch	8	0.04-0.16	0.05-0.23
Continuous	18	0.0-0.6	0.11-10.0
Integrated	12	0.01-0.4	0.03-2.0
Ion exchange	3	0.01-0.38	0.02-1.0
Evaporation	3	0.05-1.0	0.16-1.5
Electrolysis	2	0.01-0.03	0.32-5.0
Reverse osmosis	2	0.1	0.03
Media effluent		0.06	0.3

As a result of gradually diminishing natural resources and more stringent environmental protection laws, there will be increased incentives to recover and reclaim in effluent treatments. Electrochemical techniques are poised to play a major role in this respect.

1.13. The Objective Of The Project

This project adapted the electrochemical processes for treatment of electroplating effluent containing heavy metals reported by several research groups.[24,26,45,48,72-78]

These processes generally combined electrolytic and chemical precipitation / coprecipitation techniques. Simulated heavy metal effluent samples were treated by using electrolysis with cheap and readily available metals (such as stainless steel and aluminium plates) as electrodes. Low D.C. currents were used. At the anode surface, competing anodic processes could occur, viz:-

$Fe = Fe^{2+} + 2e^-$ (if stainless steel used as anode) (15)

$Cr = Cr^{3+} + 3e^-$ (if stainless steel used as anode) (16)

$Ni = Ni^{2+} + 2e^-$ (if stainless steel used as anode) (17)

$Al = Al^{3+} + 3e^-$ (if aluminium used as anode) (18)

$6H_2O = O_2 + 4H_3O^+ + 4e^-$ (19)

$2\ Cl^- \rightarrow Cl_2 + 2e^-$ (in the presence of NaCl) (20)

$Cl_2 + 4H_2O \rightarrow 2H_3O^+ + 2HClO + 2e^-$ (in the presence of NaCl) (21)

$HClO + Cl^- + H_3O^+ \rightarrow Cl_2 + 2H_2O$ (22)

The reactions (19-21) would increase the solution acidity.

At the cathode surface, possible competing cathodic processes are:-

$M^{n+} + ne^- = M$ (23)

$H_3O^+ + 2e^- = H_2 + OH^-$ (24)

$O_2 + 4H_3O^+ + 4e^- = 6H_2O$ (in acidic condition) (25)

$2H_2O + 2e^- = H_2 + 2OH^-$ (26)

Steel anodes corrode to give ferrous ions (Fe2+), nickel (Ni^{2+}), chromium ion (Cr^{3+}) in reactions (15-17) and other alloying metals found in steel; or, if aluminium electrodes were used, Al^{3+} ions would be produced. At the cathode, hydrogen gas is liberated by reactions (24 and 26). Due to hydrogen evolution, hydroxyl ions (OH^-) are also available. This led to local pH changes[25,46,79,80] at the electrode surface and caused hydroxide formation:

$Fe^{2+} + 2(OH^-) = Fe(OH)_2$ (for stainless steel anodes) (27)

$Al^{3+} + 3(OH^-) = Al(OH)_3$ (for Aluminium anodes) (28)

Besides this, other heavy metal hydroxide $M(OH)_n$ may be formed, if M is other than Al or Fe;

$M^{n+} + n(OH^-) = M(OH)_n$ (29)

This method of wastewater treatment is based on the mechanism in which co-precipitating heavy metal ions with a carrier precipitate which is formed in-situ within the aqueous solution during electrolysis. Depending on the source anode, the carrier precipitate is amorphous aluminium hydroxide or ferric hydroxide, $Fe(OH)_3$ formed by the oxidation of ferrous ions to ferric ions. Oxygen formed during oxygen evolution at the anode in reaction (19) can be the oxidizing agent. This reaction also led to the formation of hydrogen ions which may be the cause of decreasing solution pH during the electrolysis process.

Aluminium / Ferric ions (the cationic carrier precipitate precursors) which are attracted to the cathode and hydroxide ions (the anionic carrier precipitate precursors) are caused to chemically react in the vicinity of the cathode and precipitate out as carrier precipitate particles (sludge). As the ferric / aluminium hydroxides (carrier precipitate particles) are formed, heavy metal ions (coprecipitant precursors) are removed from the aqueous solution by adsorption onto the surface of ferric hydroxide and / or by "occlusion" within the interior of ferric / aluminium hydroxide (sludge). The term "occlusion" refers to the mechanical entrapment of foreign ions within a precipitate particle by physical encapsulation within the particle walls and by chemical bonding within the particle structure to form a continuous three dimensional network.[48] Heavy metal ions may also be removed from the aqueous solution by reduction to metal at the cathode. Using this electrochemical method of treatment, a heavy metal-rich aqueous solution can be transformed into a liquid solid mixture where the liquid-phase heavy metal concentrations are substantially lower than their initial concentrations. By segregating the liquid-phase of the mixture from the amorphous solid-phase (sludge), a stable aqueous effluent is produced which can be discharged substantially free of heavy metals.

In this project, treatment of nickel, copper, chromium as the heavy metals in both artificial and industrial electroplating effluent samples were studied.

1.14. Potentiodynamic Studies

Since the treatment process involved alkalization of the cathodic layer, which is the direct result of cathodic hydrogen evolution, and the dissolution rate of the anode under an applied current, the most convenient method for studying the phenomena at the electrodes is by using the potentiodynamic method. From the potential-current plot, the rate of anode metal dissolution and hydrogen evolution (OH^- formation) can be observed. In addition, potential ranges at which passivation of anodes under different solution conditions can also be obtained from the polarization plots.

If an external potential E is applied to a metal electrode (polarization of the electrode from equilibrium potential or E_{cor} value), a change of dissolution (corrosion) rate will occur. The result is summarized in the adoption of the Bulter-Volmer[81,82] equation for electrochemical kinetics, according to which

$$I = I_{cor}\{\exp(\alpha EnF/RT)-\exp(-\beta En'F/RT)\} \qquad (30)$$

where I is the measured current, I_{cor} is the corrosion current, F is Faraday's constant, R is the universal gas constant, T is the absolute temperature, E is the applied potential, n and n' are valencies of the ions which are oxidized and reduced respectively, and α, β are coefficients related to the potential drop through the electrochemical double layer.

During anodic polarization, the metal may form soluble cations or form a passive film. Passivation is the formation of a film on the surface of the electrode which will retard the dissolution rate depending upon the properties of the film.

In this study, potentiodynamic studies were made of the electrode (as cathode and as anode) behaviour of stainless steel and aluminium in the different effluent solutions at 25.0°C.