Chapter 2: Literature Review

2.1 NICKEL

Nickel alloy was known by people about thousands of years ago. It is a silver-white metal. Its atomic number and atomic weight are 28 & 58.71 respectively. Nickel is a transition metal and the lightest element of group VIII of the Periodic Table. It has high ductility,. good thermal conductivity, moderate strength and hardness, and fair electrical conductivity which makes it suitable for readily rolling, forging and polishing (Adamec and Kihlgren,1967). At ambient temperature it is ferromagnetic in nature, and it melts at 1452^0C but it becomes paramagnetic above the curie point (353^0C). This element can exist in formal oxidation states from -1 through to + IV but the only important state in aqueous solution is + II. The metal is highly insoluble in water and is quite resistant to attack by air at ordinary temperatures. However, in the finely divided state, nickel is reactive to air and under some conditions may be pyrophoric. In dilute mineral acid, the metal is easily dissolved but in concentrated nitric acid it is rendered passive, which means it is not readily attacked by the acid. Nickel is ubiquitous in the environment. About 0.008% of Earth is composed of nickel (Boldth,1976), which is not evenly distributed. Most of it is contained in the igneous rocks; deposits that are commercially extracted contain about 1% nickel as a minimum. World production of nickel is approximately 0.8×10^6 tones per year (Papp,1986) and the single largest use of nickel together with chromium is in the manufacture of stainless steels.

2.1.1 Nickel in the Environment

2.1.1.1 Behavior of nickel in aquatic environment

Increased industrial activities such as metal plating, finishing and other anthropogenic activities introduce nickel into the aquatic environment.

The aquatic environment considered are: 1) Streams, 2) Lakes, 3) Estuaries and 4) Oceans. Most of the heavy metals in the aquatic environments are strongly influenced by the reaction with soluble species and particulates. Nickel, like other metal ions in the first transition series, is octahydrally coordinated in aqueous systems. It is a fairly mobile metal in natural water and stays in solution in ionic form at high pH values. Figure 2.1 shows the distribution of nickel species as a function of pH for a non saturated solution, and as can be seen, in natural waters (pH= 5 to 9) the free ion , Ni^{2+} dominates. The distribution of nickel in natural water may also be affected by the presence of suspended particulates. Perhac (1972) found that about 85-97% of total nickel present in stream water is in the insoluble form. In typical freshwater, ionic nickel constitutes 90% of the total nickel, and under oxidized conditions $Ni(OH)_2$ accounting for about 1% of the nickel compounds. The solubility of nickel sulfide is quite low (Sillen and Martell, 1971) but under anoxic conditions, 99% of the nickel is considered to be precipitated as nickel sulfide (Healy, 1972). The hydrolysis of nickel in water is as follows:

$$Ni^{2+}\ H_2O = NiOH + H^+ \qquad (2\text{-}1)$$

$$Ni^{2+}\ H_2O = Ni(OH)_2 + H^+ \qquad (2\text{-}2)$$

$$Ni^{2+}\ H_2O = Ni(OH)_3 + H^+ \qquad (2\text{-}3)$$

$$Ni^{2+}\ H_2O = Ni(OH)_4 + H^+ \qquad (2\text{-}4)$$

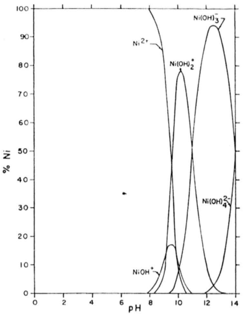

Fig.2.1 : Nickel hydrolysis distribution diagram (Source: Nriagu, 1980).

2.1.1.2 Nickel in the atmosphere

The largest anthropogenic source of nickel is the burning of fuel and residual oils, emitting 26,700 MT nickel per year globally (Schmidth, 1980). Atmospheric nickel is considered to exist mainly in the form of aerosols. Its chemical composition and particle sizes depends mainly on its sources. The spatial distribution pattern of nickel is also governed by its source and meteorological factors. There is little information available about the chemistry of nickel in the environment (Nriagu,1980). The transport of nickel from the atmosphere usually takes place by precipitation. Cycling of nickel through the atmosphere allows for transport of this metal from a variety of sources to nearly every type of ecosystem on Earth.

2.1.1.3 Nickel in the Soil

Nickel is present in the soil in variable quantities. This divalent metal ion (Ni^{2+}) is dominant in the soil environment and its solubility in the soil depends mostly on the pH. The hydroxy -complex $Ni(OH)^{+}$ and Ni^{2+} ions are the most likely major forms in soil solution above pH 8. In acid soils, Ni^{2+}, $NiSO^{2}_{4}$, $NiH(PO_4)$ are important although the relative proportions would depend on the levels of SO^{2+}_{4} and $PO^{2-}_{4.}$ The mobility of nickel in soils increases as the pH and CEC (Cation exchange capacity) decreases (Alloway,1995). Sanders *et al.*, (1987) observed that in sewage amended soil, the solubility of nickel increases at lower pH, especially when it is below pH 6.

2.1.2 Usage of Nickel

Nickel is a very useful mineral commodity which has experienced an exponential growth in demand during this century. The major industrial uses of nickel are in the production of ferrous alloys electroplating and electroforming operations. In order to improve the physical, chemical and mechanical properties of the finished product, nickel is used as an alloying metal. In practice, nickel increases the strength and toughness of steel and cast iron at high temperature and provides resistance to corrosion in a variety of environments. Various Ni-steel alloys were developed in the nineteenth century and their resistance to corrosion resulted in their use for manufacture of motor vehicles, armanents, aircrafts and tableware. Other major uses are as alloys, in Ni-Cd batteries, in electronic components, as catalysts for hydrogenation of fats, and methanation, and in petroleum products. The principal sources of nickel bearing wastewaters are electroplating industries, basic steel plants and foundries. The effluents generated from these industries contain nickel in various concentrations and should be treated properly before discharging to a watercourse; otherwise nickel contamination would occur in the soil or water which could be causes of toxic exposure to living organisms (Waldron 1980).

2.1.3 Nickel Toxicity

The first commercial application of nickel which started in the early nineteenth century was in a copper-nickel-zinc alloy, known as German silver. At present, we use many objects that contain nickel. The route that metal contamination can take place in the environment depends on whether they were discharged into the air, water or land as well as on the physical state they were discharged in, i.e. gaseous, liquid or particulate form. There are two major sources of nickel contamination in the environment, one is the natural source and the other is the man-made source. Robinsons and Robinsons (1971) have shown that the contribution of natural sources for the global emission of nickel is higher than the man-made sources and it is a function of the elemental composition of particles derived from them (Table 2.2). Apart from this, industrial processing is considered as a potential route of nickel released to the environment. In wastewaters, industrial sources account for over 50% of the observed nickel while residential sources supply up to 25% (Nriagu,1980).

Table 2.2: Global Emission of Air Particulates by Natural and Man-Made Sources

SOURCE	**EMISSIONS (10^9 kg/year)**
Natural	
Soil dust	200-500
Gas-particle conversion	900
Photochemical (from hydrocarbons)	200
Volcanoes	4-25
Forest fires	3-5
Meteoric dust	0.0036
Sea salt	1000
Man-made	
Particulate emission	30-90
Gas- particle conversion	200-250
Photochemical (from hydrocarbon)	15

Source : Robinsons and Robinsons (1971)

The conclusion that can be made from the natural occurrence and man-made uses of nickel is that man's perturbation of his environment is responsible for a greatly increased flux of nickel to the environment.

2.1.3.1 Effect of nickel on marine and fresh water organisms

Nickel occurs in the aquatic environment mainly in the form of divalent cation. Many aquatic plants and animals have the capability of bioaccumulation of nickel and some organisms bioconcentrate it in their specific organs or tissues. It is found from various reports that on the basis of water characteristics, aquatic organisms can tolerate nickel up to certain concentrations (Nriagu, 1980). Pickering (1974) conducted a comprehensive study with fathead minnow for nickel toxicity and found that nickel concentration up to 1.6 mg/L did not affect survival and growth of the first generation of fish, which were 6 weeks of age at the onset of exposure but after 5 months of treatment, both fecundity and egg hatchability were sharply reduced at a mean nickel concentration of 730µg/l.

2.1.3.2 Effects of nickel on human health

Metals like nickel have some adverse effects on human health. Since it is present in the soil and water, it could be transported into the human body by drinking water and from the soil through plant as foodstuffs. The significant routes of nickel entry into the human body are inhalation, oral intake, parenteral administration and percutaneous absorption. There are no reports of death in humans resulting from the oral intake of nickel except for nickel carbonyl. According to Sunderman (1970) the initial symptoms of nickel carbonyl poisoning are mild and transitory and it may be extended up to nausea, vomiting, insomnia and irritability. Persistent symptoms include, constrictive chest pains, dry cough, cyanosis, sweating, visual disturbance and weakness etc.

2.1.4 Recommended Environmental Quality Standards (EQS)

Environmental quality standards recommended by Water Research Centre (WRc, 1984), are given in Table 2.3. The values given are based on the chemistry and behavior of nickel in the environment, and the effects of nickel in the environment and on human, fish, other biota, agricultural crops, etc.

Table 2.3: Environmental standard quality by WRc, 1984

Use		**Average concentration (μg/L)**
Fresh water		
Direct abstraction to potable supply		50*
Protection of fresh water fish		
Total hardness	less than 50	50
as mg $CaCO_3$/L	50-100	100
	100-200	150
	greater than 200	200
Protection of other freshwater life and associated non-aquatic organisms		
Total hardness	less than 50	8
as mg $CaCO_3$/L	50-100	20
	100-200	50
	greater than 200	100
Irrigation of crops		150
Abstraction for food processing industry		50*
Bathing and contact water sports		500
Saltwater		
Protection of salt water fish and shellfish		30
Protection of other saltwater life and associated non-aquatic organisms		30
Bathing and contact		500

* Indicates mandatory values. (WRC,1984)

2.2 ADSORPTION

Adsorption is an effective and important means of controlling the extent of pollution due to metallic species in industrial effluent. It is termed as a process of collecting soluble substances that are in solution on a suitable interface. Adsorption occurs on the surfaces because of attractive forces of the atoms and molecules that make up the surfaces. A number of reports are available on the removal of metal ions from wastewater using different types of adsorbent. Bhattacharya *et al.*(1985) conducted studies on adsorption of Cd from wastewater using crushed coconut shell and coal in a batch process. They have studied the first order rate constant for the forward and the reverse reaction for both adsorbents and found that the cadmium adsorption for the two sorbents was a function of the pH of the reactants. Their study indicated the mechanism of sorption in terms of electrostatic forces and chemical interactions with the aid of zero point of charge (pH zpc).

Activated carbon plays an important role in the removal of dissolved contaminants and recovery of materials from water and wastewater. An experiment was done by Young *et al.*,(1987) who found that about 70% of Zn and Cd could be removed from the wastewater by using activated carbon adsorption following hydroxide precipitation. They also remarked that in the absence of chelating agent or other interference, removal of Zn exceeded 70% and sulfide removal exceeded 50% over the pH range 7 to 10 by the activated polishing step. For water with a high sulfide content, removal exceeded 74%. On the other hand, in the presence of interfering agents like ammonia or cyanide, the removal efficiency is reduced to 50%. Finally, they concluded that the activated polishing step may have potential for H_2S removal.

Huang *et al.*,(1978) has conducted several studies on heavy metal removal from wastewater by adsorption process. In one of their investigations, they studied the effects of hexavalent chromium concentration, carbon dosage, pH and mixing on the rates of reduction and adsorption in batch experiments. They concluded that the efficiency of hexavalent Cr removal, either by reduction or adsorption, is enhanced by increasing carbon dosages and hydrogen ion concentrations. The initial stage of chromium removal is very fast due to reduction of the Cr(vi) species, which usually occurs to completion within the first two hours of the reaction time. The later stage of Cr(vi) removal is much slower since only adsorption is occurring and the hydrogen ion concentration has been reduced by the reduction and hydrolytic reactions. The magnitude of the total Cr removal is decreased by the production of Cr^{3+}; however, the reduction mechanism may be eliminated and the efficiency of the total chromium removal is greatly magnified by the hydrolytic reaction. Metals like chromium could be removed from the wastewater by different methods but each has some demerits.

Jung.*et al.*,(1977) employed activated carbon to remove Cr^{+} from wastewater. In their work, they explicated the mechanism of adsorption and the interaction of metal with activated carbon. In order to verify the adsorbed chromium state they performed an extraction study at pH 9 and found that the extracted chromium was in hexavalent state. They also observed that the adsorption of Cr+ from the water is pH dependent and the degree of reduction of Cr(vi) to Cr(iii) is also the function of pH and the amount of activated carbon in the solution. Although activated carbon adsorption has shown effectiveness for the removal of organic and inorganic pollutants from wastewater, poor adsorption was observed for some heavy metals (Peters *et al.*, 1985). In the presence of organic complexing agents, adsorption could be improved substantially. When complexing agents are present in the wastewater, heavy metal hydroxide precipitation is inhibited, thus causing an adverse effect on removal efficiencies. Therefore, in the case of removal of heavy metal chelates or by deliberate addition of chelates to heavy metals, adsorption by activated carbon provides an alternate separation technique. Bhattacharya *et al.*,(1987) conducted an experiment with ligands to establish adsorption behavior of several metals from single and two metals systems in the presence of complexing agents. In their experiment, they investigated metal-ligand complex formation of cadmium, nickel, barium and ferric ion respectively with EDTA and found that in most of the systems, M^{+2} and $MH(EDTA)^-$ are predominant at lower pH, and at higher pH most metal ions chelate completely with EDTA in a one to one ratio to form $M(EDTA)^{2-}$. Rubin *et al.*,(1987) also reported that the use of activated carbon to remove Cd^{2+} from wastewater in the presence of a chelating agent, is a function of pH. At low cadmium to carbon ratios, EDTA appeared to enhance adsorption. In another study, they demonstrated the effectiveness of 1,10-phenanthroline as a chelating agent for the removal of Cd^{2+} from wastewater.

Activated carbon adsorption appears to be a particularly competitive and effective process for the removal of heavy metals. However, the use of activated carbon is not suitable for developing countries due to its high cost (Pandey *et al.*,1985). For this reason, the use of low cost material for metal removal from wastewater has been highlighted recently. Pandey *et al.*,(1985) used fly ash as an adsorbent for the removal of Cu(ii) from industrial wastewater and noted that removal of Cu(ii) from aqueous solutions is highly concentration and pH dependent. The pH of the solution affects the surface charge of the adsorbent and the degree of ionization and speciation of adsorbate. With increase in pH of the solution from 3.0 to 8.0, the extent of removal increases from 13.93 to 100 percent. In this study, wood ash was used as an adsorbent for the removal of Ni(ii) from the wastewater.

2.2.1 Kinetics of Metal dsorption

In this work, the effect of time on adsorption equilibria was investigated. The quantitative aspects of metal chemistry in the natural environment and in technological systems must ultimately rest on an understanding of the kinetics of slow versus fast reactions (Pankow *et al.*,1981). However, adsorption kinetics can be extremely diverse and complex under the kinds of chemical conditions encountered in natural water and wastewater systems. Morel (1983) pointed out that aquatic chemical kinetics is an extremely complicated and largely undeveloped discipline and is still awaiting systematic treatment. The key parameters used in kinetic description of metals in aquatic systems are the rate constant k, ΔH^0, ΔS^0 and ΔG^0 .

2.2.2 Effect of pH

The pH of solution exerts a strong influence on the adsorption process. This is due to the fact that hydrogen ions attach themselves to the adsorption sites and pH influences the ionization characteristics of many compounds (Elliot and Huang, 1981). Some adsorbents have affinity for H^+ or OH^- ions and can directly affect the solution pH and adsorption capacity. In general, the extent of cationic metal adsorption increases with the increase of pH. On the other hand, the anionic metal adsorption reaches the optimum point at a lower range of pH. This is attributed to the fact that both the surface acidity and the hydrolysis of the metal ions are pH dependent. Generally, the extent of metal ion adsorption increases abruptly at a particular pH. The pH at which adsorption density increases abruptly is referred to as the pH of the adsorption edge. Apart from this, the influence of pH on adsorption is not evident for several metals ions. This is due to the fact that adsorption takes place at a wide pH range. Therefore, on the basis of adsorption pH, metal ions can be divided into three major groups (Greene,1985)

1) Those which bind stongly at low pH values (pH 2.0-5.0)
2) Those which bind at high acidic pH values (2.0-7.0)
3)Those which are independent of pH range.

Pandey *et al.*, (1985) reported that the removal of metal increases from 13.93 to 100% with the increase in pH from 3.0 to 8.0 . Stumm and Bilinski (1972) suggested that the adsorption of metal ions at the solid-solution interface is not governed by the 'free' metal concentration but by the much stronger adsorbed hydroxo, sulfato, carbonato and other metal species.

$$M^{Z+}{}_{aq} + nH_2O \rightarrow M(OH)^{(z-n)} + nH^{+} \qquad (2\text{-}5)$$

The pH $_{max}$,where maximum adsorption of the metal takes place seems to be related to the pK of the first hydrolysis product of the metal. The exact nature and distribution of hydroxo complexes depend on the solution pH. Bhattacharya *et al.*, (1984) observed that the adsorption of cadmium by low cost adsorbents like Giridih coal and crushed coconut shell is pH dependent. At pH 3.0, adsorption did not occur but an increase in pH by 2.0 increased the adsorption to about 80 %. In order to explain the variation of sorption of cadmium as a function of pH, they established the zero point of charge for the adsorbent which revealed that the pH zpc for Giridih coal and crushed coconut shell were 7.0 - 7.2 and 6.8 respectively. Low *et al.*, (1994) showed that the percentage of Cu and Ni uptake from electroplating wastewaters increases from 3.90 to 80.2% with the rise in pH from 3.90 to 4.5 for adsorption on banana pith.

The solution pH would influence both aqueous metal chemistry and surface binding sites of the sorbents. At low pH values the surface of the sorbent would be closely associated with the hydronium ions (H_3O^+) that hinder the access of metal ions to the surface functional groups owing to repulsive surface forces by the metals. At higher pH, more functional groups on the surface of the sorbent would be available for binding with the metals. The rate of sorption increases with increasing pH to the point where the metal ions precipitate.

2.2.3 Effect of coincidental ions

In industrial effluents, heavy metal ions including alkaline and alkaline earth metals and various anions are always encountered. These ions may affect the adsorption of heavy metals by adsorbents. Coincidental heavy metal ions and alkaline or alkaline earth metal ions may compete with each other for the same binding sites on particle surface wall, resulting in decreased adsorption of heavy metal ions (Crist *et.al.*, 1981; Nakajima *et.al.*,1981). On the other hand, the formation of complexes between heavy metal ions and anions decrease adsorption by reducing the amount of *free heavy metals ions. The effects of the coincidental ions on the metal adsorption* in the wood ash system at various concentrations are examined in this section.

2.2.4 Adsorption kinetics and equilibria

The adsorption of a substance from one phase to the surface of another in a specific system leads to a thermodynamically defined distribution of that substance between the phases when the system reaches equilibrium; that is when no further net adsorption occurs. The whole process usually takes place in three steps; macrotransport, microtransport and sorption. The movement of material from the water to the liquid-solid interface by advection and diffusion processes is termed as macroscopic transport. Microscopic mass transfer refers to movement of solute under the influence of its own molecular or mass distribution and finally, the process of attachment of the sorbate and the sorbent is known as sorption (Weber *et al.*, 1991). Commonly, the amount of adsorbed material per unit of adsorbent increases with increasing concentration.

The extent of nickel ion adsorption is greatly dependent on the chemistry of nickel ion in the solution. Ahrland *et al.*,(1958) classified nickel as a transition element in terms of its stability with the first ligand atom of the periodic groups (V), (VI), i.e. F, O, N or with a later member of the groups (I, S, P). Pearson (1973) interpreted metal ions in terms of Lewis acid-base interaction in the complex formation reactions and termed nickel ion as a borderline metal ion. Nieboer and Richardson (1980) classified metal ion, using the terminology of Ahrland *et.al.*, (1958). They classified metals as class A (soft metal), borderline and class B (hard metal) based on the equilibrium constants that describe the preferential formation of metal ion-ligand complexes (Table 2.4). According to their classification, soft metal ions have the preference for ligands in the order: O> N> S while hard metal ions show the opposite preference sequence: S>N>O. The borderline metal ions form an intermediate group and bind to any of these ligands without any preferential sequence. There is a sharp distinction between class A and borderline metal ions, but the separation between class B and borderline metal ions is not as distinct. The adsorption characteristics of class B metal ions increase among the borderline ions in the following order: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Co^{2+} \approx Fe^{2+} > Ni^{2+} > Mn^{2+}$. Therefore the nickel ion is regarded as borderline ion. Nevertheless, nickel has higher affinity towards hard ligands. Nickel being a relatively harder metal, is expected to form ionic bonds with hard ligands.

Apart from the chemical characteristics of a metal ion, the chemical speciation of the metal ion also plays an important role (Forbe *et al.*,1974) in adsorption which is mainly pH dependent. The electrostatic interaction between the charged adsorbate species and the surface of the adsorbent might be affected by the function of pH (Bhattacharya *et al.*,1987). For pH > pH_{zpc}, the surface functional groups are negatively charged. Adsorption is then favorable for positively charged species present in the solution. On the other hand, at pH < pH_{zpc}, the surface of the adsorbate is positively charged; therefore, it favors the adsorption of negatively charged species. Thus chemical speciation of a metal ion in aquatic condition refers to the set of all concentration values of its various chemical species present in the system (Pankow,1981). Metals can exist either as 'free' or in a complex form in solution. Free metal ions may be coordinated with water molecules by hydrolysis to form hydroxo species. Stumm and Morgan (1981) established two general rules for the hydrolysis of cations:

(1) the tendency of metal ions in solutions to hydrolyze increases with dilution and with increasing pH.

(2) the fraction of polynuclear complexes in a solution decreases on dilution. Cation hydrolysis is more significant at high pH where hydroxyl ions are in abundance.

$$M^{2+} \xrightarrow{OH^-} MOH^{+} \xrightarrow{OH^-} M(OH)^{2} \xrightarrow{OH^-} M(OH)^{3-} \xrightarrow{OH^-} M(OH)^{2-4} \qquad (2\text{-}6)$$

where, M = divalent metal cation

Table 2.4: Classification of metal ions

***A Metal cations**	**Transition Metal Cations**	**B-Metal cations**
Electron configuration of inert gas; Low polarizability; "Hard spheres";	One to nine outer shell electrons; not spherically symmetric;	Electron no. corresponds to Ni, Pd and Pt Low electronegativity; High polarizability; soft spheres,
H^+, Li^+, Na^+, K^+, Be^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Al^{3+}, Sc^{3+} , La^{3+}; Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}	Fe^{2+} Co^{2+}, Ni^{2+}, Cu^{2+}, Cr^{2+}, Mn^{2+}, V^{2+}, Ti^{3+}, V^{3+},Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}	Cu^+, Ag^+, Au^+, Hg^+, Pb^{2+}, Cd^{2+}, Hg^{2+}, Zn^{2+}, Sn^{2+}, Tl^{3+}, Au^{3+}, In^{3+}, Bi^{3+}

Pearson(1973)

Hard acids	**Borderline**	**Soft acids**
All A-metal cation plus Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Uo^{2+}, Vo^{2+} Ligand atom preference: N>> P C>>S F >>Cl	All bivalent transition metal cations plus Zn^{2+} Pb^{2+} , Bi^{3+} Qualitative generalization: Preference by hard acids ------------------------------ F,O,N=Cl, Br, I, S=C ------------------------------ Preference by soft acids.	All B-metal cations minus Zn^{2+} , Pb^{2+} , Bi^{3+} Ligand atom preference: P>> N S>>O I>>F

Source : Ahrland *et al.*, (1958)

The hydrolysis and metal adsorption are probably related as the rate of adsorption of metals on adsorbent surface often increases with pH of the solution. Therefore, the adsorption of metal ions at solid-solution interface is not governed by the free metal ions but by the concentration of the hydroxo- metal complexes that are more strongly adsorbed onto the adsorbent (Stumm and Bilinski,1972).

$$M^{z+}_{aq} + nH_2O \quad M(OH)^{(z-n)} + nH^+ \qquad (2\text{-}7)$$

The pH_{max} where maximum adsorption of the metal takes place seems to be related to the pK of the first hydrolysis product of the metal. Since the extent of metal ions adsorption varies with changes in pH, these variations in adsorption are therefore related to the speciation of organic ligands on the surfaces which are a function of pH (Stumm,1992)

2.2.4.1 Chemical reaction

A number of steps are involved in the transfer of an adsorbate to the adsorption layer, including transport to the surface by convection and/or molecular diffusion, and attachment to the surface. The later may include steps like formation of a bond, dehydration, surface diffusion, and association processes of the adsorbed constituents. In a simplified way, it can be distinguished as:

1) transport of a solute to the interface,
2) the transfer from the interface to the adsorption layer.

The adsorption process involves a reaction between an adsorbate and an adsorbent resulting in a change in the physical and chemical form of the adsorbate. The resulting chemisorptive bond is usually stronger than that derived from the physical Van der waals forces. Most naturally occurring solids carry on their surface functional groups such as -OH, -SH and -COOH. These functional groups contain the same donor atoms as in functional groups of solute ligands. In the adsorption process, the presence of hydroxide ions enhances the removal reaction. It is known that both oxides and metal ions are highly hydrated in aqueous media. Novak *et al.*,(1987) has generalized the structure of the adsorbed water at the metal ion or oxide surface in the following manner:

i. Hydrolysis reactions are likely to produce different types of hydroxyl sites; e.g., amphoteric sites, particularly on oxide surfaces

ii. Layers of physisorbed water; i.e., the hydration sheath, are held by hydrogen-bonding interactions.

iii. Adsorbed water can be highly structured. Adsorption of the hydration sheaths must occur for a metal ion to adsorb on a hydrous oxide.

Hydrolysis models have several important implications regarding metal ion adsorption mechanisms. First, adsorption of metal ions must occur by disrupting the metal oxide hydration sheaths. This reaction normally carries a positive free energy of adsorption (James *et al.*, 1972). A final implication of hydrolysis models is that precipitation of metals ions on the alumina surface should contribute to the sorption process (Farley *et al.*,1985). Menzel and Jackson (1950) proposed that the presence of one hydroxyl ion would alter one adsorbed metal ion to be readily accommodated in the surface lattice for further adsorption.

An alternative interpretation for the coincidence of adsorption and hydrolysis involves surface complex formation between 'free' metal ions and deprotonated surface functional groups as

$$\mathrm{SiOH} + \mathrm{M}^{z+} = (\mathrm{SiO})\mathrm{M}^{(z-1)} + \mathrm{H}^{+} \qquad (2\text{-}7)$$

$$2\,(\mathrm{SiOH}) + \mathrm{M}^{z+} = (\mathrm{SiO})_2\,\mathrm{M}^{(z-2)} + 2\mathrm{H}^{+} \qquad (2\text{-}8)$$

A similar result has been reported by James *et al.*, (1973) for the adsorption of metal ions on a silica surface, considering the hydroxo species in one case and the deprotonated surface in the other.

2.2.4.2 Ion Adsorption

The surface charge may arise from the chemical reactions at the surface. The preferential adsorption of one type of ion on the surface can arise from Van der Waals interactions and from hydrogen bonding. The charge of the particle usually depends on the degree of ionization and consequently on the pH of the medium. Once the adsorber is charged, the surface charge will influence the distribution of ions in the polar medium. Oppositely charged ions are attracted to the surface and ions of the same charge are repelled.

The surface charge, at the phase boundary, may be caused by lattice imperfections at the solid surface and by isomorphous replacement within the latice (Stumm and Morgan, 1996). It can be measured by the electrophoresis. Electrophoresis is also known as the electrokinetic effect as a result of the relative motion of the mobile and immobile components of the electric double layer. Stern (1923) suggested that the interface be divided into two regions, the first being a compact layer of ions adsorbed at the surface and the second a diffuse layer. The electrokinetic potential is the potential drop across the mobile part of the double layer and that is responsible for the electrokinetic phenomena. In an electric double layer model, the potential of the solution decreases exponentially with distance from the surface, eventually reaching zero in the bulk solution. It is assumed that the liquid adhering to the solid particles (ash) surface and the mobile liquid are separated by a shear plane. The potential of the shear plane is known as the electrokinetic or zeta potential. It can be determined by measuring the particle velocity under the influence of an electric field. The zeta potential reflects the potential difference between the plane of shear and the bulk phase (Stumm and Morgan,1996). The pH at which the electrophoretic mobility is zero is called the iso-electric point (P*I*) or point of zero charge or zero zeta potential. The point of zero charge of salt type minerals depends on pH and on the concentration of all potential determining ions. At pH values below P*I* , the particles have a net positive zeta potential and at pH above P*I* , the particles carry a net negative potential. As such, metal cation adsorption increases when pH is greater than P*I* of the particles. At pH lower than P*I*, metal cations are repelled, resulting in a low metal cation adsorption.

In the adsorption process, kinetics and equilibrium of sorption are two important physio chemical parameters.The kinetics of sorption, describing the solute uptake rate, which in turn governs the residence time of sorption reaction, is one of the important characteristics defining the efficiency of sorption. In an adsorption process, there is a definite distribution of metal ions between the liquid and solid phases and the distribution ratio is a measure of the equilibrium in the adsorption process. The quantity of adsorbate that can be taken up by an adsorbent is a function of the characteristics and concentration of adsorbate and temperature. The adsorption isotherm is a batch equilibrium test which provides data relating adsorbate adsorbed per unit weight of adsorbent to the amount of adsorbate remaining in the solution (Bernardin, 1985). The most commonly used adsorption isotherm is the Langmuir adsorption isotherm. It is valid for monolayer adsorption on a surface containing a finite number of identical sites. It was developed by assuming that a fixed number of accessible sites are available on the adsorbent surface, and all of which have the same energy which leads to adsorption. Equilibrium is reached when the rate of adsorption of molecules onto the surface is the same as the rate of desorption of molecules from the surface.

2.2.5 Adsorption Models

The Langmuir and Freundlich isotherms are most frequently used to represent data on adsorption from solution.

For a solid -liquid system, the Langmuir adsorption isotherm is as follows.

$$q^* = q^m C^* / K_d + C^* \qquad (2\text{-}9)$$

q^* = Solid phase equilibrium concentration of sorbate (mMol metal/g dry weight)

C^* = Liquid phase equilibrium concentration of sorbate (mMol)

q^m = Adsorption capacity (mMol metal/g dry weight)

K_d = Langmuir equilibrium parameter (mMol)

Small changes of environmental factors such as pH, temperature, contact time, doses and filtration etc. affect adsorption isotherms significantly. Thus, in this study the effect of pH and biomass concentration on nickel adsorption were investigated to obtain the optimum time required for the adsorption process to reach equilibrium.

The Freundlich equation has the form

$$x/m = K\, C_e^{\,1/n} \qquad (2\text{-}10)$$

$x/m = (q_e)$ = amount adsorbate adsorbed per unit weight of absorbent

C_e = equilibrium concentration of adsorbate in solution after adsorption

K, n = empirical constants

The commonly used log-log linear transformation of this equation is popular because such equations are easy to use. However, the Freundlich equation does not express q (x/m) as a linear function of C at low concentrations. Moreover, it does not provide for a maximum value of q (Rubin *et al.*, 1987). As a result, the Freundlich equation predicts infinite surface coverage at infinite concentration, a condition which does not occur. Therefore its application is limited to ranges of intermediate surface coverages.

The Langmuir model predicts that, under constant temperature and equilibrium, simple adsorption should obey a function of the form

$$x/m = \frac{Q_o b.C_e}{1+bC_e} \qquad (2\text{-}11)$$

where, x/m = amount adsorbed per unit weight of adsorbent
Q_o, b = empirical constants,
C_e = equilibrium concentration of adsorbate in solution after adsorption,

Here Q_o is a maximum surface coverage which represents the formation of a monomolecular layer on the surface of the adsorbent. The monolayer capacity of an adsorbate indicates the amount adsorbed by one gram of the adsorbent in a full-up monolayer. It can be expressed as moles, grams or cubic centimeters, per gram of adsorbent.

The Langmuir adsorption isotherm was developed on the following basis;

1) A fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy.
2) The process is reversible and equilibrium is reached when the rate of adsorption of molecules on the surface is the same as the rate of desorption of molecules from the surface.

At equilibrium concentration, the rates of adsorption and desorption are equal. The correspondence of experimental data to the Langmuir equation does not mean that the stated assumption is valid for the particular system being studied because departure from the assumptions can have a canceling effect. The constant in the Langmuir isotherm can be determined by plotting $C_e/(x/m)$ versus C_e and can be rewritten as

$$\frac{C_e}{(x/m)} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \tag{2-12}$$

The Langmuir equation is strictly applicable only to the adsorption of gas molecules by simple crystalline materials with homogenous surfaces such as mica and platinum. These simple adsorbents have only one elementary type of adsorption site with a single adsorption energy potential. The adsorption of gas molecules on solids which contain more than one elementary type of adsorption sites should follow a related but more complex function. The implication of adsorbent heterogeneity is that if the equilibrium gas pressure is varied over several orders of magnitude, q can show a continuous increase. The exact shape of the adsorption isotherm for a heterogeneous adsorbent will depend upon the distribution of 1/b values, or more specifically, upon the frequency distribution of the adsorption energy sites on the adsorbent. The adsorption on ash, which is a highly heterogeneous solid, should follow this type of function.

Inspite of these limitations, the simple Langmuir equation is often used to describe adsorption from solution by heterogeneous solids. The Langmuir equation is usually regarded as characteristic of adsorbents whose pores are so narrow that there is a space for only one molecular layer on the walls (Gregg,1961)

2.2.6 Effect of the coincidental ions

The formation and the stability of metal-ligand complexes are influenced by the degree of ionization of the ligand molecules and its functional groups. The complex formed is especially stable if the ligand is of chelating character. Chelates are formed by ligands which contain at least two donor atoms, thus forming a ring by the co-ordination at two sites. As an initial step, it is important to understand the nature of the binding mechanisms of metal ions onto various binding sites on the surface of the adsorption site. Several possible species may exist at equilibrium in solutions containing metal ions and ligands such as: ML, ML_2, MHL, MH_2L, MHL_2, MH_2L_2, MOHL, $M(OH)_2L$, $MOHL_2$. In the case of a ligand to molar ratio (L/M) less than one, or weak metal-ligand bondings, precipitation may occur. In solution containing metal ions and ligands, the major components that exist at equilibrium are ML, MHL, and MOHL. At the pH range of 5 to10, the predominant species in most divalent metal-ligand system is ML except those metal ions which form weak metal-ligand bondings where metal precipitation may occur (Bhattacharyya *et al.*,1987).

Batch adsorption experiments were carried out for all equilibrium studies. Equilibrium data obtained from single metal studies give a better understanding of the mechanisms involved in the metal binding process. However, multisolute mixtures are always encountered in industrial effluents where solutes coexist in solution and compete for binding sites on the wood-ash .

In hydrolysis, water molecules act as ligands that serve as electron donors and thus coordinate with metal ions to form hydroxo complexes. The formation of a hydroxo complex affects the adsorption of metal ions to particle surfaces. Other ligands that can replace water molecules around a metal ion are chemical species that have a nonbinding pair of electrons to share with the metal. These include simple anions such as the halides Cl-, F-, Br-, I-, and more complex inorganic compounds such as sulfate, nitrate, acetate, ammonia, phosphate and cyanide. They are commonly found in industrial wastewater and they form a single bond with metal ions and are called monodenate (Meites,1980). Organic molecules with suitable functional groups containing oxygen, nitrogen, sulfur atoms as electron pair donors, e.g. R-COO- ; R--OH ; R-NH_2 ; R-SH, can donate one or more pairs of electrons to a single metal ion, depending on the number of above functional groups. Thus they can be further subdivided into bidentate ligands such as oxalate ion, tridenate ligands such as diethylenetriamine.

EDTA (ethylene diamine tetra acetic acid) is a very well known complexing agent. If a base contains more than one ligand atom, and thus can occupy more than one coordination position in the complex, it is referred to as a multidenate complex former and in this pattern EDTA is considered as hexadenate since it has six pairs of electron to form a complex with a metal ion. Complex formation with multidenate ligand is called chelation, and the complexes are called chelates. Most metals of interest in wastewater have a coordination number of six and thus form octahedral complexes (Cotton and Wilkinson,1972). Complexes with monodenate ligands are usually less stable than those with multidenate ligands (Stumm and Morgan,1981). It is of interest to investigate the effect of EDTA on the adsorption behavior of nickel because this potential complexing agent is often found in wastewater. EDTA is present in metal finishing due to its use as a chelating agent in the plating operation (Davis and Sundy, 1992)

Metal ion adsorption capacity will therefore depends on the relative affinity of the metal ion towards the ligands on particles surface and those in the aquatic surrounding. The system attains higher adsorption yield if the metal ion forms more stable complexes with the ligands on the particle surfaces and vice-versa.

Huang *et al.*,(1990) reported in one of their studies that there is a distinct similarity between the adsorption of the 'free' EDTA ions and the Ni(II)-EDTA complexes, a 'ligand like' adsorption. Using a double-labeling technique, Bowers and Huang (1986) reported that a one to one stoichiometric relationship exists between the amount of Ni(II) and EDTA and the Ni-EDTA adsorbed as a whole. The mechanism of nickel-EDTA adsorption is brought about by the formation of hydrogen bonding between the oxygen atoms and the surface protons. They also observed that the adsorption of other M(ii)-EDTA complexes is indistinguishable at a metal to EDTA concentration of 10^{-4} M.

In the present study, Na^+, K^+, So_4^{-2}, Cl^- and EDTA which are commonly found in electroplating effluents, were selected for adsorption studies.

2.3 MEMBRANE SEPARATION

A membrane can be viewed as a semi-permeable barrier between two phases. This barrier can restrict the movement of molecules across it in a very specific manner. This barrier can be solid, liquid or a gas. The semi-permeable nature of a membrane ensures that separation takes place under appropriate conditions. The manner in which the membrane restricts molecular motion can take many forms. Size exclusion, differences in diffusion coefficients, electrical charge and differences in solubility are some examples.

In a membrane process, the separation is accomplished by a driving force which may be pressure, concentration, temperature or electrical potential (Richard, 1987). In many cases, the transport rate (permeation) is proportional to the driving force and the membrane can be categorized in terms of an appropriate permeability coefficient. Table 2.5 lists the commercially important membrane processes and their applications. The use of driving force as a means of classification is not altogether satisfactory because apparently different membrane processes can be applied for the same separation. For example, desalination of water can be accomplished by electrodialysis, reverse osmosis and evaporation.

Table 2.5 : Membrane Separation and Applications

Membrane separation	**Driving force**	**Applications**
Microfiltration	Hydrostatic pressure	Clarification, sterile filtration
Ultrafiltration	Hydrostatic pressure	Separation of macromolecular solutions
Nanofiltration	Hydrostatic pressure	Separation of small organic compounds and selected salts from solution
Reverse osmosis	Hydrostatic pressure	Separation of microsolutes and salts from solutions
Gas permeation	Hydrostatic pressure, concentration gradient	Separation of gas mixtures
Dialysis	Concentration gradient	Separation of microsolutes and salts from macromolecular solutions
Electrodialysis	Electrical potential	Separation of ions from water and non-ionic solutes

(Scott, 1996)

2.3.1 Reverse osmosis

Reverse osmosis is a pressure driven process. The transport mechanism is primarily solution-diffusion rather than sieving action as in the case of microfiltration and ultrafiltration (Bell and Cousins, 1994). Reverse osmosis rejects particles as small as 10^{-3} to 10^{-4} μm (10 to 1 Å), which include ionic materials and dissolved salts (Scott, 1996). Usually, reverse osmosis works on the concept of cross-flow filtration. The transmembrane pressure in the system forces water through the membrane. The concentrated or rejected solution is usually recycled to the process (Chang,1996). The different types of membrane modules commonly used in the reverse osmosis process are:

i) tubular

ii) spiral-wound

iii) hollow fiber
iv) plate and frame

Among these, spiral - wound units are not easily plugged by suspended solids. Moreover, it has low concentration polarization, low contamination and high durability. It is the most widely used configuration in the reverse osmosis process (Matsuura, 1994).

Three types of semipermeable membrane materials can be used in reverse osmosis units:

i) cellulose acetates (acetate, diacetate and triacetate)
ii) aromatic polyamide
iii) thinfilm composite membranes.

Reverse osmosis membranes are sensitive to pH. However, thin film composite membranes are least affected by pH (ranges from 1 to 12) and are commonly used in manufacturing membranes.

The recovery of heavy metals from electroplating rinse waters has been one of the most successful applications of reverse osmosis. In this process, 99% of the drag-out nickel salts can be recycled in watts nickel baths (Huang and Kaseoglu, 1993). The recovery of chromium from low pH chromic acid rinse water is now possible with the application of a thin film composite membrane since it can withstand a wide pH range (Huang and Kaseoglu, 1993). It is possible to achieve zero discharge in certain applications where the concentrate is completely recycled. In this study, we used reverse osmosis to achieve economic benefits associated with chemical recovery and the reduction of the cost of hazardous waste disposal.