CHAPTER 2

LITERATURE REVIEWS

2.1 Nickel chemistry

Nickel (Ni) is the third element in Group VIII in the periodic table. It has an atomic number of 28, with an atomic weight of 58.69 g/mol. Its electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$. Nickel ion commonly occurs with a valence of 2 (divalent cation, Ni^{+2}) rather than 1, 3, or 4. Ni^{+2} is natural aqueous species. In reducing conditions, nickel would present in insoluble nickel sulfides. Nickel would form complexes with hydroxide, carbonates, and organic ligands in aerobic conditions.

Nickel and its compounds are widely used in various industries such as manufacture of rechargeable batteries, electronic components, coinage, enamel frits, ceramic glazes, stainless steels and other corrosion resistant alloys. They are used as catalysts in hydrogenation of fats and oils and paint pigments. They also can be introduced in electroplating process in order to produce hard tarnish resistant surface. (Stokinger HE,1981)

Toxicity of nickel: The main health concern is if workers are exposed to certain compounds of nickel. Direct contact to nickel and its compound can cause an allergic dermatitis. Inhaling gaseous nickel compound would cause acute effects such as headache, giddiness, nausea, and vomiting. Exposure to nickel-containing dust can also result in sensitization, conjunctivitis, pneumonitis, and asthma. An increased incidence of lung and nasal sinus cancer occurs in long-term exposure to some kinds of nickel ores. (Stokinger HE, 1981)

Nickel in water: The maximum allowable nickel concentration in the industrial discharge effluent is 1 mg./L, which is issued by the Department of Industrial Works, Ministry of Industry, Thailand.

2.2 Metal plating process

Nickel plating is a widely used in industry. Three basic processes are used in nickel plating: physical, chemical, and electrochemical processes. The physical process used is abrasive blasting the surfaces. Blasting removes scale, debris, and excessive oxide from the surface and allows pickling to be more effective. The industry also uses chemical process to eliminate oil or grease and to use in cleaning, pickling, etching, coating, and electroless plating. The electrochemical process is used in plating, electrocleaning, electroplishing, and anoding. Figure 2.1 illustrates a typical or electrochemical process in which the workpiece enter the process (US EPA, 1992).
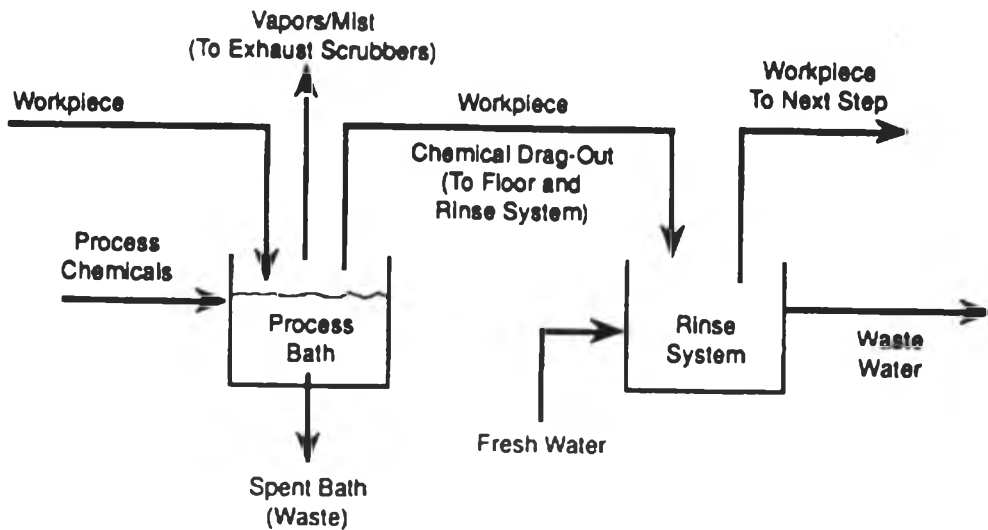

Figure 2.1 Typical metal plating process step (US EPA, 1992).

2.2.1 Waste generation

The metal plating process generates wastewater, solid waste, and air emissions. The wastes generated in the process are summarized in Table 2.1 wastewater, solid waste, and air emissions are described below:

Wastewater

1. Wastewater consists of rinsed water, cooling water, steam condensate, boiler blowdown, wash water, and exhaust scrubber solution.

2. Plating baths are contaminated or spent electroplating or electroless plating baths.

3. Spent process baths. The etchants and cleaners that are contaminated or spent.

4. Strip and pickle baths. The acidic solution used to strip metals from workpiece racks or parts. Commonly used acids are nitric, sulfuric, hydrochloric, and hydrofluoric acids.

5. Exhaust or scrubber solutions. The solutions collected in exhaust and air emission control devices.

Solid waste

1. Industrial wastewater treatment sludge is contaminated with metals such as cadmium, copper, chromium, nickel, tin, and zinc.

2. Miscellaneous solid wastes such as absorbants, filters, empty containers, and abrasive blasting residues.

Air emissions

Air emissions include vapors from degreasing and solvent cleaning from plating operation.

Table 2.1 Waste generated in metal plating industry (US EPA, 1992).

Waste	Potential Hazards	Waste Stream	Process
Alkali (hydroxide)	Corrosivity	Wastewater	Cleaning, etching
Acid (nitric, sulfuric, and hydrochloric)	Corrosivity	Wastewater	Cleaning, pickling, etching, bright dipping
Surfactants	Aquatic toxicity	Wastewater	Cleaning
Oil and Grease	Aquatic toxicity	Wastewater, spent solvent	Cleaning
Cadmium, Zinc, Nickel, Copper, and other metals	Toxicity	Plating bath, drag-out, rinse water, spent titters, sludge	Plating
Perchloroethylene, Trichtoroethylene, and other solvents	Inhalation, derma	Spent solvent (liquid or sludge), air emissions	Cleaning
Cyanide	Toxicity	Plating bath, drag-out, rinse water, other wastewater	Plating, tumbling, stripping, heat treating, desmutting
Chromates	Toxicity	Plating bath, drag-out, rinse water, sludge, other wastewater, mist	Plating, chromating, etching
Water	-	Rinse water, drag-out, process bath, air emission (evaporation), cooling water, boiler blowdown	Various

2.2.2 Metal plating wastewater Treatment

Various treatment techniques have been used for treating wastewater generated from metal plating process. Those techniques can be used individually or combined together. Details of the techniques are explained below.

1. Precipitation technique

Metals enter the plating bath contain impurities. They can be precipitated from the bath by using precipitating reagents such as zinc sulfide. Like other chemical reaction, care must be taken to ensure that the reagents are compatible with bath constituents. Peroxide is normally used for removing iron and chromium in acidic baths. Precipitant would then be used in elevated pH to remove the impurities along with batch filtration.

Metal ion can be removed with cation resins and chelated anion resins. Using a reducing agent and sand filter or other media column to precipitate the metal on the media surface can attain low effluent metal concentrations (US EPA, 1992).

2. Filtration technique

Filtration technique is mainly employed to remove accumulated solid. The continuous use of the system would increase its effectiveness. This technique is commonly applied to eliminate copper sulfate , nickel sulfonate, and nickel chloride (US EPA, 1992).
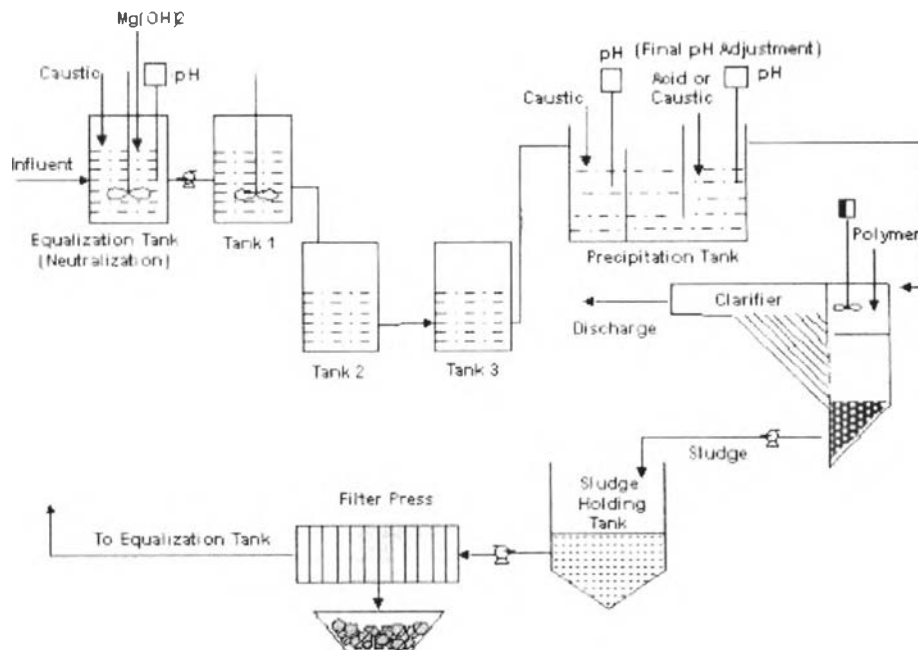

Figure 2.2 Precipitation and filtration techniques are available for treating wastewater from metal plating process (Ratana and Sultan, 2001).

3. Electrocoagulation

This technique introduces electricity into the bath to conduct electrochemical process. The process can simultaneously remove heavy metals, suspended solids, emulsified organic, and many other contaminants from water. Metal plates in tank containing with contaminants are charged with direct electrical current. The plate material is discharged into the stream where ionic and non- ionic contaminants would be subjected to the electrical charge, electrolysis products, and the plate elements. Products from this process are variable depending on the species present in the water. But most products are generally stable and can be removed from the wastewater. (Kaspar, 1999)

4. Coagulation / flocculation

Coagulants are used for water and wastewater treatment. Coagulation is a process for transforming small particles into larger aggregates (flocs) and for adsorbing dissolved organic matter onto particulate aggregates, therefore the impurities can be removed in subsequent sedimentation / flotation and filtration stages. The coagulation process consists of three sequential steps: coagulant formation, colloid / particle destabilization, and particle aggregation. Coagulant formation, colloid / particle destabilization are promoted in a rapid mixing stage, where treatment chemicals are added and dispersed throughout the water to be treated. Particle aggregation (floc formation) is then promoted in a flocculation stage where interparticle collisions create large floc particles amenable to separation from the treated water. In water and wastewater treatment practice, the term *coagulation* and *flocculation* are not synonymous. Coagulation is used to describe the initial process whereby the original colloid dispersion is destabilized, principally by charge neutralization. *Flocculation* describes the subsequent process whereby the destabilized colloids in the micron and sub micron size range undergo aggregation and particle growth into millimeter sized flocs (Jiang , 1998).

5. Sedimentation

Sedimentation is employed for the removal of suspended solids from wastewater. The process can be considered in three basic classifications, depending on the nature of the solids present in the suspension: discrete, flocculent, and zone settling. In discrete settling the particle maintains its individuality and does not change in size, shape, or density during the settling process. Flocculent settling occurs when the particles agglomerate during the settling period with a resulting change in size and settling rate. Zone settling involves a flocculated suspension which form a lattice structure and settless as a mass, exhibiting a distinct interface during the settling process. Compaction of the settled sludge occurs in all sedimentation but will be considered separately under thickening(Wesley, 2000).

6. Activated carbon

Activated carbon is employed for the treatment of toxic or nonbiodegradable wastewater and for tertiary treatment following biological oxidation. Powdered activated carbon (PAC) can be adding to the activated sludge process for enhanced performance. The addition of PAC has several process advantages, namely, decreased variability in effluent quality and removal by adsorption of nonbiodegradable organic, reduction of inhibition in industrial wastewater treatment, and removal of refractory priority pollutants (Wesley, 2000).

7. Ion exchange

Ion exchange can be used for the removal of undesirable anion and cation from wastewater. Cations are exchanged for hydrogen or sodium and anions for hydroxyl ions. Ion exchange resins consist of an organic or inorganic network structure with attached functional groups. Most ion exchange resins used in wastewater treatment are synthetic resins made by polymerization of organic compound into a porous three-dimensional structure. The degree of crosslinking between organic chains determines the internal pore structure, with higher crosslink density giving smaller pore sizes. From a kinetic viewpoint, a low degree crosslinking would enhance diffusion of ions through larger pores. However, physical strength decreased and swelling in water increases as crosslink density is lowered. The functional organic groups are usually introduced by reaction the polymeric matrix

with a chemical compound containing the desired group. The number of functional groups per unit mass of resin determines exchange capacity (Wesley, 2000).

8. Chemical oxidation

Chemical oxidation generally refers to the use of oxidizing agents such as ozone, O_3, hydrogenperoxide, H_2O_2, permanganate, MnO_4^-, Chloride dioxide, ClO_2, Chlorine, Cl_2 or $HOCl$, or oxygen, O_2, These reactions frequently require one or more catalysts in order to increase the rate of reaction to acceptable levels. Catalysts include simple pH adjustment, transition metal cations, enzymes, and a variety of proprietary catalysts of unreported composition. Chemical oxidation is typically applied to situation where organic compounds are nonbiodegradable, toxic, or inhibitory to microbial growth. However, chemical oxidation is also effective for the destruction of many inorganic compounds and the elimination of odorous compounds, such as oxidation of sulfides (Wesley, 2000).

Criteria of wastewater treatment

1) wastewater properties

2) the discharge standard

3) wastewater treatment area is used

4) cost of operating and monitoring

5) safety of operation

6) recycle or reuse

2.3 Oxygenation of ferrous iron (II) in highly buffered waters

The oxygenation of ferrous ion (II) occurs in the presence of oxygen. Ferrous ion (II) is naturally found as hydrated ferrous oxide form. It has low solubility. Since, the aeration raises the pH of the water by the release of CO_2 and provides oxygen for oxidation of Fe (II) to Fe (III). The oxygenation of ferrous ion (II) is slower in lower alkalinity solution (Stumm, 1985).

The stoichiometric relationship describes the oxidation of Fe (II):

$$2\,Fe^{2+} + 5\,H_2O + 1/2\,O_2 \longleftrightarrow 2\,Fe\,(OH)_3(s) + 4\,H^+$$

2.4 Inner-sphere and outer-sphere surface complexes

Surface complexation is a reaction of surface functional group with ions or molecules. There are two categories of surface complexation on structural groups. The first type is *inner-sphere*. It is a reaction of functional group with bound ions or molecules without water. The second is *outer-sphere*. It interposes at least one water molecule between functional group and the ion or molecule. Generaly, the outer-sphere surface complexes are involved with electrostatic bonding mechanisms. They are less stable than inner-sphere complexes, which are involved with either ionic or covalent bonding or the combination of both (Stumm, 1995).

Hydroxyl group in goethite can be protonated to form a Lewis acid site. It can be exchanged to allow the formation of an inner-sphere complex with the oxyanion, HPO_4^{2-}. This surface complex is shown in Figure 2.3. It consists of a HPO_4^{2-} bound through its oxygen ions to pair Fe (III) cations (bi-nuclear surface complex, the configuration of the o-phosphate unit) and is especially compatible with the grooved structure of the goethite surface, thus providing stereochemical enhancement of the stability of the inner-sphere complex.

The outer-sphere surface complex mechanisms of adsorption involve almost exclusively electrostatic bonding, whereas, inner-sphere complex mechanisms are likely to involve ionic as well as covalent bonding. Which covalent bonding depends significantly on the particular electron configurations of both the surface group and the complex ion. It is appropriate to consider inner-sphere surface complexation as the molecular basis of the term "specific adsorption", correspondingly, outer-sphere surface complexation are the molecular basis for the term "nonspecific adsorption".

There is a consensus that ions adsorbed specifically, like HPO_4^{2-} are not to be considered "readily exchangeable" which is in contrast to the case of outer-sphere complex mechanism of adsorption.

For systems containing more than one metal, competitive adsorption among metals is one of the major concerns. Benjamin and Bloom (1981) studied the effect of strong binding of ionic adsorbates on adsorption of trace metals on amorphous iron oxyhydroxide. They found that anions either increase or have no effect on trace metal adsorption, indicating that competition between the anions and cations for surface sites is relatively low. They suggested that anion adsorption sites be physically and electrically isolated from cation adsorption sites. For the systems in which the amount of trace metal adsorbed increased, they concluded that the most likely cause of the enhanced adsorption is that a secondary surface phase forms, and the metals bind more strongly to the new phase than they do to the original phase.
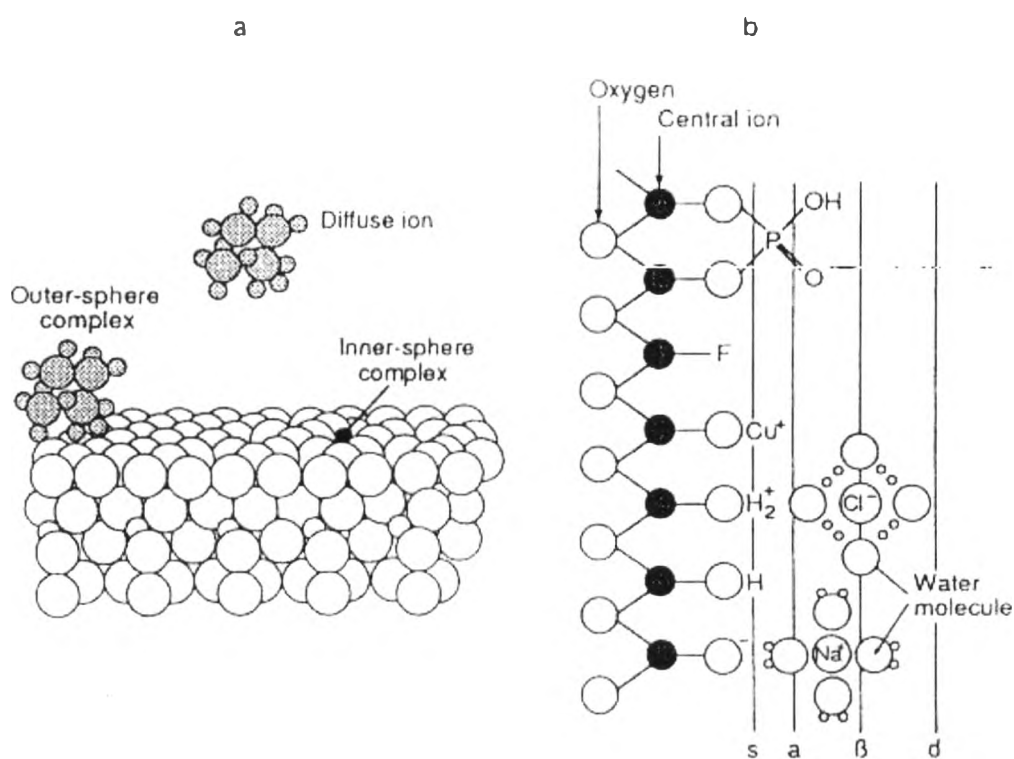

Figure 2.3 Surface complex formation (Stumm and Morgan, 1995)

(a) Surface complex formation of an ion on hydrous oxide surface.

(b) A schematic portrayal of the hydrous oxide surface, showing planes associated with surface hydroxyl groups, inner-sphere complexes, and the diffuse layer.

2.5 The coordination chemistry of the hydrous oxide water interface

Oxides, especially those of Si, Al, and Fe, are abundant components of the earth's crust. Hence, a large fraction of the solid natural waters, sediments, and soils contain such oxides or hydroxides. In the presence of water the surface of oxides are generally covered with surface hydroxyl groups, as shown in Figure 2.3.

2.6 The theoretical adsorption

The adsorption isotherms are equilibrium equations and apply to condition resulting after the adsorbate containing phase has been contact with the adsorbent for sufficient time to reach equilibrium. Generally, the amount of materials adsorbed is determined as a function of the concentration at a constant temperature. Equations are used to describe the experimental isotherm data were developed by Freundlich, by Langmuir, and by Brunauer, Emmet, and Teller (BET isotherm)

Freundlich Isotherm is defined as follows.

$$q = KC^{1/n} \qquad (2\text{-}1)$$

C is the concentration of solute after adsorption.

q is the mass of contaminant adsorbed per unit weight of the adsorbent.

K and n are constants, which must be evaluated for each solute and temperature.

The Freundlich isotherm is often expressed in its logarithmic form,

$$\log q \ = \ \log K + (1/n) \log C \qquad (2\text{-}2)$$

The constants in the Freundlich isotherm can be determined by plotting q versus C.

(Sawyer et al., 1994)

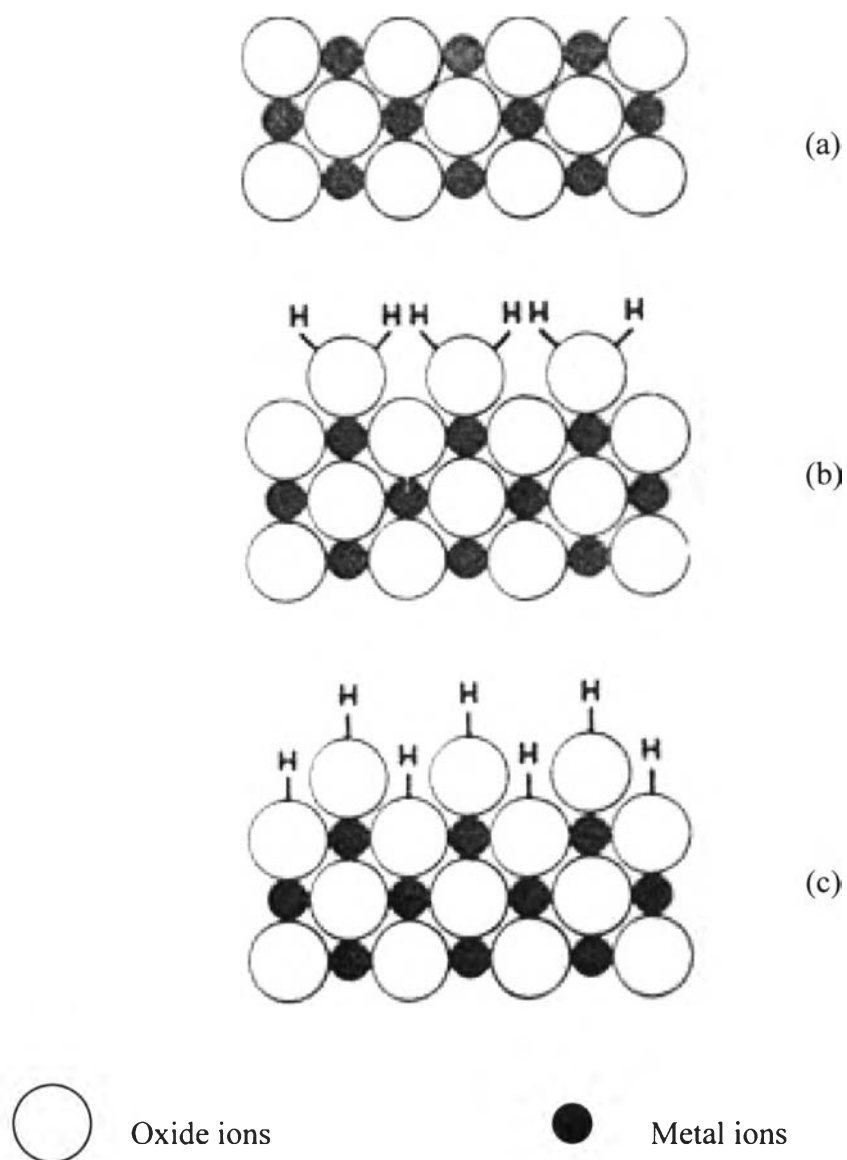**Figure 2.4** Surface complexes at oxide-water interfaces (Anderson and Rubin, 1981)

(a) Surface ions are coordinatively unsaturated

(b) In the presence of water, the surface metal ions may coordinate

   H_2O molecules.

(c) Dissociative chemisorption leads to a hydroxylated surface.

The Langmuir isotherm is used to describe general form of Langmuir , as follows.

$$C/q = a/q_m + C/q_m \qquad (2\text{-}3)$$

q_m is the maximum adsorption in grams of adsorbate per gram of adsorbent, when C is large relative to constant a .

When q approaches q_m, the coverage of the surface is essentially complete. If plotting C/q versus C. The constant a and q_m can be evaluated.

The BET type is used to multilayer adsorption, as follows.

$$C/(q(C_s\text{-}C)) = (1/bq_m) + ((b\text{-}1)/bq_m)(C/C_s) \qquad (2\text{-}4)$$

C_s and b can be contained from the slope and intercept of the straight line best fitting of the plot of the left side of equation 2- 4 versus C/C_s (Sawyer et al., 1994)

2.7 Surface complexation model

The basically concepts for all surface complexation model was summarized by Davis and Kent (1990).

1. The surface is composed of specific functional groups that react with dissolved solutes to form surface complexes in a manner analogous to complexation reactions in homogeneous solution.

2. The equilibria of surface complexation and ionization reactions can be described by mass law equations, with correction factors applied for variable electrostatic energy.

3. Surface charge and surface electrical potential result from the sorption reaction itself (Stumm and Morgan, 1996).

4. The apparent binding constants determined are empirical parameters related to thermodynamic constants by the rational activity coefficients of the surface species

Table 2.2 Adsorption (surface complex formation) equilibria
(Stumm and Morgan, 1995)

Acid-Base Equilibria for surface

$S\text{-}OH + H^+$ = $S\text{-}OH_2^+$

$S\text{-}OH + OH^-$ = $S\text{-}O^- + H_2O$

Metal Binding (M^{z+} = metal)

$S\text{-}OH + M^{z+}$ = $S\text{-}OM^{(z-1)+} + H^+$

$2\,S\text{-}OH + M^{z+}$ = $(S\text{-}O)_2M^{(z-2)+} + 2\,H^+$

$S\text{-}OH + M^{z+} + H_2O$ = $S\text{-}OMOH^{(z-2)+} + 2\,H^+$

Ligand Exchange (L^- = ligand)

$S\text{-}OH + L^-$ = $S\text{-}L + OH^-$

$2S\text{-}OH + L^-$ = $S_2L^+ + 2OH^-$

Ternary Surface Complex Formation

$S\text{-}OH + L^- + M^{z-}$ = $S\text{-}L\text{-}M^{z+} + OH^-$

$S\text{-}OH + L^- + M^{z-}$ = $S\text{-}OM\text{-}L^{(z-2)+} + H^+$

$S\text{-}OH$ = oxide surface

2.8 Related study

Ratanatamskul (1993) studied the effect of iron bed height on the removal of phosphorus. The average phosphorus loading was 5.3 mg/l/d. The phosphorus removal rate increased rapidly with increasing column iron bed height. The phosphorus removal rate reached a maximum value of 4.3 mg/l/d. However, increasing iron bed heights above 45 cm. did not give significant improvement. This studied suggests that an increase in iron bed height resulted in a decrease in phosphorus removal capacity. The reason for this observation might be due to insufficient oxygen supply at the lower part of iron bed inside the long column, which could not cause a complete oxidation of iron material to free ion oxide and hydroxide forms on the iron surface. The observation of the experimental system also showed that iron bed layers could be separated into two parts so called the upper and lower part. The upper part contained brown iron oxide layer that was in contrast to black deoxidized iron layer at the lower part of the column. The lower part of the column seemed, thus, not effective in the removal of phosphorus.

The ability of the ferric hydroxide precipitate to sorb ions with heavy metals was characterized in single and multi-adsorbate systems by Manzion et al., (1994). Heavy metals could be sorbed both as cations (Cr^{+3}, Pb^{+2}, Cu^{+2}, Zn^{+2}, Ni^{+2}, Cd^{+2}) in neutral to high pH and as anions (SeO_4^{-2}, CrO_4^{-2}, AsO_4^{-3}) in neutral to mildly acidic pH.

Khaodhiar (1997) studied the removal of copper, chromium, and arsenic from synthetic groundwater using composite iron oxide adsorbent. Two types of composite adsorbents were iron oxide coated sand and magnetite coated sand. The result was concluded that copper and arsenate were strongly adsorbed or formed inner sphere surface complexes with the iron oxide coated sand surface, while chromate was weakly adsorbed or formed outer sphere surface complex with the iron oxide coated sand surface. The presence of arsenate in the solution slightly increase the amount of copper adsorbed while the presence of chromate did not affect copper adsorption by iron oxide coated sand. The presence of copper and/or chromate did not affect arsenate adsorption. The presence of copper increases chromate adsorption that is mainly by electrostatic force. The presence of arsenate significantly decreased chromate adsorption due to electrostatic force and competitive effects.

Jurek et al., (1998) found that the wastewater from a metal pickling facility, treating with lime precipitation supernatant with ferric chloride at 30 mg/l dose removed both Ni and Cr to 0.01 mg/l range in unfiltered samples. Ferric salts are capable of removing heavy metals to low ppb levels from complex matrix with metals present in various forms such as dissolved, colloidal, emulsified, and particulate.

Ongwandee (1999) explored methodology of metal plating wastewater treatment with using a stable aqueous solution of sodium borohydride (SBH) containing 1.2 % $NaBH_4$ and 4 % NaOH, removing heavy metals, namely copper plating, nickel plating, and chromium plating. The nickel waste with concentration 380 mg/L can be respectively processed with adjusting pH to 8.5 with caustic, adding sodium bisulfite ($NaHSO_4$) at 0.5 times of amount nickel in wastewater, and adding SBH until the pH of solution increased to 9 .This process can removed total nickel from wastewater less than 1 mg/L according to effluent Thai industrial standard.

Lai et al., (2000) applied an iron oxide coating onto the sand surface. The utilization of the adsorbent properties of the coating and filtration properties of the sand media was developed. The competitive adsorption of iron-coated sand for copper and lead ions from water was investigated by batch and column experiments. Among the two metal ions studied, the coated sand had greater affinity for the removal of lead ions compared to copper ions at a concentration of 5 x 10^{-5}M, 1 x 10^{-4}M, and an interval of pH = 2.5 - 6.5. From the column experiment results, the iron-coated sand in a continuous treatment unit could remove both copper and lead ions simultaneously.

Pratomsrimake (2000) removed nickel from synthetic wastewater using an iron waste column. The pH was a very important parameter in removal efficiency. The efficiency was more than 90 % at pH over 8. The dissolve oxygen was effected to the removal efficiency by the removal rate was depend on concentration of dissolve oxygen. In the aerated status, dissolve oxygen concentration was about 7.8 mg/L. It would be the highest removal rate. The presence of anions, sulfate and chloride ions increased the efficiency a little bit, but the cations, zinc and copper, showed no effect. The continuous column, the height of iron waste had effected to removal efficiency. The height was varied from 20 to 60 cm. The removal rate increase rapidly related to the height. But after the height was increased more than 60 cm. The rate was

increased with no significant. For the effect of flow, it was found that the increasing of flow was reduced removal efficiency. The nickel was added to the iron column with concentration of 11.14 mg/L. The average effluent concentration was 0.30, 0.77, 1.90 and 2.94 mg/L or be calculated in percentage was 97.3 %, 93.1%, 82.9%, and 73.6% at the flow of 0.5, 1.0, 1.5, and 2.0 BV/Hr respectively for 91 days operation. The adsorption of nickel was of the inner sphere complex.

Ratanatamskul et al., (2002) studied iron in steel wool is responsible for silver recovery by metallic replacement mechanism, increasing iron mass tends to increase silver recovery as the residual concentration of silver decreased significantly. A very high removal percentage is more than 99 %. The metallic replacement using steel wool does not require pH adjustment. The relationship between time scale of silver reduction in the spent solution and the metallic replacement. It was found that the silver concentration decreased very rapidly within 0.5 hours with all range of iron mass from 25 to 100 g iron in the spent solution of 500 ml. These mean that the reaction between silver and iron in steel wool is a very fast reaction. It seems that iron mass of at least 25 g iron was rather enough for the spent solution of 500 ml.