

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Surface treatment processes

Surface treatment processes in metal industries are the processes that prepare the metal surface by removal of rust or scale and making the appropriate surface before proceeding to the next processes; i.e., rolling, electroplating, electrocoating, painting and pigment product. The surface treatment efficiency depends on times, concentration of acid solution and temperature of acid solution, etc.

Surface treatment processes can be classified into 2 processes i.e. pre-cleaning process and removal of rust process.

2.1.1 Pre-cleaning process

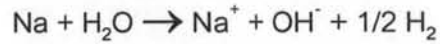
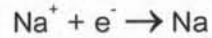
Pre-cleaning process is the cleaning of raw materials with water but some cases chemicals such as sodium hydroxide (NaOH), alkaline silicate and phosphate in rinse water have been used for increased efficiency of cleaning. Pre-cleaning is treated by dipping the raw materials in the cleaning bath or spraying the cleaning solution on the raw materials. The dust and oil are removed from the metal surface and the raw materials are transferred to the next processes [1, 6].

2.1.2 Removal of rust process

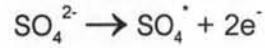
2.1.2.1 Stainless steel

Generally, removal of rust for stainless steel can be classified into several processes shown in Figure 2-1. Electric current is used for the removal of rust process which metal oxide is removed by oxygen (anode) and hydrogen (cathode). Reaction occurred at anode and cathode can be explained by

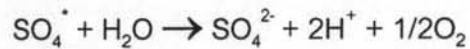
Cathode:



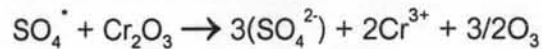
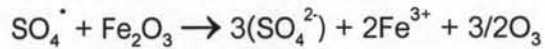
Anode:



Surface cleaning:



Oxide:



Second step of the removal of rust process with electric current is also related to using acid in the removal of rust bath. Reaction between acid and rust and electrolysis reaction are occurred at the same time in the removal of rust bath. Nitric acid and hydrofluoric acid (10% HNO_3 + 3% HF) are used for the removal of rust in the final bath [1, 7-10].

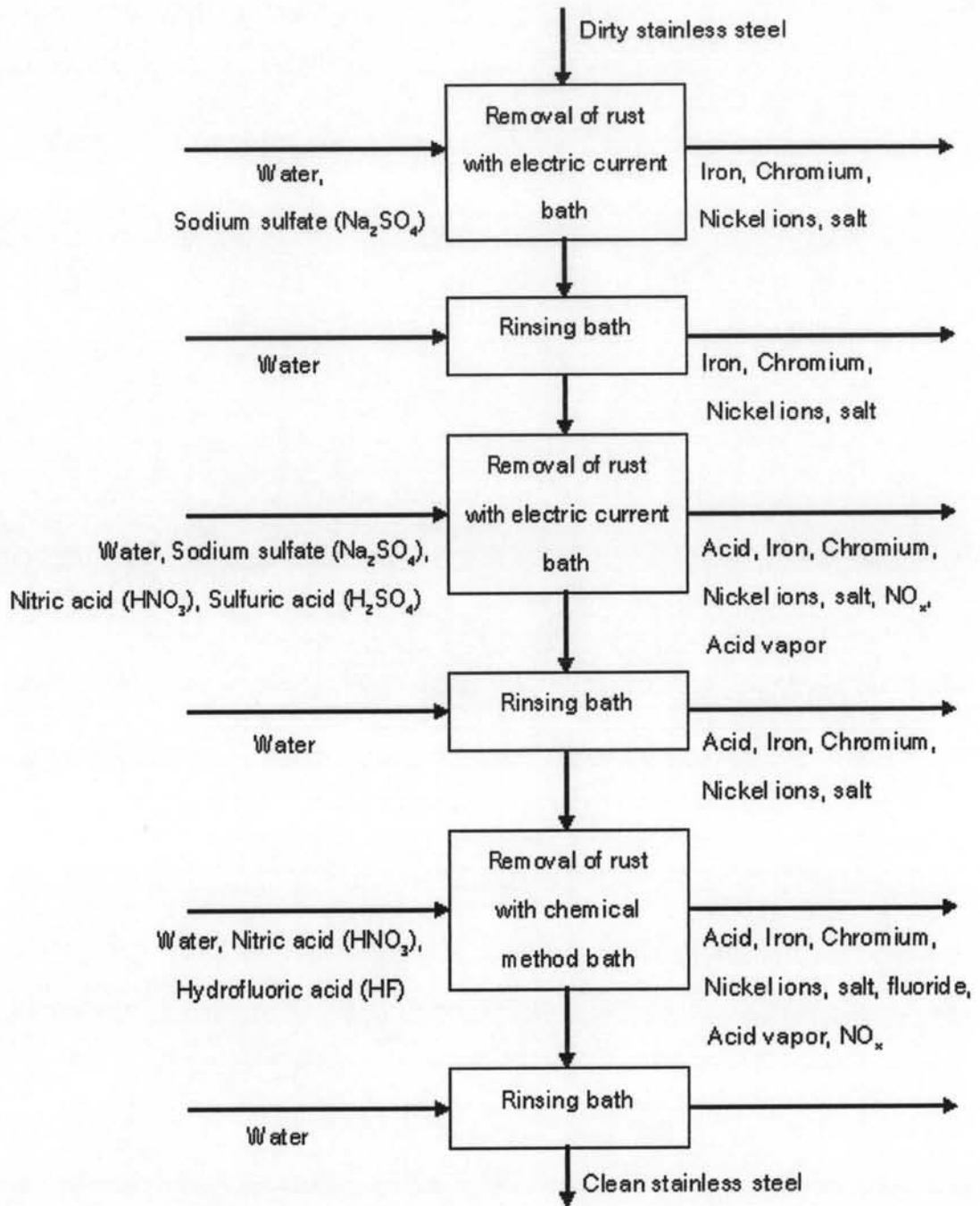


Figure 2-1 A diagram of the removal of rust process for stainless steel [1].

Figure 2-2 showed the surface treatment process at the Stainless steel Home Equipment Manufacturing Co., Ltd., where the wastewater sample was taken for this study.

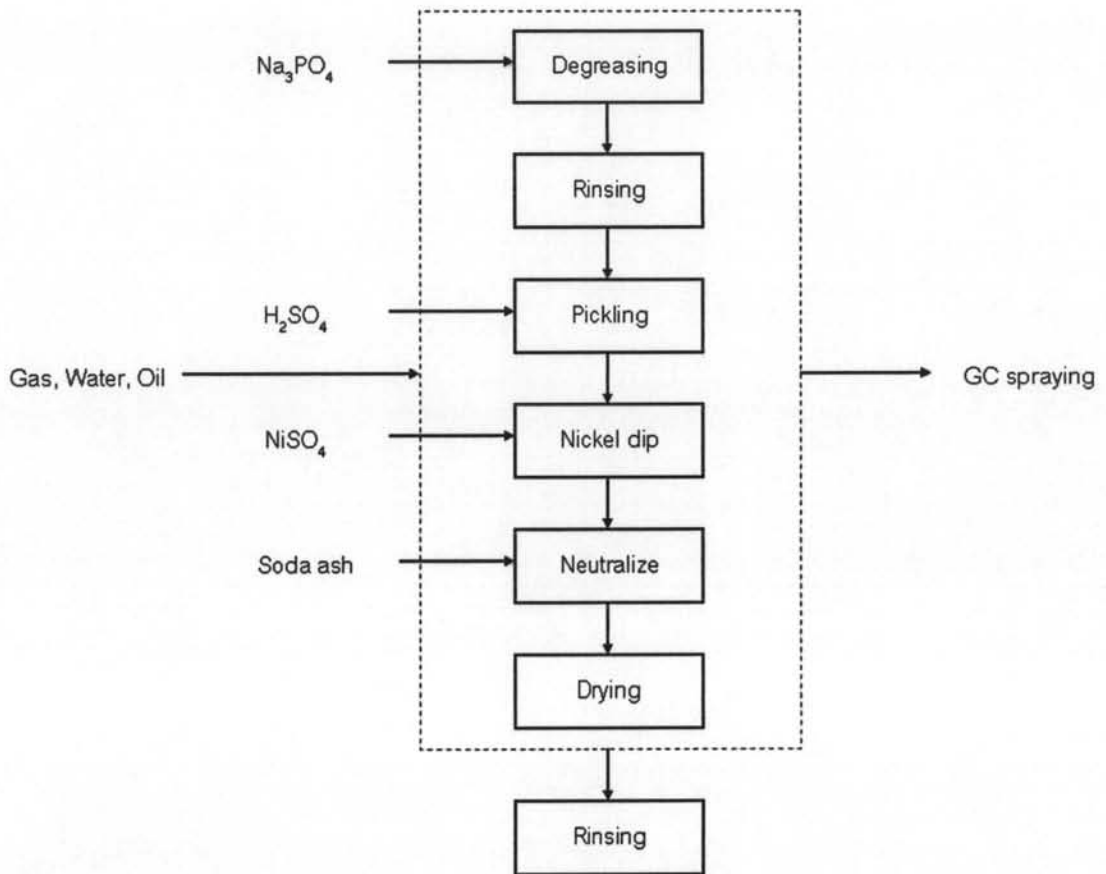


Figure 2-2 A diagram of the surface treatment process from the Stainless steel Home Equipment Manufacturing Co., Ltd.

The wastewater was taken from the pickling bath, where the sulfuric acid was used for the removal of rust process. The major waste of this process usually contains sulfuric acid (H_2SO_4), iron ions, chromium ions, and nickel ions.

2.2 Toxicity of heavy metals

The acid waste solution after stainless steel surface treatment process usually contains heavy metals mainly iron (Fe), nickel (Ni), and chromium (Cr) that are hazardous to environment and human health due to its toxicity even in very low concentration.

2.2.1 Chromium (Cr)

Chromium has three main forms chromium (0), chromium (III) and chromium (VI). Chromium (III) compounds are stable and occur naturally in the environment. Chromium (0) does not occur naturally and chromium (VI) occurs only rarely. Chromium is used in the production of stainless steel or chromium steels or chromium alloys and other alloys, catalyst in ammonia synthesis, bricks in furnaces, dyes, pigments, leather tanning, wood preserving, for greatly increasing resistance and durability of metals and chrome plating and for electroplating [11].

The health hazards associated with exposure to chromium is depended on its oxidation state. Chromium (VI) is danger to human health, mainly for people who work in the steel, textile industry and leather products. Chromium (VI) is known to cause various health effects. The effect of skin may be included ulceration, dermatitis and allergic skin reactions. The effect of respiration system may be included ulceration, perforation of the mucous membranes and nasal septum, irritation of the pharynx and larynx, asthmatic, bronchitis, edema, coughing, wheezing, shortness of breath and nasal itch. Other health problems that are caused by chromium (VI) such as weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer and death. Chromium (III) is considerably less toxic than the chromium (VI) but it can be toxic at high levels. The effect of chromium (III) may be caused skin irritation, skin allergy which can be occurred with itching, redness and eczema [11-13]. The Department of Environmental Quality Promotion; Ministry of Natural Resources and Environment has set industrial effluent standards for chromium (III) chromium (VI) and total chromium to be 0.75 mg L^{-1} , 0.25 mg L^{-1} , and 0.50 mg L^{-1} , respectively [17].

2.2.2 Iron (Fe)

Iron has two main forms; i.e., iron (II) or ferrous compounds and iron (III) or ferric compounds. Iron has played an important for the several industrial sectors such as pig iron, alloy of iron, stainless steel, alloy steels, wrought iron, cast iron, carbon steel. The effect of iron may be caused conjunctivitis, retinitis and pulmonary carcinogens [14]. The Department of Environmental Quality Promotion; Ministry of Natural Resources and Environment has set industrial effluent standards for iron to be 10 mg L^{-1} [17].

2.2.3 Nickel (Ni)

Nickel compounds are also used for nickel plating, stainless steel cutlery, to color ceramics, to make some batteries and as catalysts that increase the rate of chemical reactions [11]. Nickel may cause health problems such as higher chances of development of lung cancer, nose cancer, larynx cancer and prostate cancer, sickness and dizziness after exposure to nickel gas, lung embolism, respiratory failure, birth defects, asthma and chronic bronchitis, allergic reaction, skin rash and heart disorders [11, 15, 16]. The Department of Environmental Quality Promotion; Ministry of Natural Resources and Environment has set industrial effluent standards for nickel to be 0.2 mg L^{-1} [17].

Therefore, the wastewater treatment process is required for reuse or recovery and removal of heavy metals ion prior to releasing to the environment

2.3 Wastewater treatment process

The wastewater treatment process is the process of removing contaminant from wastewater, both runoff (effluent) and domestic. It includes physical, chemical and biological processes to remove physical, chemical and biological contaminants. The removal of heavy metals can be treated by single process or multiple processes depending on the suitability.

2.3.1 Chemical precipitation

Chemical precipitation is the most common technique and a widely used, proven technology for the removal of dissolved (ionic) metals and other inorganic ions, suspended solids, fats, oils, greases and some other organic substances from wastewater. Chemical precipitation is a method of causing contaminants that are either dissolved or suspended in solution to settle from a solution as a solid precipitate, which can be filtered, centrifuged or otherwise separated from the liquid portion. Precipitation is facilitated through the use of coagulant, an agent which causes smaller particles suspended in solution to gather into larger aggregates. The ionic metals can be transformed to insoluble forms (precipitates) by the chemical reaction between the soluble metal ions and the precipitating reagent [5, 18-20].

The effectiveness of the chemical precipitation process depends on several factors, including the type and concentration of ionic metals present in the solution. The precipitating agent used, the reaction conditions, especially the pH of the solution and the presence of other constituents may inhibit the precipitation reaction.

The advantages of using chemical precipitation in wastewater treatment process are that it is a well-established technology with ready availability of equipment and many chemicals, low maintenance and unsophisticated operation.

The disadvantages of using chemical precipitation are that the volume of waste sludge may be increased up to 50 percent from the addition of treatment chemicals and large amounts of chemicals may need to be transported to the treatment location [21, 22].

2.3.2 Ion exchange

Ion exchange is very similar to adsorption; both processes involved mass transfer from a fluid to a solid phase. Ion exchange is a process in which ions held by electrostatic forces to charge functional groups on the surface of a solid are exchanged for ions of similar charge in a solution in which the solid is immersed. Ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay and soil human. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). Also, amphoteric exchanger is able to exchange both cations and anions simultaneously. However, the simultaneous exchange of cations and anions can be more efficiently performed in *mixed beds* that contain a mixture of anion and cation exchange resins or passing the treated solution through several different ion exchange materials [5, 18, 23].

Ion exchangers can be unselective or have binding preferences for certain ions or classes of ions, depending on their chemical structures, size of the ions and their charges or their structures. Ion exchange resins are widely used in different separation, purification and decontamination processes. Actual process design depends on the waste to be treated, pollutant concentration, flow rate and other operating conditions [24].

The advantages of using ion exchange are that it demands low energy, the resin can be selected for removal of certain ions, recycle of water and recover of chemicals.

The disadvantages of using ion exchange are that it produces a concentrated solution which needs to be further treated, it usually runs as a batch process, it is difficult to find a suitable resin for treatment of a waste solution containing mixed metal ions, limited concentration ability, excess regenerate required, feed concentration must be closely monitored and ion exchange column takes time to regenerate [5, 21, 22].

2.3.3 Membrane separation processes

The membrane can be defined as a semi-permeable barrier between phases, which can restrict the transport of molecules or ionic species in a selective manner. Membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid and can carry a positive or negative charge or be neutral or bipolar.

Membrane separation process can be used for separation and preconcentration of solution or gas and solid mixtures by using of concentration difference, pressure difference, electric potential difference and temperature difference as driving forces such as particle filtration, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), gas separation, pervaporation, reverse osmosis (RO), dialysis (D), diffusion dialysis (DD) and electrodialysis (ED), etc.

Several membrane separation processes have been extensively used for food, beverage, pharmaceutical, textile, chemical, electroplating, and surface finishing industries, as well as medical application, and waste treatment process.

The type of membrane can be classified such as microporous membrane has pores size between 0.01 to 10 microns (μm) in diameter, nonporous membrane is used for transport by diffusion under the driving force of pressure or concentration and electrical gradient, electrically charged membrane may be microporous or nonporous which can be fixed with positively or negatively charged ions, anisotropic membrane, ceramic, metal and liquid membranes [26]. The principal types of membranes are shown in Figure 2-3.

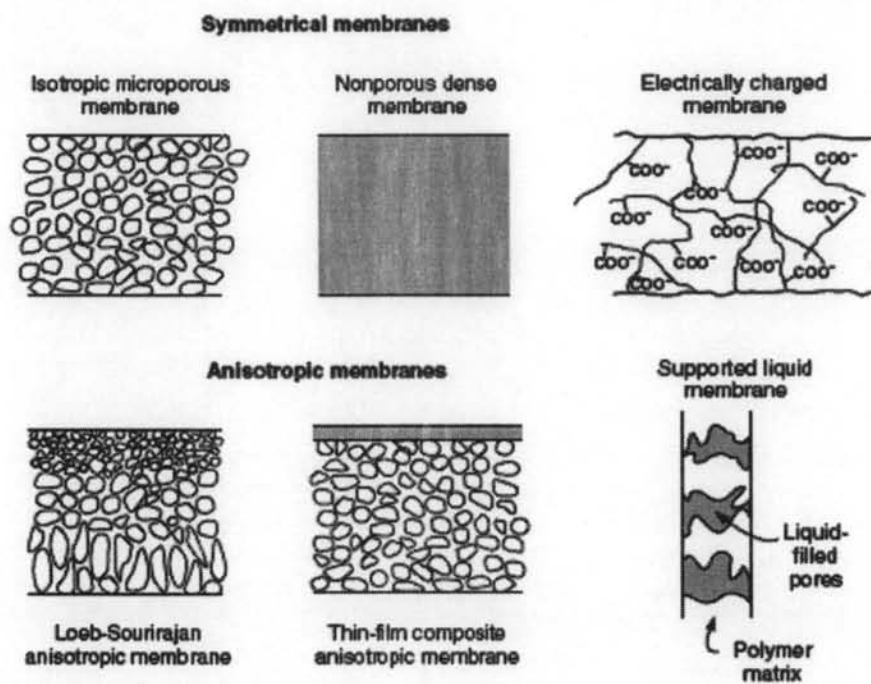


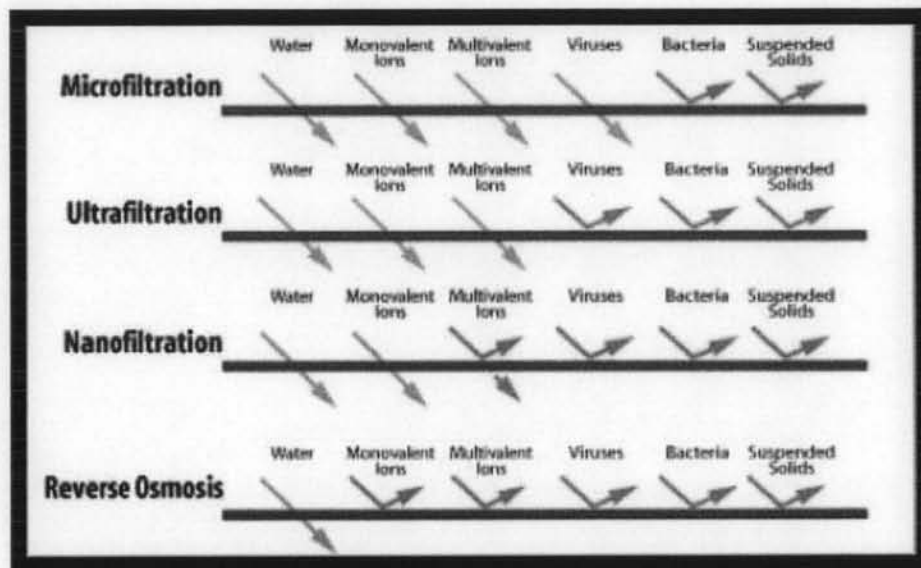
Figure 2-3 The principal types of membranes [26].

2.3.3.1 Filtration processes [24-27]

The filtration process can be summarized in Table 2-1 and Figure 2-4.

Table2-1 The membrane filtration processes characteristics

Types	Pressure	Pore size
Microfiltration (MF)	100 to 500 kPa	0.05 to 10 μm
Ultrafiltration (UF)	100 to 800 kPa	0.003 to 0.1 μm
Nanofiltration (NF)	0.3 to 4 MPa	-
Reverse osmosis (RO)	1 to 10 MPa	-



Membrane Process Characteristics

Figure 2-4 The membrane filtration processes characteristics [25].

The advantages of using the membrane filtration processes are such as reduction the amount of treatment chemical, small floor space requirements, low operating costs, achieves modest concentration, very compact, high separation rate can be achieved and no chemical used.

The disadvantages of using the membrane filtration processes are such as limited concentration range of operation, membrane sensitive to pH, some materials fractionally rejected, scale formation that can be a serious problem, flux rate (the rate of feed water flow through of the membrane) that gradually declines over time, fouling of membrane due to feed highs in suspended solids and expensive compared to conventional treatment [18, 21, 22].

2.3.3.2 Dialysis process

Dialysis process is a membrane separation process which the concentration difference is used as a driving force. Dialysis is controlled by diffusion of solute through the pores of membrane and diffusion of solute through the two concentration boundary layers or mass transport films at both surfaces of membrane [24, 27].

The advantages of using dialysis processes are such as low energy consumptions, simple plant, stable and easy operation and low operating cost.

The disadvantage of using dialysis processes are relatively slow process and limited degree of selectivity [2, 27].

2.3.3.3 Electrodialysis process

Electrodialysis process is an electrochemical membrane separation process which is used to transport ions from one solution through ion exchange membranes to another solution under the influence of an electrical potential difference.

Electrodialysis process is useful for the separation and concentration of salts, acids and bases from aqueous solution, the separation of monovalent ions from multivalent ions, the separation of ionic compounds from uncharged molecular, the production of potable water from brackish water, the desalination of salt water, the demineralization of whey, the radioactive wastewater treatment by using radiation resistant membranes and the deacidification of fruit juices, etc [24, 26-31].

The advantages of using electrodialysis process are such as achieving higher concentration than reverse osmosis or ion exchange, no chemical being used and high energy efficiency.

The disadvantages of using electrodialysis process are such as that the membranes are sensitive to flow distribution, pH and suspended solids, feed must be filter and susceptible to fouling, etc [21, 22, 27, 30].

2.4 Electrodialysis process (ED)

2.4.1 Principle of electrodialysis (ED)

The principle of electrodialysis (ED) is displayed in Figure 2-5 that ionic components in solution transport through ion exchange membranes from one solution to another under an electric potential difference as a driving force.

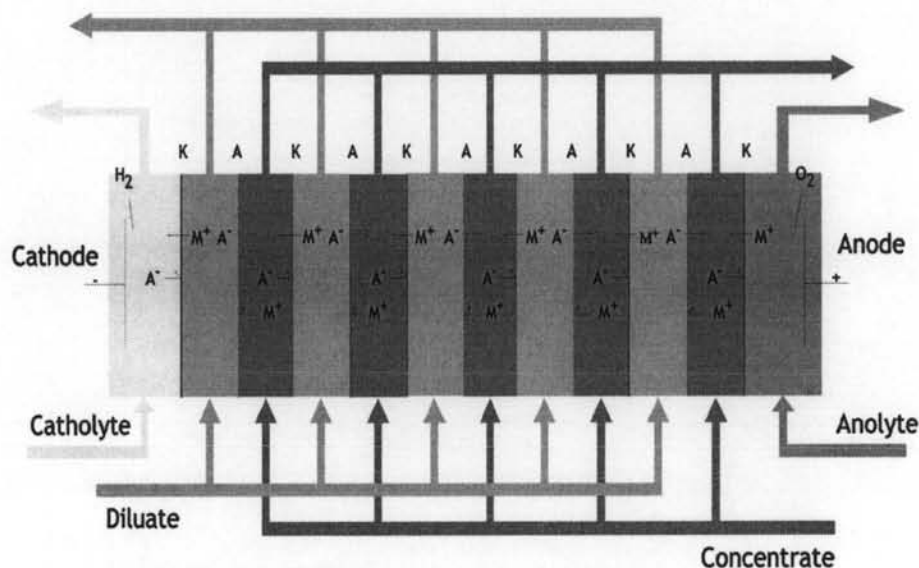


Figure 2-5 A diagram of the principle of the electrodialysis process [31].

K = Cation exchange membrane

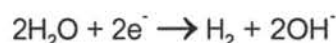
A = Anion exchange membrane

M⁺ = Cation and A⁻ = Anion

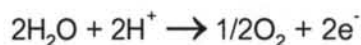
The electrodialysis cell consists of a stack of cation exchange membranes (CEM), anion exchange membranes (AEM) and spacers. The membranes are alternatively arranged between two end plates that contain the electrodes (cathode and anode) producing the electric potential. The cell pair in the ED cell stack is separated into one diluate compartment and one concentrate compartment [24, 27, 28]. The negatively charged ions in the solution are migrated toward the anode, passing through the AEM and retained by the CEM while the positively charged ions in the solution are migrated toward the cathode, passing through the CEM and retained by the AEM. In addition to the diluate solution and concentrate solution in the ED cell stack; there are

two electrode rinse solutions circulating around to the anode and the cathode. The catholyte solution contains excess cations, which typically release hydrogen gas due to reduction of the hydrogen ions at the cathode while the anolyte solution contains excess anions, which typically release typically oxygen gas due to the oxidation of the hydroxide ions. The reactions taking place at each electrode are illustrated below [26, 28-33].

At the cathode:



At the anode:



2.4.2 Ion exchange membranes (IEM)

Ion exchange membranes are used in charge separation process, of the electrodialysis. The characteristics of membranes include selectivity between ions of opposite charge, high ionic conductivity, low electrical conduction, long-term chemical stability, mechanical strength and resistance to fouling [26]. Ion exchange membrane is a synthetic membrane that is permeable to either positively or negatively charged ions in a solution, which can be classified into cation exchange membranes (CEM) and anion exchange membranes (AEM), respectively depending on the type of ionic group located on the polymer backbone of the membrane material. [26, 28-33].

The anion exchange membrane (AEM) is the membrane whose backbone contains positively charged functional group such as $-\text{NH}_3^+$, $-\text{RNH}_2^+$, $-\text{R}_2\text{NH}^+$, $-\text{R}_3\text{N}^+$, $-\text{R}_3\text{P}^+$ and $-\text{R}_2\text{S}^+$ etc., which allow anions to go through but reject cations. The cation exchange membrane (CEM) is the membrane whose backbone contains negatively charged functional group such as $-\text{SO}_3^-$, $-\text{COO}^-$, $-\text{PO}_3^{2-}$, $-\text{HPO}_3^-$ and $-\text{C}_6\text{H}_4\text{O}^-$ etc., which allow cations to go through but reject anions [28-33]. The characteristics of AEM and CEM are shown in Figure 2-6.

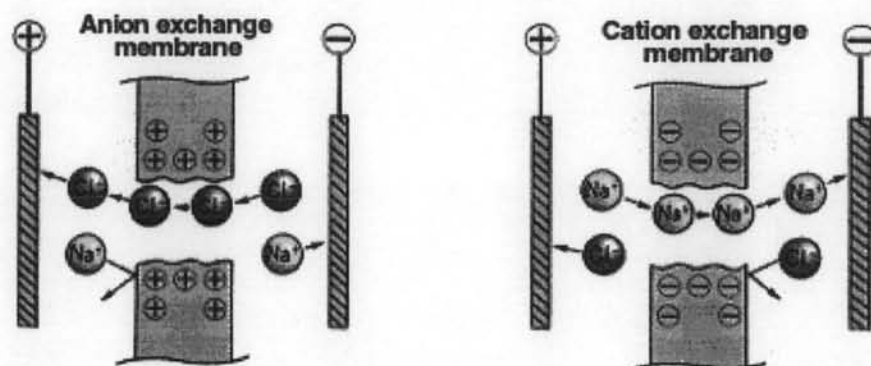


Figure 2-6 The characteristics of AEM and CEM [32].

AEM = Anion exchange membrane

CEM = Cation exchange membrane

2.4.3 Types of eletrodialysis process

The electro dialysis process is taken place inside the electro dialysis cell (stack). The solutions are circulated through the cell pairs from a storage vessel. The solution is not finally treated by passing the ED cell one time but needed to pass the ED cell several times. The electro dialysis process can be operated as batch mode and continuous mode operations (see Figure 2-7).

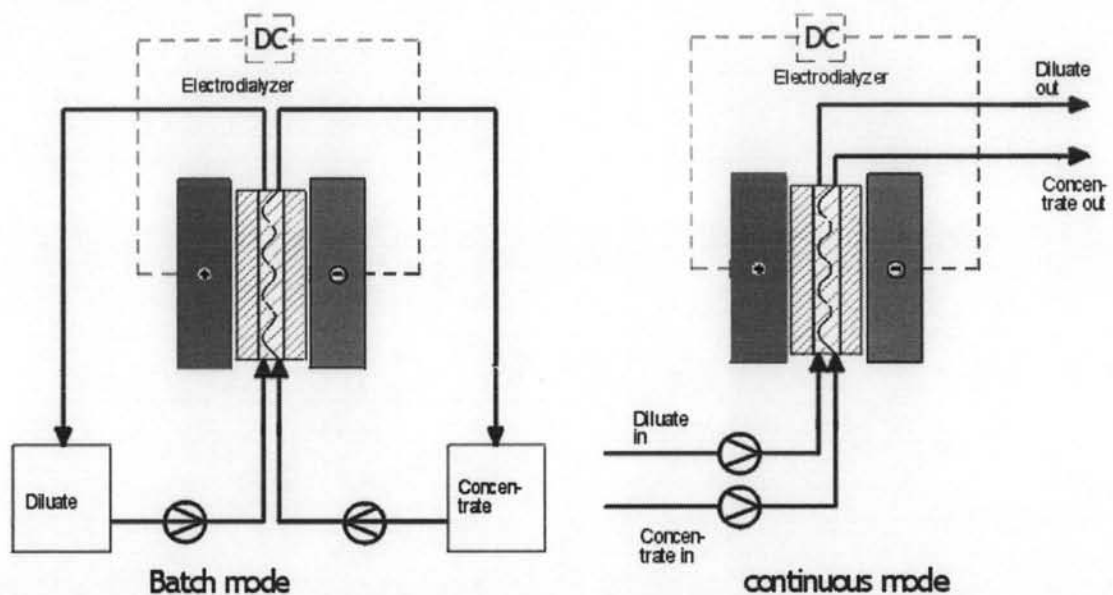


Figure 2-7 Diagrams of the batch mode operation and the continuous mode operation [31].

In batch mode operation, the diluate and/or concentrate solutions are recirculated through the electrodesalination stack until the final product or concentrate quality is achieved.

The advantages of using batch mode operations are that variations in recirculation rate do not effect performance, changes in feed solution only modify the production rate and changes in membrane properties only effect production rate.

The disadvantages of using batch mode operation are that membranes are never at equilibrium, variable current density through membranes and performance difficult to evaluate [30, 31, 34].

In continuous mode operation, the feed is passed through a sufficient number of stacks placed in series to produce the final desired product quality. Therefore, the module has to treat the solution in one go which needed a certain time and a certain velocity of solution corresponds with a certain process length.

The advantages of using continuous mode operations are that no recirculation reservoir, minimum control instrumentation, minimum power requirements and stage voltages readily adjusted to conform with actual stack resistances.

The disadvantages of using continuous mode operations are that feed water or temperature changes require plant adjustment, production rate must be balanced with flow velocity and increasing membrane resistance may put plant out of operation [30, 31, 34].

2.4.4 Evaluation of electrodialysis process

2.4.4.1 Current density (i) [39]

The current density is a measure of the density of electrical current. The current density is the driving force of the process since it determines the quantity of equivalent grams transported across the membranes. Current density can be used for determination applied voltage and total resistance of the membrane stack. Since total resistance of the membrane stack is not available. Current density can be used for calculation of a general definition. The assumption of constant concentration in the cell compartments as follow:

$$i = dl / dA_m = I / A_m$$

where:

I = current (A) which I can be measured in each run

A_m = active membrane area (cm^2)

i = current density (A cm^{-2})

2.4.4.2 Current efficiency (η) [46]

Current efficiency is the net transfer of chemical equivalents from the diluate to the concentrate compartments divided by the net passage of electrical equivalents across the membrane stack over some interval of time. The current efficiency is calculated from a material balance on the membrane stack and can be based on the conditions that exist in the diluate or the concentrate compartments. Current efficiency can be calculated as follow:

$$\eta = z F V_D \Delta C / N \int_0^t I(t) dt$$

where:

- η = current efficiency
- z = charge of the ion
- F = Faraday constant (96,500 A s mol⁻¹)
- V_D = diluate stream volume (L)
- ΔC = inlet concentration in diluate tank – outlet concentration in diluate tank (mol L⁻¹)
- N = number of cell pairs
- I = current (A)
- t = time (s)

2.4.4.3 Specific power consumption (SPC) [40]

The specific power consumption (SPC) is referred to the electrical energy over time that must be supplied to an electric appliance to maintain its operation which usually a result of energy used to perform the intended function of the device plus additional "wasted" energy. Specific power consumption (SPC) can be described as the energy needed to treat unit volume of solution which can be calculated as follow:

$$\text{SPC} = [E \int_0^t I(t) dt] / V_D$$

where:

E = Applied stack potential (V)

I = Current (A)

SPC = Specific power consumption (kW h m⁻³)

V_D = dilute stream volume (m³)

t = time (s)

2.5 Literature Reviews

Choi and Jeoung [35] studied the removal of zinc ions in wastewater by electrodialysis. The effect of operation parameters such as the initial concentration of diluate solution, the flow velocity and the applied voltage were studied by using the experimental electrodialysis model: TS-1-10 of Tokuyama. Zinc ions in solution were effectively removed by the CMX cation exchange membranes and AMX anion exchange membrane. It was found that increase in the initial concentration of diluate solution, the flow velocity and the applied voltage increased the removal ratio as well as increased the energy consumptions whereas the effect of the flow velocity on the energy consumption was unimportant.

Costa et al. [36] evaluated the electrodialysis process for the treatment of metal finishing wastewater. The cation exchange membrane Nafion[®] 450 and anion exchange membrane Selemion AMP were used in this work. In the metal finishing wastewater contained ions of Zn, Ni, Cu, Fe and Al as well as of Na and CN⁻ in alkaline pH was treated by ED. The results showed that each metallic ion exhibited a different rate of extraction from the treated solution and was dependent on the galvanostatic or potentiostatic operation mode. Zn, Ni and Cu ions can be extracted under galvanostatic control. For Al ions, higher extraction was observed when the experiment was conducted in a potentiostatic mode. Fe ions were exhibited an unexpected behavior not being removed in the same way as the other ions. The results of best extraction were obtained in 2-3 hours of treatment.

Tzanetakis et al. [37] compared the performance of ion exchange membrane for electrodialysis of nickel and cobalt. Two cation exchange membranes; the perfluorosulfonic Nafion[®] 117 and a new sulfonated PVDF membrane, were compared under similar operating conditions. The effect of flow rate, current density, salt concentration and temperature on the performance of each membrane was studied. The performance was characterized in terms of transport properties, current efficiencies and concentrations of metal ions transported through each membrane. The performance of the PVDF membrane was as good as; if not slightly better than, that of the commercial Nafion[®] 117. Corrugated membranes results in an increase of 60% on actual membrane area and produced a significant improvement in the amount of transported metal ions for both systems. The use of corrugated Nafion[®] 117 membrane in particular, enabled enhancement in current efficiencies for both system when the same amount of charge had passed.

Marder et al. [38] studied the cadmium electroplating wastewater treatment using a laboratory-scale electrodialysis system. The cation exchange and anion exchange membrane were Nafion[®] 450 and Selemion AMP, respectively. Removal of cadmium and cyanide was limited by cadmium compound precipitation on the cation exchange membrane. Successive changes of synthetic wastewater on the diluate compartment of the electrodialysis cell were applied to avoid the cadmium compound precipitation. This solution can be reused in the cadmium electroplating bath. When the wastewater contained other metals (copper, chromium or iron), reuse of cadmium and cyanide in the deposition bath is not possible, since transport of these former metal ions occurred with cadmium and cyanide ions. The results demonstrated that the percent extraction of cadmium and cyanide and the current efficiency (ce) were depended on the concentration of ions in the wastewater.

Güvenç and Karabacakoglu [40] studied the use of electrodialysis to remove silver ions from model solutions and wastewater. The experiment was used in the batch electrodialysis system and carried out using two different types of ion exchange membranes. Membranes were used in this work; i.e., type 1: anion exchange membrane (Ionac MA-3457) and cation exchange membrane (Nafion[®] 424) and Type 2: anion exchange and cation exchange membrane (A-501 and K-501). The effect of applied potential, pH value and initial silver concentration on the duration of electrodialysis and energy consumption were studied. Full removal of silver ions was achieved from model solution and the sample of rinse water. The removal rate of silver ions of 99.6% was achieved with ion exchange membrane type 1 after 110 min with energy consumption of 3.96 kW h m⁻³ whereas the removal rate of silver ions of 99.8% was achieved with ion exchange membrane type 2 after 90 min with energy consumption of 4.73 kW h m⁻³. Therefore, it is obvious that one can be preferred either relatively lower electrodialysis duration or lower energy consumption for the treatment of wastewater.

Bonev and Nenov [41] studied the copper recovery from acidic wastewater by ED. The MA-40 (anion exchange membrane) and MK-40 (cation exchange membrane) were utilized for electro dialysis process. The separation of sulfuric acid was achieved at short period of recirculation. At time of recirculation 4 hours the concentration of copper in concentration compartment was around 25 mg L^{-1} , while the concentration of sulfuric acid was 15 g L^{-1} . At higher extent of sulfuric acid was transferred into the concentration compartment, the selectivity of membranes towards heavy metals was not satisfactory.

Sadrzadeh et al. [42] studied the separation of different ions from wastewater at various operating conditions using electro dialysis. The effect of important factors on separation of the monovalent (Na^+), divalent (Cu^{2+} , Zn^{2+} and Pb^{2+}) and trivalent (Cr^{3+}) ions were studied. Two types of different membranes were used due to different ion exchange capacity. Membranes were used in this work i.e. type 1: anion exchange membrane (AR204SXR412) and cation exchange membrane (CR67MK111). It was found that increasing concentration, voltage and temperature improved cell performance but separation percent (SP) was decreased with increasing flow rate. The performance of an electro dialysis (ED) cell was almost independent on the type of ions but it was only depended on the operating conditions and the cell structure. It was confirmed by the experiments conducted on a mixture of ions that the SP of monovalent ions was larger than divalent and trivalent ions ($S_{\text{Cr}} < S_{\text{Cu}} < S_{\text{Zn}} < S_{\text{Pb}} < S_{\text{Na}}$). The ions of similar valence, SP was restricted by molecular weight and electrochemical activation energy of the ions ($S_{\text{Pb}} < S_{\text{Cu}} < S_{\text{Zn}}$).

The study of the literature reviews showed that the electro dialysis process could be used for the removal of several ions from the wastewater solution and the high removal rate (%) of several ions could be achieved in short period.