Chapter 1 : Introduction

1.1 Significance of Research

A wide variety of chemicals are discharged as waste by process industries in Malaysia. These wastes contain a high volume of hazardous chemicals which affect the environment. A proper handling and safe disposal of these wastes is necessary to prevent the deterioration of environmental quality and to reduce the risk to human health.

It has been found that approximately 487,100 MT of schedule wastes were generated in Peninsular Malaysia in 1995 (DOE, 1996). Heavy metals represent 7.12 % of the total waste volume. Hence, a proper treatment technology is essential for removal of heavy metals from industrial effluents.

In recent years, there has been a growing interest in Malaysia for the treatment of liquid effluents containing heavy metals. Studies on this area were mostly restricted to physico-chemical treatment of the effluents. In this work the feasibility of using membrane process for concentrating the effluents and recovering process water has been studied. It is concluded from the experimental data and the available information that recovery of high quality process water from effluents containing Ni and Cr by membrane process is more economical than ion exchange process for medium scale electroplating industries. Moreover, the concentrate which contains Ni and Cr in higher concentrations may be recycled to the process. It is envisaged that the membrane technology will be appropriate for small and medium scale electroplating industries in Malaysia for treating wastewater.

1.2 Industrial Wastewater and Heavy Metal Pollution

There as been a growing concern in Malaysia about pollution of heavy metals in water. Industries such as electroplating, metal finishing, circuit board production and so on contribute large amount of heavy metals as pollutant to the environment (Lee and Hong, 1995). Metal finishing industry produce a large quantity of heavy metals as waste (DOE, 1985; 1989). In addition to heavy metals these waste streams contain acids, bases, solvents and oils. Table 1.1 shows the typical waste components found in metal finishing industries and Table 1.2 shows the characteristic of the wastewater in Malaysia.

Table 1.1: Metal finishing operations and typical wastes

Source	Waste
Degreasing	Solvents, oils
Cleaning	Alkalis, metals, chelates, solvents
Pickling	Acids, metals, chromates
Metal plating	Acids, metals, cyanide, alkalis, chelates
Etching	Metals, acids, chelates
Conversion coating	Chromate, phosphates, metals

(Higgins, 1989)

Table 1.2: Characteristics of metal finishing wastewater

Metal Finishing Operation	Some Common Constituents
Acid pickling bath	Fe, Cu, Zn, Ni, Cd
Alkaline pickling and cleaning bath	Al, Zn
Acid and alkaline plating bath	Cu, Zn, Ni, Sn, Cd
Chromic acid-based bath	Cr, Al, Zn, Cd
Phosphoric acid-based bath	Fe, Zn, Mn
Metal polishing bath	Cu, Ni, Fe, Al
Cyanide solutions	Cu, Zn, Cd, other precious metals

(Pickett, 1978)

According to Rosnani (1986), industries are the major source of metal pollution in rivers. In addition to this, a study by Babji *et al.* (1986) on tissues of fishes collected from the downstream of heavy industries, further suggests that industries mostly contribute heavy metals in wastewater. The DOE Water Quality Monitoring Program in 1992 confirmed that heavy metal pollution in rivers was due to industrial activities (DOE, 1993). Although several Acts and Regulations have been legislated to control pollution (see Appendix 1), the degree of heavy metal pollution is still on the rise.

1.3 Various Techniques of Treatment Technology

There are various techniques for separating heavy metals from effluents generated by industries. The physico - chemical treatment which is the conventional technology employed to treat heavy metal waste includes chemical precipitation, ion exchange, evaporation and membrane technology (Volesky, 1987).

1.3.1 Chemical Precipitation

The removal of heavy metals can be accomplished by chemical precipitation processes in which metal ions in solution are converted to a solid phase or sludge by the addition of chemicals. The sludge, usually comprising insoluble hydroxides, is dewatered and stabilized prior to disposal. It is important to neutralize the pH of the effluent so that metal hydroxides are produced. The yield of insoluble precipitates from this neutralization is dependent upon the concentration of heavy metals in the effluent and the pH. Each metal has an optimum pH at which it will almost completely precipitate (Chang, 1996). The high volume of sludge which is difficult to dispose leads to the generation of hazardous pollutants. Furthermore, the use of stabilizing agents such as cement and fly ash before sludge disposal increases the disposal cost dramatically (Darnall, 1991).

1.3.2 Ion Exchange

Ion exchange is a process in which mobile ions are held by electrostatic forces to the solid surface of the resin and the exchanged ions from the resin become mobile and enters the solution. Ion exchange resins are made in the form of very small spheres or beads, so that when packed in columns, they present an enormous surface area to the effluent and each bead has on its surface thousands of functional groups (Robert, 1991). The use of ion exchange resins can be regenerated and used over and over again. Cationic resins are regenerated by mineral acids.

However, ion exchange process can remove ionized species. Thus unionized materials still remain in the solution. It also requires a large volume of resins for treatment of concentrated effluents. A high concentration of salt residue is produced in the regeneration process (Higgins, 1989). Furthermore, the presence of divalent calcium and magnesium in electroplating wastewater can compete with the heavy metals for the binding sites on the resins. The binding of these ions to the resins limits the removal of heavy metals from the wastewater (Darnall, 1991).

1.3.3 Evaporation

Evaporation is the oldest method for the recovery of metal salts from electroplating wastewater. Most electroplating solutions require regular additions of chemicals to replace materials which are lost as drag-out. As a process, evaporation is energy intensive but produces effluent with low metal concentrations and meets the discharge standards (Higgins, 1989).

1.4 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. The 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. Table1.3 lists the commercially important membrane processes and their applications.

Table 1.3 : 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)

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 pervaporation. Based on applications, membrane filtration is classified as follows (Figure 1.1).

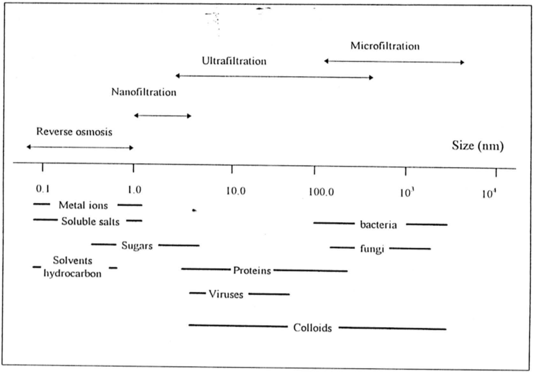

Figure 1.1 : Application size range of membrane filtration processes.

1.4.1 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 is 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 thinfilm 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. Reverse osmosis systems would achieve economic benefits associated with chemical recovery and the reduction of the cost of hazardous waste disposal (Robert, 1991).

1.5 Comparison of Different Separation Technologies

A comparative study on four different methods of heavy metal treatment has been done by Chang (1996). The study involves the technical and economic analyses of reverse osmosis, ion exchange and precipitation processes which are summarized in Table 1.4. The total annual cost includes the cost of operation , maintenance, labour, chemicals, regulatory compliance and waste disposal (Chang, 1996).

Table 1.4: Evaluation of three different separation technologies

Evaluation	Reverse osmosis	Ion Exchange	Precipitation	Evaporation
Waste quantity	low	low - medium	substantial	low
Water recovery	high	high	low	medium
Effluent TDS	20 - 35 ppm	1 - 10 ppb	1000-3000 ppm	≈ 50 ppm
Operation / Maintenance	≈ $3K / yr.	≈ $3K / yr.	$5 - 8K / yr.	≈ $3K / yr.
Chemical usage	low	medium	medium - high	zero - low
Permit	no	no	yes	yes
Energy	low	low	medium	medium - high
Space	medium	medium	large	small - medium
Labour	medium	medium	high	high
Overall	good	good	fair	fair - good
Capital costs and capacity	$30 - 40K 20 litres / min.	$25 - 40K 20 litres / min.	$40 - 65K 20 - 50 litres / min.	$20 - 40K 200 - 400 litres / hr

(Chang, 1996)

1.6 Objective and Scope of Research

This study covers the recovery of heavy metals (i.e. nickel and chromium), and the production of high quality water from effluents containing Ni and Cr salts. This technology is very important not only from the view point of environmental protection but also for the recovery of valuable materials.

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

The objectives of this study are to establish following.

1) The relationship between permeate flow rate and trans-membrane pressure drop (TMP) for different feed concentrations.
2) The effect of TMP on concentration of heavy metals in the permeate.
3) The economic feasibility of reclaiming high quality process water from the effluent.

The other objective was to gather experimental data for the modification of surface force pore - flow (SFPF) model developed by Sourirajan (1981). This is one of the most established models for prediction of separation efficiency in RO processes. This model assumes uniform pore size on the membrane surface. The present work is aimed at necessary modification of this model by considering the effect of pore size distribution on the separation efficiency of sodium chloride (aqueous). The application of SFPF model to aqueous nickel and chromium salts is not included in the scope of the present work.