Separation of Zinc Chloride ($ZnCl_2$) Metal Using Membrane Process

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CERTIFICATION OF APPROVAL

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Approved by,

(   )

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(MOHAMAD HAZEEM BIN MOHD)

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ABSTRACT

Nowadays, heavy metals are widely utilized as a main material to produce catalyst in petrochemical industry and they are also very harmful chemical substance that needs to be treated before can be discharged. The objective of this research is to investigate the separation behavior of heavy metal using membrane process. In this study, three commercial membranes; AFC 99 (Reverse Osmosis-RO), AFC40 (Nanofiltration-NF) and CA 202 (Ultrafiltration-UF) membranes were tested to determine the flux and salt rejection in aqueous solution. Zinc chloride ($ZnCl_2$) was used in the experiments to prepare the aqueous solution. Effects of cross flow velocity, pressure, types of membranes and feed concentration towards the flux and salt rejection of those membranes were investigated. Experiments showed that the cross flow velocities had a significant effect on permeate flux values. In addition, the permeate flux increases almost in linear form as the cross flow velocity increased. Similarly, permeate flux increased as operating pressure was increased. Other parameters that affect the flux are types of membrane. From the result, the CA 202 membrane produced the highest flux followed by AFC 40 and AFC 99 respectively. For concentration effect, the flux decreased with increasing of $ZnCl_2$ concentration. Variations in pressure and cross flow velocity also affected the salt rejection, which decreased with increasing of feed concentration. Salt rejection at low cross flow velocities was lower than those conducted at high cross flow velocities and independent of the pressure. From the experiment, the AFC 99 has the highest rejection recorded which was 98% followed by AFC 40 (84%) and CA 202 (58%) membranes respectively. This work shows that the membrane separation processes, particularly AFC 99 (RO), can be used to selectively remove $ZnCl_2$ from wastewater.

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND OF STUDY

Natural gas and crude distillates such as naphtha from petroleum refining are used as feedstock to manufacture a wide variety of petrochemicals that are in turn used in the manufacture of consumer goods. The basic petrochemicals manufactured by cracking, reforming, and other processes include olefins (such as ethylene, propylene, butylenes, and butadiene) and aromatics (such as benzene, toluene, and xylene). Thus, much of the present day, catalytic process is widely used and become the backbone in petrochemical manufactured mainly to increase the production rate of reaction. Indeed, heavy metals like Ni, Mo, Co, Rh, Pt, Pd, etc., are widely utilized as a catalyst in petrochemical industries. The reason heavy metal is used as a catalyst is due to the characteristic of the heavy metal catalyst itself which is very active for catalyzing various reactions (Farrauto and Bartholomew, 1997).

However, after a periodical time use of catalyst, it will become inactive due to the poisoning effect of foreign material and impurities, which deposit on the surface of the catalyst. Poisoning effect involves strong chemical interaction of a component of the feed or products with active sites on the catalyst surface. Catalysts are also deactivated by sintering which causes loss of active surface area and therefore lowers catalytic activity (B. Singh, 2009). In general, catalysts deactivated by thermal degradation, phase separation or phase transformations, cannot be reactivated easily and therefore replacement of the catalyst is necessary. In such cases, fresh catalysts have to be substituted and the spent catalyst will be carry away to the wastewater facilities.

Heavy metals are natural components of the Earth's crust. Most of Heavy metals are very harmful and dangerous to people and environment. They cannot be degraded or destroyed. Some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. Nevertheless, at higher concentrations they can lead to poisoning. Due to its dangerous and hazardous, the heavy metal treatment in industry must be taken into consideration before can be discharge to environment.

Environmental pollution decrease is a major concern in modern petrochemical industry. Nowadays, it is strictly prohibited to discharge the contaminants with high concentration to environment freely. In response to the growing problems, the International Petroleum Industry Environment Conservation Association (IPIECA) and state government which is Environmental Quality Act 1974 (EQA 1974) have instituted environmental regulations to protect the quality of surface and ground water from heavy metal pollutants.

1.2 PROBLEM STATEMENT

Nowadays, catalyst is widely use in petrochemical industrial mainly to enhance the production rate of the process. Most catalyst used is heavy metals. After a period of time, the catalyst will become inactive and need to be substituted. The inactive catalyst will be carry away to the wastewater treatment. Due to heavy metal's ability to increase chemical oxygen demand (COD) level of the effluent, the separation of heavy metals in wastewater is compulsory and must meet the regulatory requirement.

The conventional method of heavy metals separation is by using precipitation. However, this method needs neutralization of the solution. The disadvantages of this method are it consumes amounts of reagents for neutralization of the acid and precipitation of metals, as well as generation of large amounts of valueless liquid wastes (Zielinski, Buca and Famulski, 1998). In order to avoid higher negative impact to environment, researchers have been conducted on various methods and possibilities of separation as an alternatives approach. One of them is by using membrane process.

1.3 OBJECTIVES AND SCOPE OF THE STUDY

The objectives of the research project are:

- To investigate the separation behavior of heavy metals using membrane process.
- To investigate the factors affecting the separation of heavy metals.
- To evaluate the parameters of membrane performance to reach the optimum separation of wastewater containing heavy metals
- To compare the performance of different type of membrane used

The scope of study for the research is to study on the characteristic and behavior of the membrane as well as the effects of applied pressure, cross flow velocity, feed concentration and types of membrane that suite to separate the selected heavy metals.

CHAPTER 2: LITERATURE REVIEW

2.1 INDUSTRIAL WASTEWATER

Wastewater can be defined as a combination of the liquid or water-carried wastes removed from residence, institutions and commercial and industrial establishment, together with such groundwater, surface water, and storm water (Metcalf and Eddy, 2004). Wastewater that accumulates in the stream will decompose and this will lead to nuisance condition including the production of malodorous gases. Wastewater also contains several nutrients, which can stimulate the growth of aquatic plant. However, high concentration of contaminant will cause mutagenic and carcinogenic to living things.

2.1.1 Wastewater Characteristics

Industrial wastewater is characterized in term of physical, chemical and biological constituent. The important of physical constituents are color, temperature, density and conductivity content. The chemical constituents of wastewater are divided into two classes which are inorganic and organic. For organic chemical classes, the characteristic that been considered are chemical oxygen demand (COD), nitrogenous oxygen demand (NOD), total organic compound (TOC) and etc. For inorganic chemical classes, the characteristic that been considered are pH, alkalinity, chloride, metals, various gases and etc. Lastly, the biological constituent may contain of coli form organism, specific microorganisms and toxicity (Metcalf and Eddy, 2004).

Wastewater treatment was developed to treat and remove the physical, chemical and biological contaminants from water to ensure protection of public health and environment. The effluent that discharged into any inland waters shall be analyzed and have parameter limits based on Environmental Quality (Sewage and Industrial Effluent) Regulation, 1979 - Regulation 8. Parameter limits of effluent to be discharged into inland waters (see appendix A).

(1) No person shall discharge effluent, analyzed in accordance with regulation 7, which contains substances in concentrations greater than those specified as parameter limits of-

- *(a) Standard A, as shown in the third column of the Third Schedule, into any inland waters within the catchment areas specified in the Fourth Schedule; or*
- *(b) Standard B, as shown in the fourth column of the Third Schedule, into any other inland waters.*

2.1.1.1 Temperature

The temperature of wastewater is commonly higher compare to the local water supply, because of the addition of warm water from households and industrial activities. The temperature of water is very important parameter because of its effect on chemical reactions and reaction rates, aquatic life, and the suitability of the water for beneficial uses (Metcalf and Eddy, 2004). The optimum temperatures for wastewater to be discharge are in the range from 25°C to 35°C which is suitable for bacterial activity.

2.1.1.2 pH Value

The typical ranges of pH that suitable for the existence of most biological life are 6 to 9 which has minimum impact to environment. Wastewater with an extreme concentration of hydrogen ion is difficult to treat by biological means and if the concentration is not altered before discharge, the wastewater effluent may alter the concentration in the natural water (Metcalf and Eddy, 2004).

$$pH = -\log_{10}[H^+]$$

2.1.1.3 Biochemical Oxygen Demand (BOD)

Biological Oxygen Demand (BOD) is one of the most common measures of pollutant organic material in water. BOD indicates the amount of organic matter present in water. Therefore, a low BOD is an indicator of good quality water, while a high BOD indicates polluted water. This determination involves the measurement of the dissolved oxygen used by microorganism in the biochemical oxidation of organic matter. If the oxygen available is sufficient, the aerobic biological decomposition of an organic waste will continue until all of the waste is consumed (Metcalf and Eddy, 2004).

2.1.1.4 Chemical Oxygen Demand (COD)

The COD test is used to measure the oxygen equivalent of the organic material in wastewater that can be oxidized chemically using dichromate in an acid solution (Metcalf and Eddy, 2004). COD measurements are commonly made on samples of waste waters or natural waters contaminated by domestic or industrial wastes. Chemical oxygen demand is measured as a standardized laboratory assay in which a closed water sample is incubated with a strong chemical oxidant under specific conditions of temperature and for a particular period of time.

2.2 HEAVY METALS

Heavy metals are the metals of relatively high density or of high relative atomic weight. The specific gravity of the heavy metals is normally greater than five. Some of the metals are essential for many biological systems including humans at certain concentrations. However, they can exert toxic effects at high concentration. The examples of heavy metals are lead (Pb), zinc (Zn), copper (Cu), chromium (Cr), mercury (Hg) and nickel (Ni). These heavy metals cannot be degraded or destroyed.

2.2.1 Effects of Heavy Metals to Humans

Heavy metals are considered as one of the serious environmental contaminants because of their high toxicity. Heavy metals normally enter a water supply by industrial waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers and seas. They affect human health because the body cannot break it down upon ingestion or inhalation. Thus, they can lead to poisoning and harmful to human body.

Table 2-1: Effect of Heavy Metals to Humans

Heavy Metals	Source	Effects
Chromium	Metal alloys and pigments for paints, cement, paper, rubber, and other materials.	Low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage too circulatory and nerve tissue.
Copper	Drinking water from copper pipes, as well as from additives designed to control alga growth.	Anemia, liver and kidney damage, stomach and intestinal irritation
Lead	Batteries, radiators for cars and trucks, paint	Problems in the synthesis of hemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system

(M. Stoeppler, 1992)

2.2.2 Heavy Metals in Wastewater

Catalyst technology can be classified into three areas of important activity in the world which are petroleum refining, chemical production and environmental cleanup. Catalyst usage is a very important in petrochemical manufactured generally to increase and enhance the production rate of reaction and selectivity of a chemical reaction. Indeed, most of heavy metals like Ni, Mo, Co, Rh, Pt, Pd, etc., are widely utilized as a catalyst in petrochemical industries. This is due to the characteristic of the heavy metal catalyst itself which has active phases (metals, metal oxides and metal sulfides). These active phases are typically dispersed in the pores of supports in the form of microcrystallites of 1-50 nm diameter; the surfaces of these crystallites contain sites active for catalyzing several of reactions (Farrauto and Bartholomew, 1997).

However, after a periodical time use of catalyst, it will become inactive due to the poisoning effect of foreign material and impurities, which deposit on the surface of the catalyst. Poisoning effect involves strong chemical interaction of a component of the feed or products with active sites on the catalyst surface. Catalysts are also deactivated by sintering which causes loss of active surface area and therefore lowers catalytic activity (B. Singh, 2009). In general, catalysts deactivated by thermal degradation, phase separation or phase transformations, cannot be reactivated easily and therefore replacement of the catalyst is necessary. In such cases, fresh catalysts have to be substituted and the spent catalyst will be carry away directly to the wastewater facilities.

2.2.3 Technology Used to Treat Heavy Metals from Wastewater

Heavy metals are among the most harmful constituents of industrial wastes and effluents. Basically the treatment process of heavy metals from industrial wastewater is a must due to their toxicity to many living things. On the other hand, heavy metals are valuable materials and should be recovered. Nowadays, there are many treatment processes for heavy metal removal from industrial wastewater which are chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion–exchange and adsorption (Oboh, Aluyor and Audu, 2009).

The effluent that discharged into any inland waters in Malaysia shall be analyzed and have parameter limits based on Environmental Quality (Sewage and Industrial Effluent) Regulation, 1979 - Regulation 8. Parameter limits of effluent to be discharged into inland waters (see appendix A). All companies in Malaysia that has chemical operation and wants to discharge their waste must comply with the guidelines provided by EQA.

2.2.3.1 Chemical precipitation

Chemical precipitation is the most commonly used method for the treatment of industrial wastewater containing heavy metals. However, this process requires a large amount of treatment chemicals to decrease the heavy metals to levels imposed by the regulations. A major disadvantage with precipitation process is it will produce a lot of sludge (Hilal, Nidal and Al-Abril, 2006). In addition, the sludge produced from the precipitation process has to be subjected to dewatering and disposal into landfills, which adds an additional cost a lot to the treatment process.

2.2.3.2 Adsorption by using Activated Carbon (CAC)

Besides that, studies on the treatment of effluent behavior of heavy metal have revealed that the adsorption method is to be a highly effective technique for the removal of heavy metal from wastewater and activated carbon (CAC) has been widely used as an adsorbent (Saifuddin & Kumaran, 2005). However, due to its extensive use in wastewater treatment industries CAC remains an expensive material for heavy metal removal

2.2.3.3 Ion-Exchange

Ion-exchange is another conventional method to treat heavy metals in wastewater. Ion-exchange resins are polymers that are capable of exchanging particular ions within the polymer with ions in a solution that is passed through them. The use of ion-exchange results in highly successful metal recovery from pre-treated waste. However, these ion exchangers are not sufficiently selective to remove certain metals from large volumes of accompanying metals and thus metal-selective resins are being developed (Cortina et al., 1998). Unfortunately, these methods are relatively expensive, requiring elaborate equipment with high operation costs, such as the regeneration or disposal of the regeneration liquid and the spent resin, and large energy requirements. Resin usage causes a large environmental burden in terms of disposal (Lee et al., 1998).

2.3 MEMBRANE PROCESS

Membrane or semi-permeable membrane is a thin of material that is capable of separating materials as a function of their physical and chemical properties when driving force is applied across the membrane (Mallevialle, Odendaal, Wiesner, 1996). In separation applications, the role of the membrane is to serve as a selective barrier that will allow the passage of certain constituents found in the liquid (Cheryan, 1998). In membrane separation, the range of particle sizes is extended to include dissolved constituents typically 0.0001 to 0.1 μm. For certain substances can pass through the membrane, while other substances are caught. The substance that pass through is called as permeate while and retentate is a substance that cannot pass through the membrane.

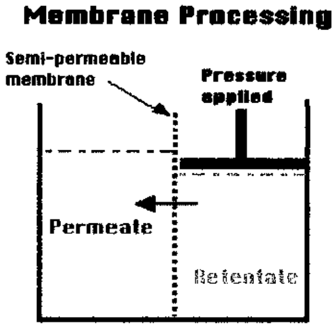


FIGURE 2-1: separation of a mixture by using membrane

2.3.1 Membrane Process Classification.

Membrane classes can be classified in a number of different ways including the type of material from which the membrane is made, the nature of the driving force, the separation mechanism and the nominal size of the separation achieved. Membrane process includes as follows:

- Reverse osmosis (RO)
- Microfiltration (MF)
- Ultrafiltration (UF)
- Nanofiltration (NF)
- Electrodialysis (ED)

The following table gives an overview and classification of membrane separation:

Table 2-2: General characteristics of membrane processes

Membrane process	Membrane driving force	Operating structure (pore size)	Typical operating range, µm	Permeate description	Typical constituents removed
Microfiltration	Hydrostatic pressure difference or vacuum in open vessels	Macrospores (>50nm)	0.08-2.0	Water + dissolved solutes	TSS, turbidity, protozoan and oocysts and cysts, some bacteria and viruses
Ultrafiltration	Hydrostatic pressure difference	Mesopores (2-50nm)	0.005-0.2	Water + small molecules	Macromolecules, colloids, most bacteria, some viruses, proteins
Nanofiltration	Hydrostatic pressure difference	Micropores (<2nm)	0.001-0.01	Water + very small molecules, ionic solutes	Small molecules, some hardness, viruses
Reverse osmosis	Hydrostatic pressure difference	Dense (<2nm)	0.0001-0.001	Water, very small molecules ionic solutes	Very small molecules, color, hardness, sulfates, nitrate, sodium, other ions
Dialysis	Concentration difference	Mesopores (2-50nm)	-	Water + small molecules	Macromolecules, colloids, most bacteria, some viruses, proteins
Electrodialysis	Electromotive force	Micropores (<2nm)	-	Water + ionic solutes	Ionized salt ions

(Metcalf and Eddy, 2004).

Based from the book entitled 'Transport Processes and Separation Process Principles', these are the classification of the membrane processes.

I. Gas diffusion in porous solid

In this type a gas phase is present on both sides of membranes, which is micro porous solid. The rates of molecular diffusion of the various gas molecules depend on the pore sizes and the molecular weights

II. Liquid permeation or dialysis

In this case, the small solutes in one liquid phase diffuse readily because of concentration differences through a porous membrane to the second liquid (or vapor) phase. Passage of large molecules through the membrane is more difficult.

III. Gas permeation in membrane

The membrane in this process is usually polymer such as rubber, polyamide and so on, and is not a porous solid. The solute gas first dissolves in the membrane and then diffuses in the solid to the other gas phase. Examples of membrane separations are helium being separated from natural gas and nitrogen from air. Separation of gas mixture occurs because each type of molecules diffuses at different rate through the membrane.

IV. Reverse osmosis

Reverse Osmosis is a water treatment process whereby dissolved salts, such as sodium, chloride, calcium carbonate, and calcium sulphate may be separated from water by forcing the water through a semi-permeable membrane under high pressure. The water diffuses through the membrane and the dissolved salts remain behind on the surface of the membrane (Aqua Pure, 2009).

V. Ultra filtration membrane process

In this process, pressure is used to obtain a separation of molecules by means of a semi permeable polymeric membrane. The membrane discriminates on the basis of molecular size, shape, or chemical structure and separates relatively high molecular weight solutes.

VI. Microfiltration membrane process

In microfiltration, pressure driven flow through membrane is used to separate micron size particles from fluids.

VII. Gel permeation chromatography

The porous gel holds back diffusion of the high molecular weight solutes. The driving force is concentration.

2.3.2 Good Membrane Properties

Below are the key properties in determining membrane performance:

- Good permeability and high selectivity
- Cost effective and free from any defects
- Good mechanical, chemical and thermal stability under operating conditions
- Low fouling tendencies and good compatibility with the operating environment

2.3.3 Theory of Membrane Process

When two adjacent volume elements with slightly different level of concentration are separated by an interface, due to the difference in the number of molecules in each volume element, more molecules will move from the concentrated side to the less concentrated side of the interface which is the opposite direction. This concept was first recognized by Fick theoretically and experimentally in 1855 (Baker, 2000). According to Fick's law of diffusion,

$$Ji = -DiC\ \frac{d(\mu i/RT)}{dx} \qquad (2.1)$$

Where *Ji* is the mass of component *i* transported or flux, kmol/m2.s, *Di* is diffusivity of component *i*, m2/s, *C* is concentration, kmol/m3, µ*i* is chemical potential of the substance diffusing, J/kmol.K, and *x* is distance, m. In most cases, activity coefficients are close to one, and Fick's first law is written as:

$$Ji = -Di\ \frac{dci}{dx} \qquad (2.2)$$

Assuming *Di* is constant, and in particular that it is independent of *Ci*, and that the concentrations in the fluid phases are in equilibrium with the membrane. Fick's law may be written:

$$Ji = -Di\ \frac{(Cf - Cp)}{z} = Di\ \frac{\Delta C}{z} \qquad (2.3)$$

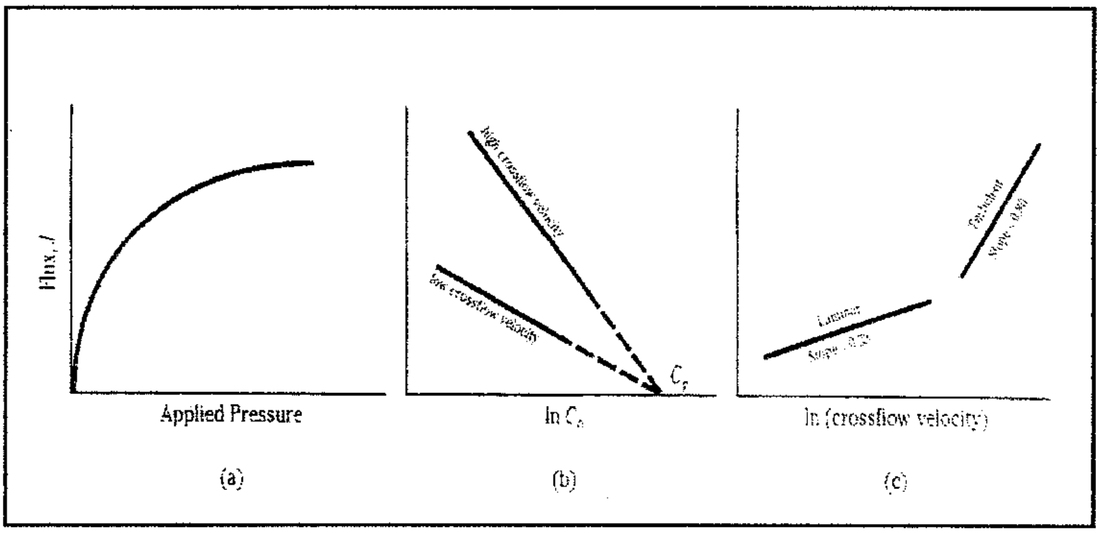


FIGURE 2-2: Typical dependence of membrane flux. (a) Applied pressure difference, (b) Solute concentration, (c) Cross-flow velocity

Solution containing macromolecular gel-forming solute will form a gel on the surface of the membrane. The gel formation will contribute to formation of dynamic membrane. Due to convective flux through the membrane a concentration of the solute at the surface C_w increases and eventually reaches a gel formation concentration C_g (FIGURE 2.2(a)). The flux, J through the membrane depends on a concentration according to the relationship;

$$J = k \, . \ln \frac{C_w}{C_b} \qquad (2.4)$$

Combining equation (2.1) and (2.4),

$$ln \frac{C_w}{C_b} = \frac{\Delta P}{v(R_m + R_p)k} \qquad (2.5)$$

As long as concentration C_w is less than C_g, C_w, will increase with pressure, but the moment C_w, equals C_g, an increase in ΔP brings about an increase of the layer resistance R_p, and the flux will no longer vary with pressure

Assuming no fouling effect, the membrane resistance, R_m can be calculated from the flux equation below;

$$J = \frac{\Delta P}{v \, . R_m} \qquad (2.6)$$

The slope obtained from the plot of flux, J versus ΔP is equal to $\frac{1}{v \, . R_m}$.

The retention of any solute can be expressed by the *rejection coefficient, R.*

$$R = \frac{\ln (C_f/C_o)}{\ln (V_o/V_f)} \qquad (2.7)$$

Where C_f = final mecrosolute concentration in the retentate

C_o = initial macrosolute concentration

V_o = initial volume

V_f = final retentate volume

This expression assumes complete mixing of retentate seldom accomplished due to concentration polarization. The apparent rejection coefficient depends on factors affecting polarization including UF rate and mixing. For material entirely rejected, the rejection coefficient is 1 (100%), for freely permeable material it is zero.

The percentage *rejection coefficient, R* also can be expressed as follow;

$$R = \frac{C_f - C_p}{C_f} \text{ x } 100\% \qquad (2.8)$$

2.3.4 Factors Affecting Membrane Performance

Concentration Polarization (CP)

The concentration polarization reduces the permeating component's concentration difference across the membrane, as a result the flux and membrane selectivity will be decrease. CP can significantly affect membrane performance in RO but it is usually controlled. Unlike in UF and electro dialysis process whereby the membrane performance is seriously affects. This is because, in RO, the solutes are dissolved salts whereas in UF, the solutes are colloids and macromolecules. The diffusion coefficients of these high-molecular-weight components are about 100 times smaller than those salts.

Pressure

Feed water pressure affects both water flux and salt rejection of membrane. Water flux across membrane has direct relationship increasing feed water pressure. Increased feed water pressure also results in increased salt rejection but the relationship is less direct than water flux. However, there is an upper limit to the amount of salt that can be excluded increasing feed water pressure. Above a certain pressure level, salt rejection no longer increases and some salt flow remains coupled with water flowing through the membrane.

Salt Concentration

Osmotic pressure is a function of the type and concentration of salts or organics contained in water. As a salt concentration increases, the osmotic pressure will increase too. If the feed pressure remains constant, higher salt concentration results in lower membrane flux. The increasing osmotic pressure offsets the feed water driving pressure and as the water flux declines, salt rejection also decrease.

Temperature

As water temperature increases, water flux increase almost linearly due primarily to the higher diffusion rate of water through the membrane. Increased feed water temperature also results in lower salt rejection or higher salt passage. This is due to a higher diffusion rate for salt through the membrane.

2.3.5 Membrane Application

Membrane technologies have seen a significant growth and increase in application in the last two decades. Membrane systems are now available in several different forms and sizes, each uniquely fitting a particular need and application. The increased use of membrane is expected to continue well into the future. Typical applications of membrane separation are discussed.

Nowadays, most of the RO systems installed in industry are desalinating brackish water or seawater. The typical salinity of brackish water is between 2000 and 10000 mg/L. the recommendation from World Health Organization (WHO) for potable water is 500 mg/L. Early cellulose acetate membranes could achieve this removal easily, so treatment of brackish water was one of the first successful applications of RO (Baker, 2000). Besides that, other applications of

RO process are seawater desalination, ultrapure water and wastewater treatment. In the 1960s and early 190s, it was thought that ultra filtration (UF) would be widely used in tertiary treatment of municipal wastewater. This application did not materialize. Ultra filtration is too expensive to be used for this application, but it is used to treat small, concentrated waste streams before they mixed with drain stream. Some UF membranes with small pore sizes have been used to remove dissolved compounds with high molecular weight such as colloids, protein, and carbohydrates. Normally, UF is used for production of high-purity process rinse water in industrial application (Metcalf and Eddy, 2004).

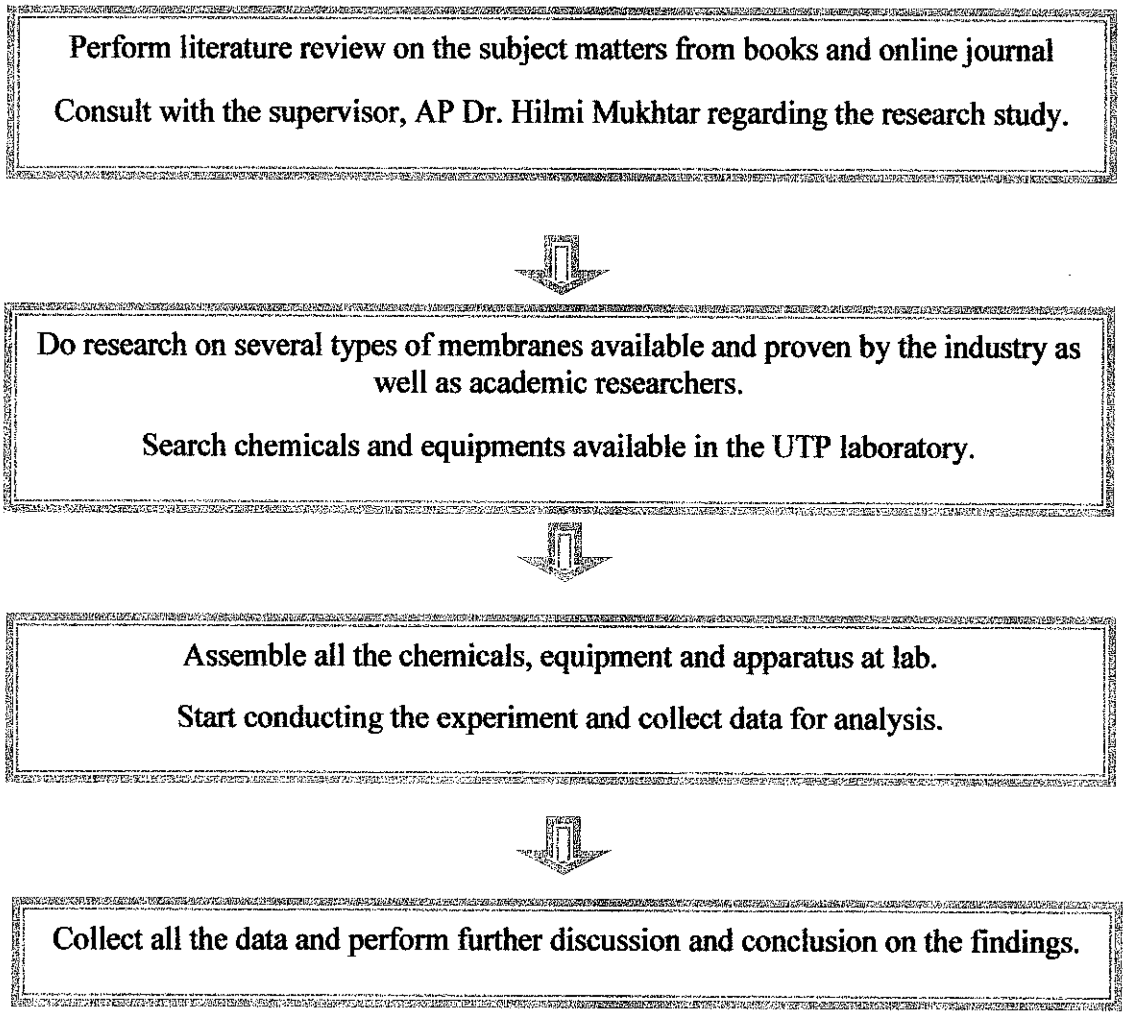
Microfiltration membranes are the most plentiful on the market, much cheaper, and commonly made of poly-propylene, acrylonitrile, nylon and polytetrafluoroethylene. In advance treatment application, microfiltration has been used as a replacement for depth filtration to reduce turbidity, remove residual suspended solids, and reduce bacterial effective disinfection.

Membrane Bioreactor (MBR) and tertiary treatment systems are the best available technologies for communities that are concerned about protecting the environment and preserving potable water supplies. MBRs provide cost-effective solutions that will meet or exceed discharge standards for years to come. Effluent from these systems is of such high quality that it can be safely discharged into the most sensitive aquatic environments or reused in irrigation, industrial processes, or groundwater recharge.

CHAPTER 3: MATERIALS AND METHODS

3.1 RESEARCH PLANNING

In this chapter, the writer will focus on the project planning throughout the semester. Below is the flow chart of methodology that will be implemented throughout this research study.



Perform literature review on the subject matters from books and online journal

Consult with the supervisor, AP Dr. Hilmi Mukhtar regarding the research study.

Do research on several types of membranes available and proven by the industry as well as academic researchers.

Search chemicals and equipments available in the UTP laboratory.

Assemble all the chemicals, equipment and apparatus at lab.

Start conducting the experiment and collect data for analysis.

Collect all the data and perform further discussion and conclusion on the findings.

3.2 MATERIALS

3.2.1 Membrane

The membrane Test Unit is specially designed to carry out the membrane processes that are widely used in biotechnology and process industries such as RO, UF and NF. The process diagram is illustrated in APPENDIX D. UF membranes are usually specified in terms of their molecular-weight-cut-off, MWCO, whereas the NF and RO membranes are specified in terms of their percentage rejection of salts. The membranes that are supplied with the Membrane Test Unit is classified as tubular type, which is widely used and have turbulent flow conditions. The system is in a cross flow configuration where the feed solution is pumped parallel to the membrane at a velocity in the range of 1 - $8ms^{-1}$ with a pressure difference of 0.1 - 0.5 MPa across the membrane. Liquid permeates through the membrane and feed emerges in more concentrated form on the exit module. TABLE 3-1 shows the properties of membrane used in the project. Detailed information for membrane was shown in APPENDIX C.

Table 3-1: Specification of membrane materials used

Membrane	***Membrane Material***	***Max pH range***	***Recommended max pressure, bar***	***Max Temperature, °C***	***Apparent Retention Character***[1]	***Pore Size, nm***
Membrane 1	*AFC99 Polyamide Film*	*1.5-12*	*64*[4]	*80*	*99% NaCl*	*< 0.6*
Membrane 2	*AFC40 Polyamide Film*	*1.5-9.5*	*60*	*60*	*60% $CaCl_2$*	*0.6 -5*
Membrane 3	*CA202 Cellulose Acetate*	*2-7.25*	*25*	*30*	*2000 MW*	*5-50*

[1] *Retention character depends on several parameters, including nature of the test solution. This information should therefore be used as a guide only.*

[2] *1 low; 5 high*

[3] *+ low; +++ high*

3 Maximum pressure limited by module

3.2.2 Equipments and Chemicals Used

In this experiment, the separation is done by using Membrane Test Unit. The equipment has the operation capability which is the pressure must not operate more than 25 bar, otherwise it will leaks. After the experiment, samples were taken for result analysis. The conductivity meters were used to determine the final concentration of the sample. The equipment and apparatus used for the experiment were summarized in the table 3-2.

Table 3-2: Equipment and apparatus

No	Equipment/Others	Function
1	Membrane Test Unit	To separate the solutions
2	Conductivity Meter	To determine the concentration of sample
3	Beaker	To place chemicals/solution
4	Pipette	To transfer small amount of chemical

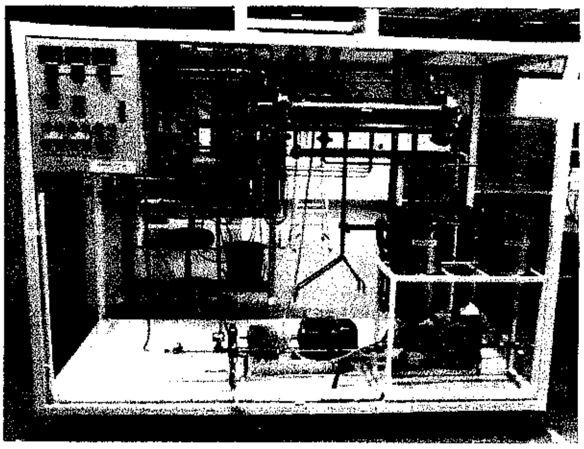


FIGURE 3-1: The membrane test unit equipment

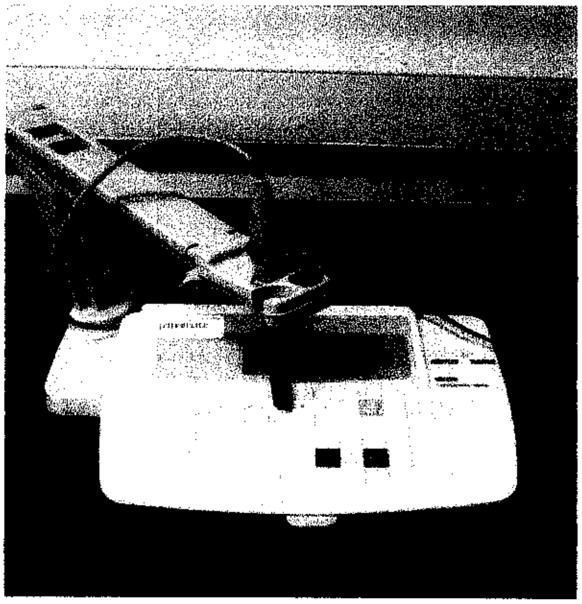


FIGURE 3-2: Conductivity meter

Table 3-3: Chemicals used

No	Chemicals	Quantity
1	zinc chloride (salt)	500 g

The detail physical properties of zinc chloride can be refer in Appendix B

3.3 METHODOLOGY

In order to obtain accurate result for heavy metal separation using membrane, several parameters need to be identified and the parameters that will affect the separation process are as follows; working pressure, flow velocity, types of membrane, types of chemical and concentration of solution.

3.3.1 Parameter

A study has been conducted to observe the removal of heavy metals by using membrane by varying the parameters of ***concentration, pressure, velocity, chemicals and membranes.***

a) Concentration

From information gathered, the typical concentration of heavy metals in wastewater is around 500 - 1000 ppm. Thus, the concentrations of solution used in this study were ***1000 ppm, 600 ppm, 300 ppm*** and ***100 ppm.***

b) Pressure

From the manual, it stated that the Membrane Test Unit can operate up to 60 bar but from the manual also the recommended maximum pressure for CA202 Cellulose Acetate is at 25 bar. The membranes will break down if operate above the recommended pressure. Furthermore, after running the equipment by using tap water, the equipment leaks and can only be operated below than 25 bar. The pressure used were ***20 bar, 15 bar, 10 bar*** and ***5 bar***.

c) Velocity

From previous experiment, the flow velocity in membrane separation affects the process obviously. This is because as we increase the velocity, we will obtain higher flux. In this experiment, the velocity used were ***8 LPM, 6 LPM, 4 LPM, and 2 LPM***

d) Chemical

In this process, the chemical used are ***zinc chloride***. (see APPENDIX B)

e) Type of membrane

The types of membranes used in this experiment were ***Polyamide Film*** for ***reverse osmosis (AFC99)***, ***nanofiltration (AFC40)*** and ***Cellulose Acetate (CA202) for ultrafiltration***. The details of membranes specifications are shown in table 3-1.

3.3.2 Experimental Procedure

Preparation of metal solution

1. Exactly salt powder was weighed using electronic balance.
2. The salt was added into a beaker containing 100 ml of distilled water. The mixture was stirred to dissolve all the metal powder.
3. The solution was then poured carefully into the 2 L volumetric flask.
4. The beaker was washed and rinsed several times with distilled water from the wash bottle. All the washing was run into the volumetric flask to make sure no metal solution remains in any of the apparatus used.
5. The volumetric flask was stirred gently so that the distilled water and salt was mixed thoroughly.
6. Distilled water was added slowly until the 2 L calibration mark in the volumetric flask is reached.
7. Repeat step 1 – 6 for twenty times to get 20 L of concentration needed.

Experimental Procedure

1. The salt solution was prepared as explain in above section. All valves were closed except V2, V5, V8, V10, V12 and V14.
2. The feed tank was filled up with the solution prepared in Step 1. The feed shall always be maintained at room temperature.
3. The maximum working pressure was set up at 25 bars.

   Note: For working pressure setting, valve, V5 was closed. A proper wrench was used to turn the adjusting screw at the pressure regulator by turning clockwise to increase and counter-clockwise to reduce the pressure.
4. The plunger pump, P1 was started. The membrane maximum inlet pressure was set to 2.5 bars by adjusting the retentate control valve (V15).
5. The system was allowed to run for 30 minutes. The collecting sample is started from permeate sampling port. The weight of permeate is recorded every 5 minute for 30 minutes.

Note: The sample was collected by open valves V7, V9, V11 and V13, simultaneously closed valves V8, V10, V12 and V14.

6. The plunger pump, P2 was stopped and valve, V2 was closed.
7. Graph flux versus concentration and pressure was plotted.
8. The procedure was repeated for different concentration of metal solution and feed water pressure.
9. Sample of each membrane was taken to be tested by using conductivity meter.

The experiments were repeated by using different pressures, different velocities. After that, 600 ppm of concentration was used followed by 300 ppm and 100 ppm. Then, sample for each of membrane was taken for COD test by using COD Test Unit. Sample was mix with 2ml of COD reagent before being tested by the test unit as follows;

Preparation of calibration curve

In analytical chemistry, a calibration curve is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration. A calibration curve is one approach to the problem of instrument calibration; other approaches may mix the standard into the unknown, giving an internal standard. The calibration curve is a plot of how the instrumental response, the so-called analytical signal, changes with the concentration of the analyte (the substance to be measured). Below is the procedure to prepare the calibration curve for zinc chloride.

1. A series of standard was prepared solution for zinc chloride in a beaker with concentration between 50 ppm to 1000 ppm.
2. The concentration was measured by using conductivity meter.
3. The reading was recorded in the table and graph is plotted as well.

Analyzing each of these standards using the chosen technique will produce a series of measurements. For most analyses a plot of instrument response vs. zinc chloride concentration will show a linear relationship. From the graph generated, the writer can measure the response of the unknown and, using the calibration curve, can *interpolate* to find the concentration of zinc chloride. Graph of calibration curve can be referring in APPENDIX E.

3.3.3 Result Analysis

The data obtained was analyzed as follows. For 10 minutes, the volume of permeate for each membrane was taken in time interval. The volume will be different for the membranes and the data was analyzed for flux and rejection.

Table 3-4: Table for collecting data

Copper sulphate, Concentration = 1000 ppm, Pressure = 4 bar, Velocity = 2 LPM										
Membrane Type	Time, s									
	60	120	180	240	300	360	420	480	540	600
AFC99										
AFC40										
CA202										

After separation, the concentration changed. Conductivity meter was used to determine the after-concentration of heavy metals solution. The data was analyzed by calculating the flux, *J* by using correlation 3.1;

$$Flux, J \left(\frac{L}{m^2 . \mathrm{h}}\right) = \frac{Volume}{Area\,.Time} \qquad (3.1)$$

$$= Weight, g\ x\ 1/Density, L\ /\ g\ x\ 1\ /\ (Area, m2\ \ x\ Time, h)$$

The area of membrane is;

$$\text{Area, m}^2 = 2\pi rL \qquad (3.2)$$

$$= 2\pi\,(0.00625\text{m}) \times (1.2\text{ m})$$

$$= 0.047\text{ m}^2$$

Graph of flux versus parameter; concentration, velocity and pressure for three types of membrane will be plotted. Rejection of separation is calculated by using below correlation;

$$Rejection, R = 1 - \frac{C_p}{C_b} \qquad (3.3)$$

Rejection is ratio of concentration of after separation, C_b with initial concentration, C_p of solution. Percent of rejection determines the percentage of how much molecules of mertal has not passed the membrane pores. Higher percent rejection shows good separation where more chemicals is separated. The conductivity meter was used to measure the final concentration. The calibration curve for zinc chloride was developed to measure the concentration (APPENDIX E).

CHAPTER 4: RESULT AND DISCUSSION

This chapter contains all experimental results which were based on data obtained from experimental work using distilled water and zinc chloride and discussion base on the graph generated.

4.1 Water Permeability

In the first part of study, the experiment was conducted to investigate the effect of parameters used on flux. The parameters that been studied in this experiment are cross flow velocity, operating pressure and type of membranes (AFC 99, AFC 40 and CA 202). The data were recorded and plotted into graph. The results are as follows;

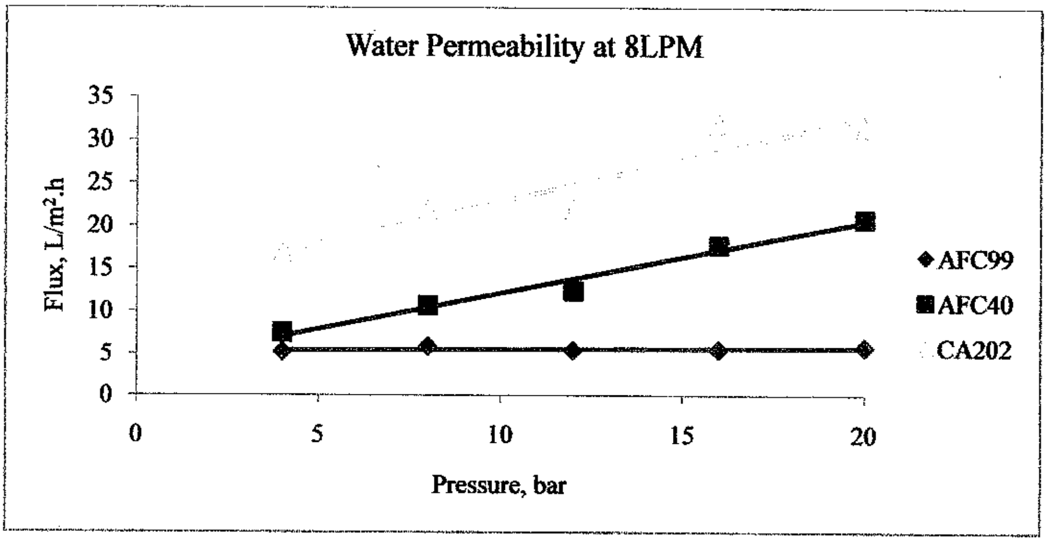


FIGURE 4-1: Water Permeability Graph at Constant Velocity 8 LPM for Different Membrane

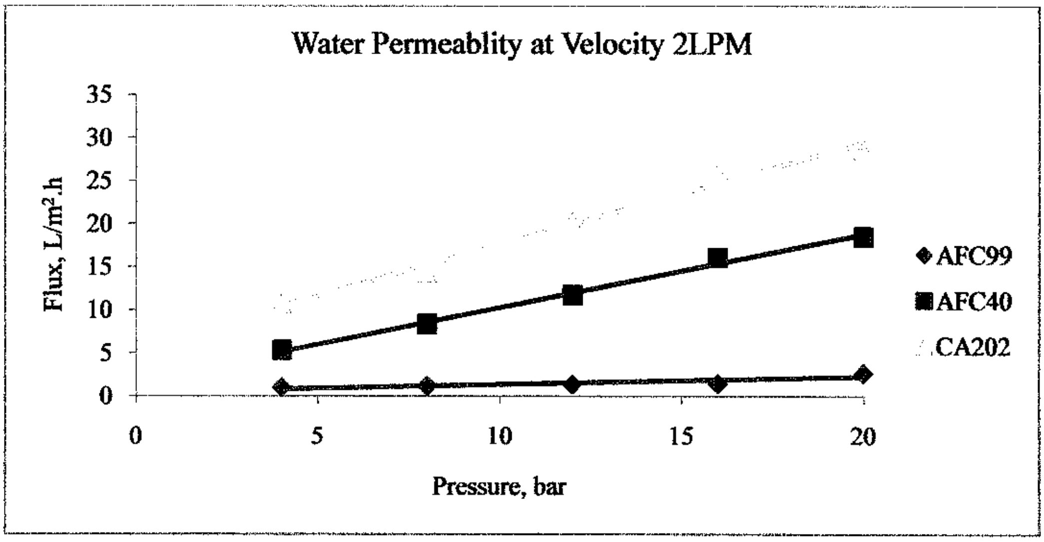


FIGURE 4-2: Water Permeability Graph at Constant Velocity 2 LPM with Different Membrane

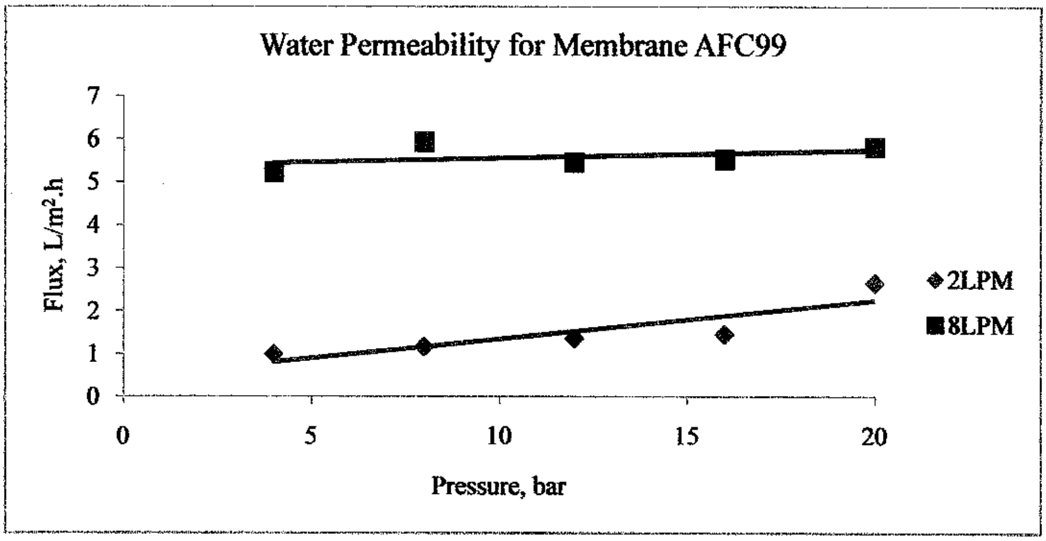


FIGURE 4-3: Water Permeability Graph at Velocity 2 and 8 LPM at Membrane AFC 99

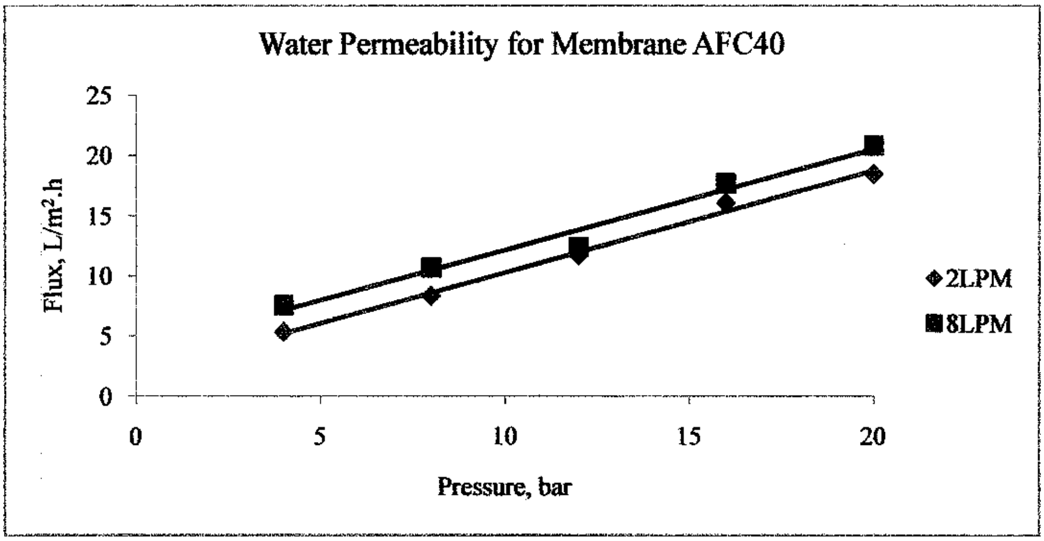


FIGURE 4-4: Water Permeability Graph at Velocity 2 and 8 LPM for Membrane AFC 40

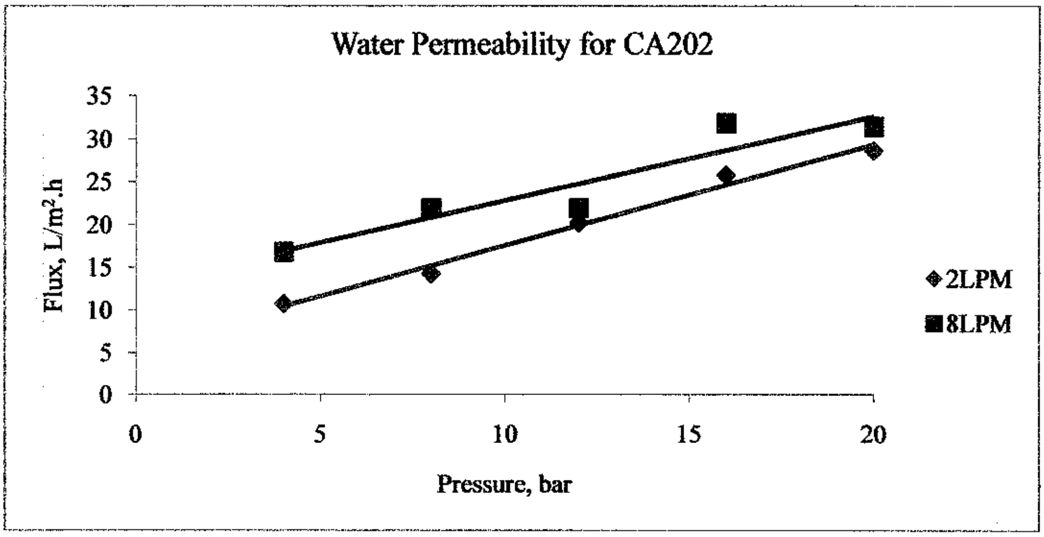


FIGURE 4-5: Water Permeability Graph at Velocity 2 and 8 LPM for Membrane CA 202

From the result obtained, the permeate flux is affected by several factors such as feed pressure and cross flow velocity. Increase in flux can be observed at high cross flow velocities due to the decrease in concentration polarization.

From the experiment conducted, the result from Figure 4-1 and 4-2 shows the effect of working pressure towards the membrane. As the pressure increase, the water flux across the membrane increase. In these studies, the highest fluxes were recorded at high pressure which was at 20 bar. This is in line with the theory, as the driving force (pressure) increase, more water flux was achieved.

Type of membrane also plays role in contributing the performance of the membrane. Membrane that has large size of pore will produce greater flux. Thus CA 202 has greater flux compare to the AFC 40 and AFC 99 respectively.

For the next experiment, the rejection study was done using Zinc Chloride, the same parameter with addition of feed concentration variables are studied. The results obtained in term of permeate flux by comparing highest and lowest value of parameter for pressure, velocity and concentration. The following graph shows comparison of flux at different membrane material and velocity variable with constant concentrations, which were at 1000 ppm and 100 ppm.

4.2 Study of Flux

Figures 4-9, 4-10, 4-14 and 4-15 show the permeate flux of difference membranes versus operating pressure. These figures show that the permeate flux increases almost in linear form as the operating pressure increased. From the result also, the AFC 99 membrane has the lowest permeate flux followed by AFC 40 and CA 202 membranes, respectively. As the solution goes through the membrane, concentration polarization is expected to occur at the surface of the membrane. Due to the rejection of heavy metal salt at all membrane (AFC 99, AFC 40 and CA 202) used, it can be seen that the permeate flux at those membranes decreases as the concentration increased.

4.2.1 Zinc Chloride Separation in Term of Flux

a) Concentration at 1000 ppm

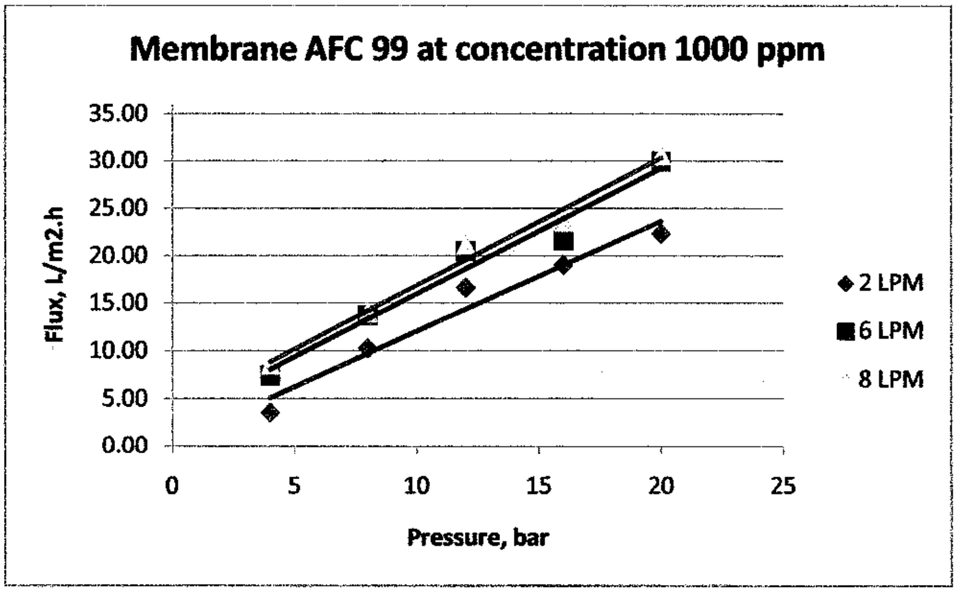


FIGURE 4-6: Flux vs. Pressure at Membrane AFC 99 with Constant Concentration 1000 ppm at Different Velocity

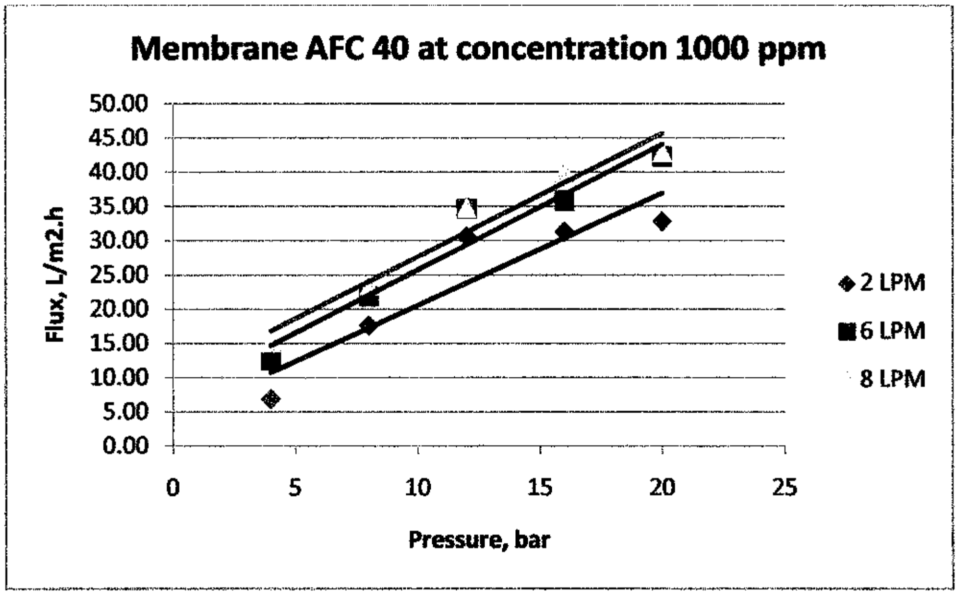


FIGURE 4-7: Flux vs. Pressure at Membrane AFC 40 with Constant Concentration 1000 ppm at Different Velocity

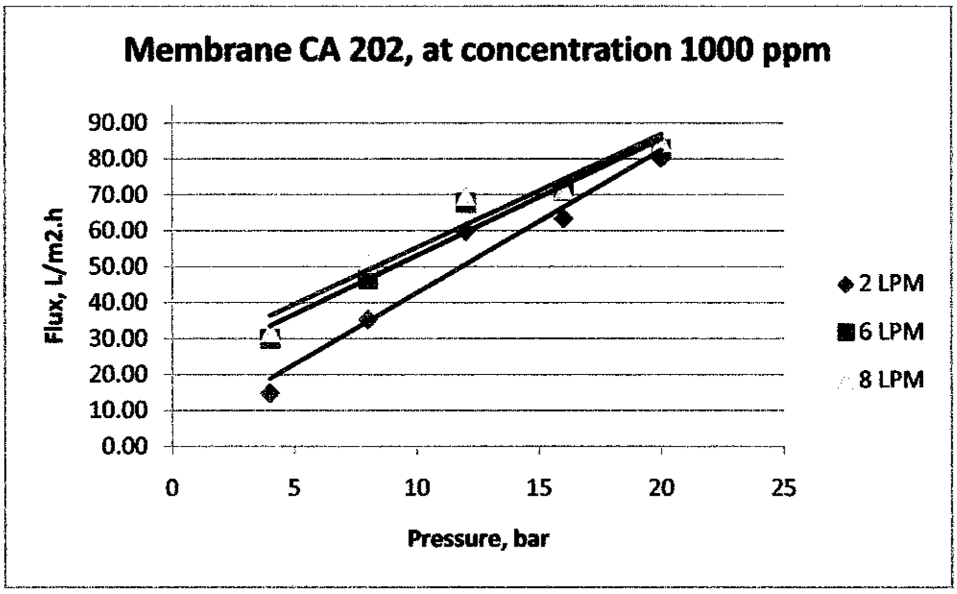


FIGURE 4-8: Flux vs. Pressure at Membrane CA 202 with Constant Concentration 1000 ppm at Different Velocity

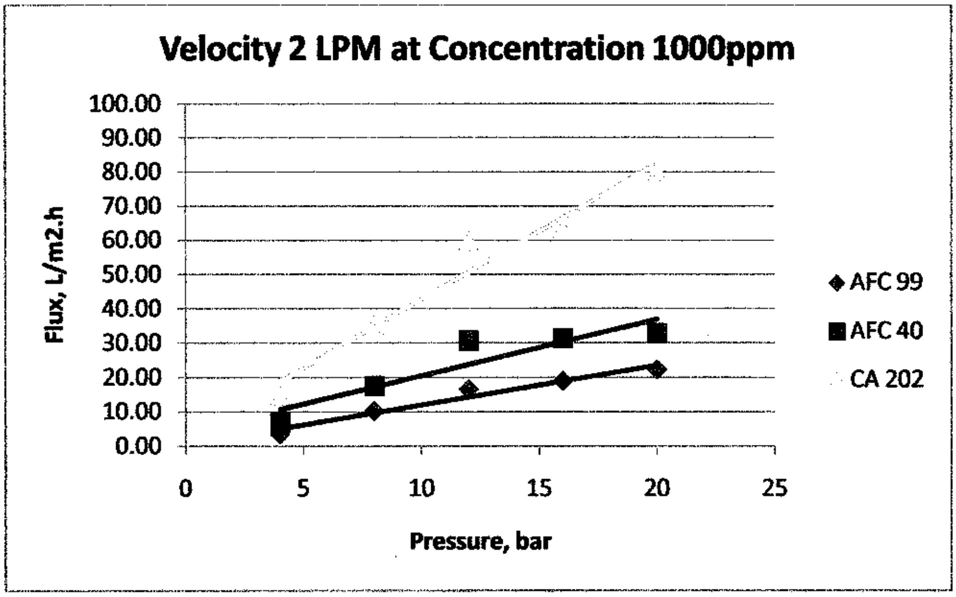


FIGURE 4-9: Flux vs. Pressure at Velocity 2 LPM with Constant Concentration 1000 ppm at Different Membrane

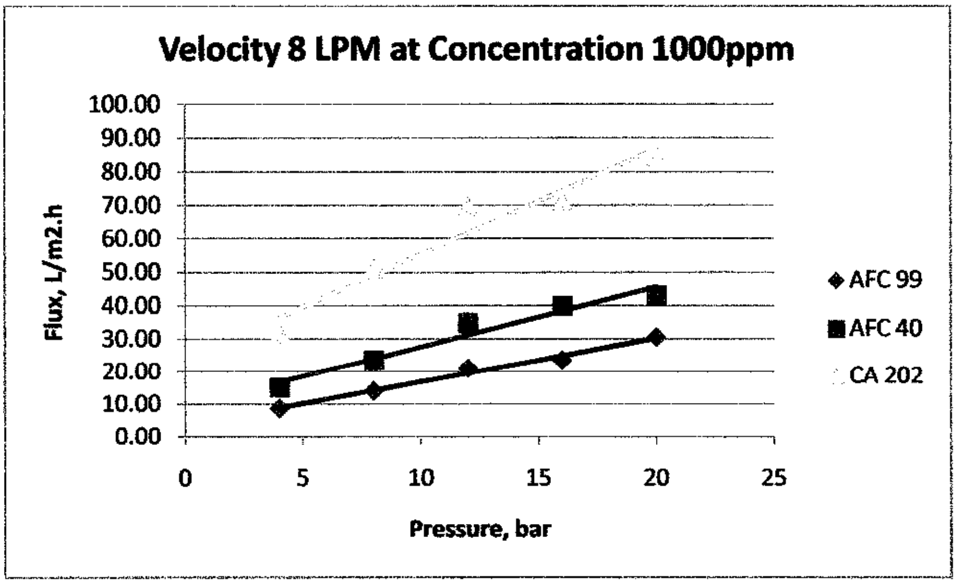


FIGURE 4-10: Flux vs. Pressure at Velocity 8 LPM with Constant Concentration 1000 ppm at Different Membrane

b) *Concentration at 100 ppm*

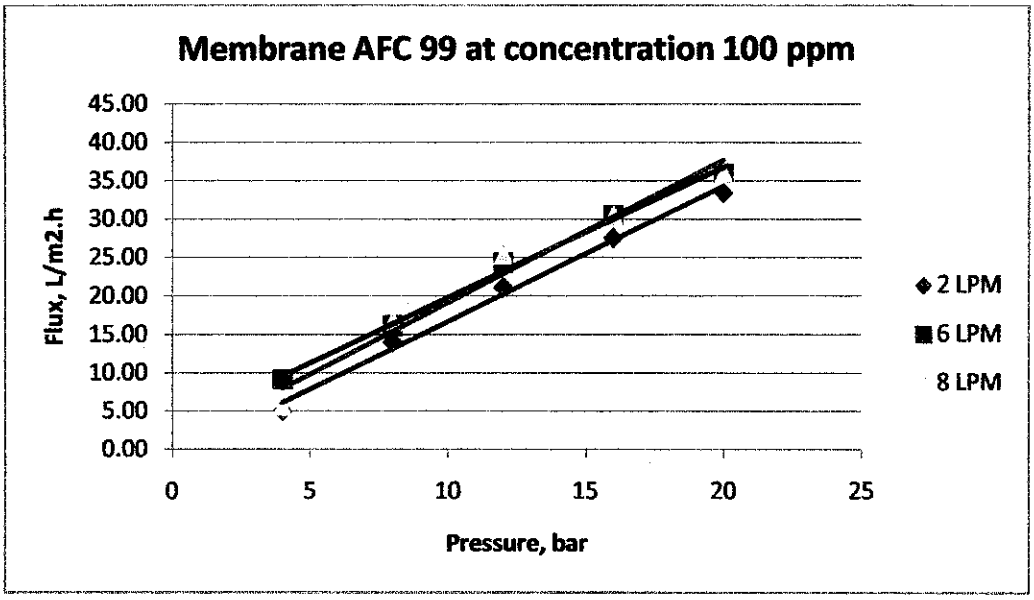


FIGURE 4-11: Flux vs. Pressure at Membrane AFC 99 with Constant Concentration 100 ppm at Different Velocity

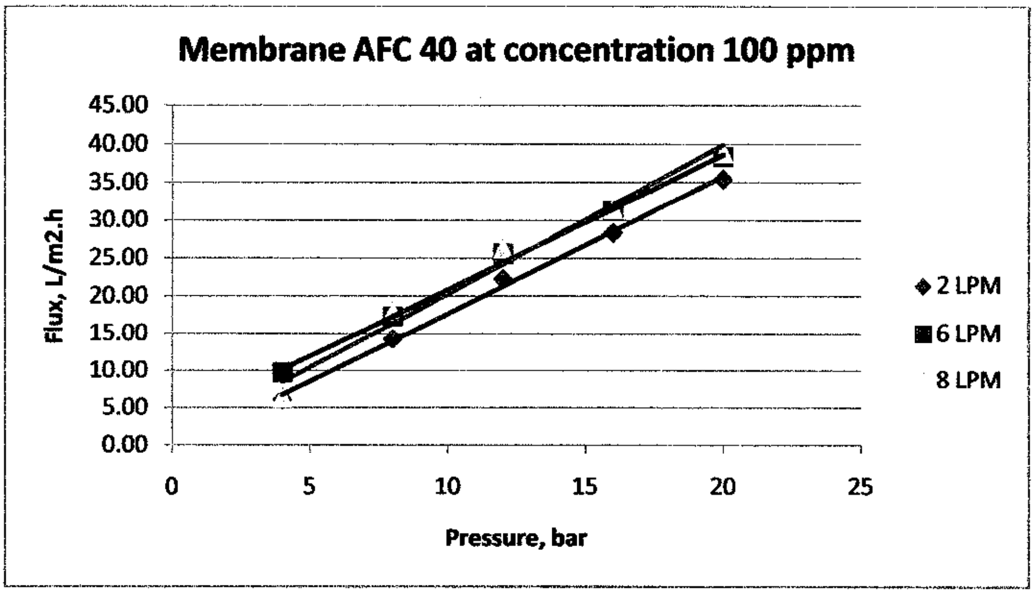


FIGURE 4-12: Flux vs. Pressure at Membrane AFC 40 with Constant Concentration 100 ppm at Different Velocity

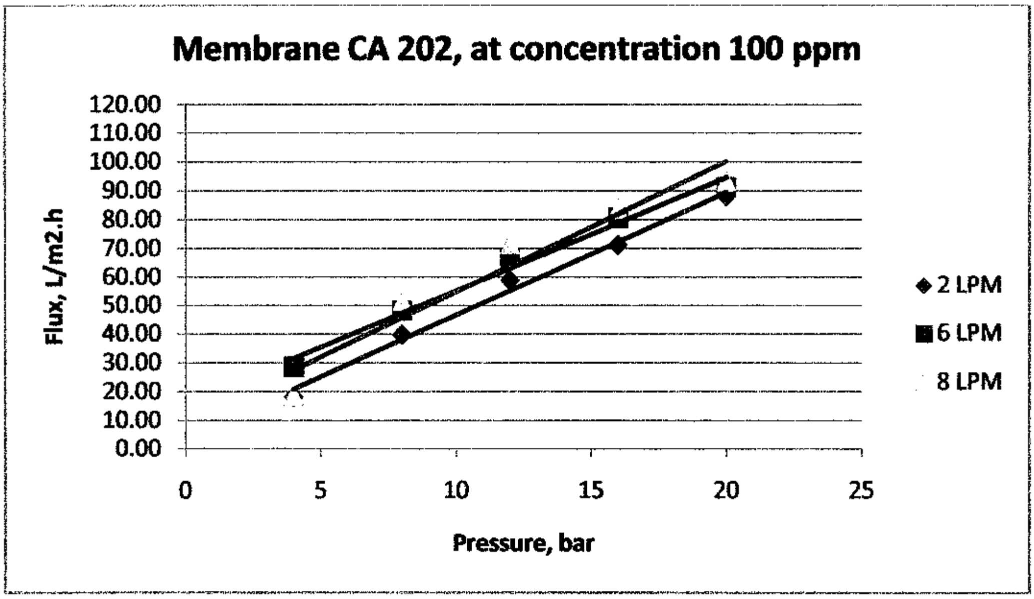


FIGURE 4-13: Flux vs. Pressure at Membrane CA 202 with Constant Concentration 100 ppm at Different Velocity

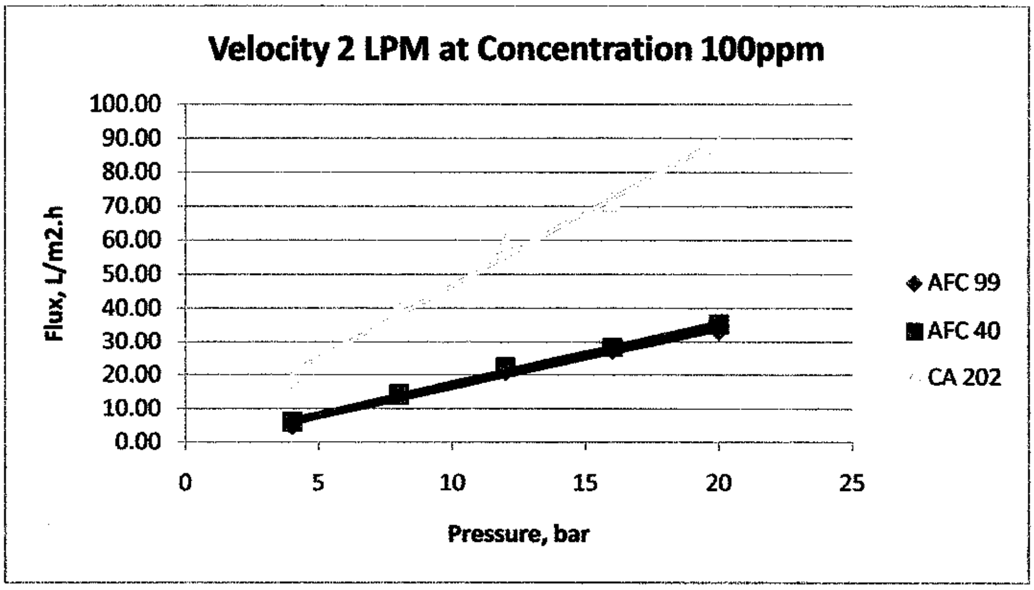


FIGURE 4-14: Flux vs. Pressure at Velocity 2 LPM with Constant Concentration 100 ppm at Different Membrane

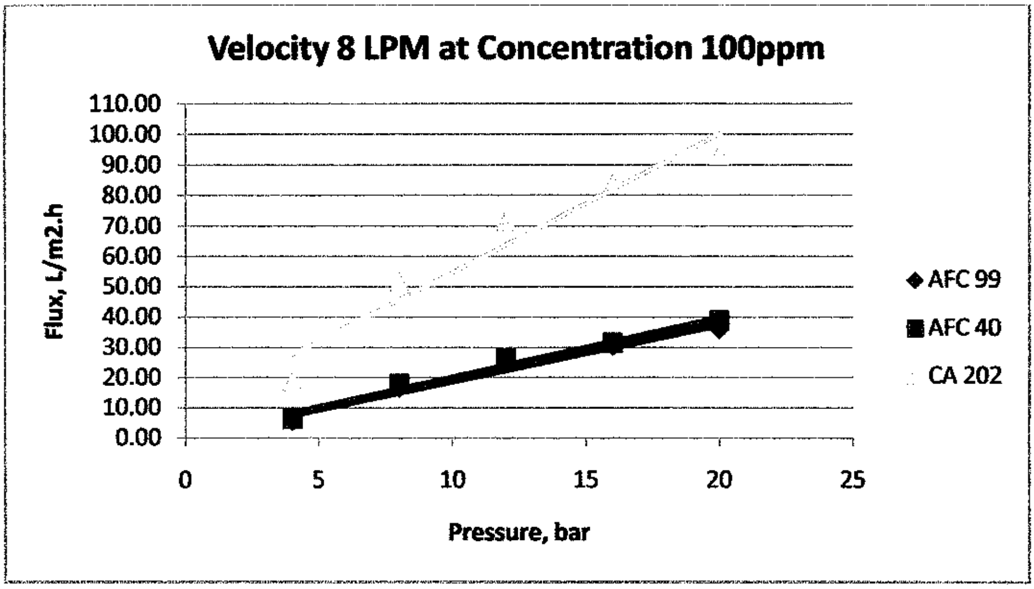


FIGURE 4-15: Flux vs. Pressure at Velocity 8 LPM with Constant Concentration 100 ppm at Different Membrane

4.2.1.1 Effect of Cross Flow Velocity

From the graph, it can be seen that greater flux can be achieved at high cross velocities due to the decrease in concentration polarization (Koyuncu *et al*, 2003). The flow velocity in membrane separation is obviously affects the process. In FIGURE 4-6, 4-7 and 4-8 shows that higher cross flow velocity tends to result in higher flux where the flow will push down the molecule to pass the membrane pores at different type of membranes which are AFC 99, AFC 40 and CA 202.

As the velocity increased, the flux will be increased. By comparing between the three graphs (FIGURE 4-6, 4-7 and 4-8) which the velocity are variables from 2 to 8 LPM, flux at membrane CA 202 shows highest flux, followed by AFC 40 and AFC 99. This is because of membrane porosity. The AFC 99, which is reverse osmosis process, has very small pore size (<0.6nm). Compare to AFC 40, the nanofiltration process, the pore size is in range 0.6-5 nm, while CA 202 has the highest pore size which is 5-50 nm.

4.2.1.2 Effects of Pressure

From all figures provided it can be concluded that the feed pressure contribute significant effect to the membrane process. As the pressure been increased (from 4 to 20 bar), the flux is increased as well. This is due to the increase of the pressure difference across the membrane (increasing the net pressure) as well as increasing the driving force for the process. In addition, the increase in water permeability as a function of pressure is caused by the increase in the driving force. Hence, increasing the operating pressure, has enhanced the separation of zinc chloride.

4.3 Study of Salt Rejection

Salt rejection was also evaluated at different operating conditions such as pressure, feed concentration, cross flow velocity and types of membrane. Rejection increased with increasing pressure (Koyuncu *et al.*, 2003). From the experiment conducted, the highest rejection was obtained at highest pressure which is at 20 bar and lowest concentration which is at 100 ppm. The result of rejection measurement at different cross flow velocities and salt concentrations are shown in FIGURE 4-19, 4-20, 4-24 and 4-25.

From the experiment, the result show that the AFC 99 membrane has the highest rejection (98.8%) compare to AFC 40 (84%) and CA 202 (58%) at the highest cross flow velocity (8 LPM) and at lowest concentration (100 ppm). This is due to reduction of concentrations polarization on membrane surface.

However, due to the concentration polarization effect on the membrane surface, the rejection of heavy metal salt decreased as the heavy metal salt concentration increased. As can be observed in Figure 4-20 and Figure 4-25, as the feed concentration of the salt increases from 100 ppm to 1000 ppm, the observed rejection was reduced from 99% to 90%.

4.3.1 Zinc Chloride Separation in Term of Rejection

a) At feed concentration 1000 ppm

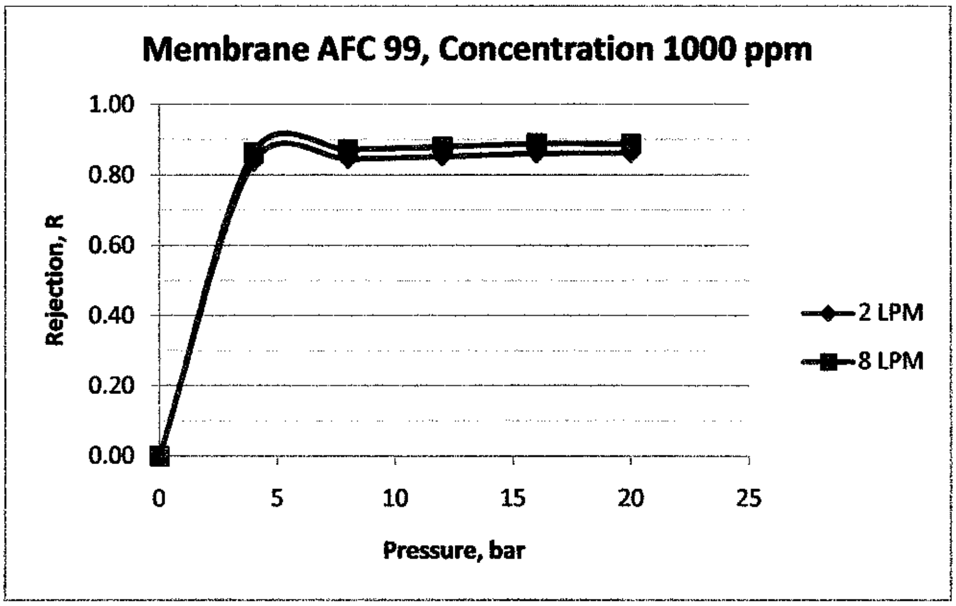


FIGURE 4-16: Rejection vs. Pressure at Variable Velocity with Constant Concentration 1000 ppm and Membrane AFC 99

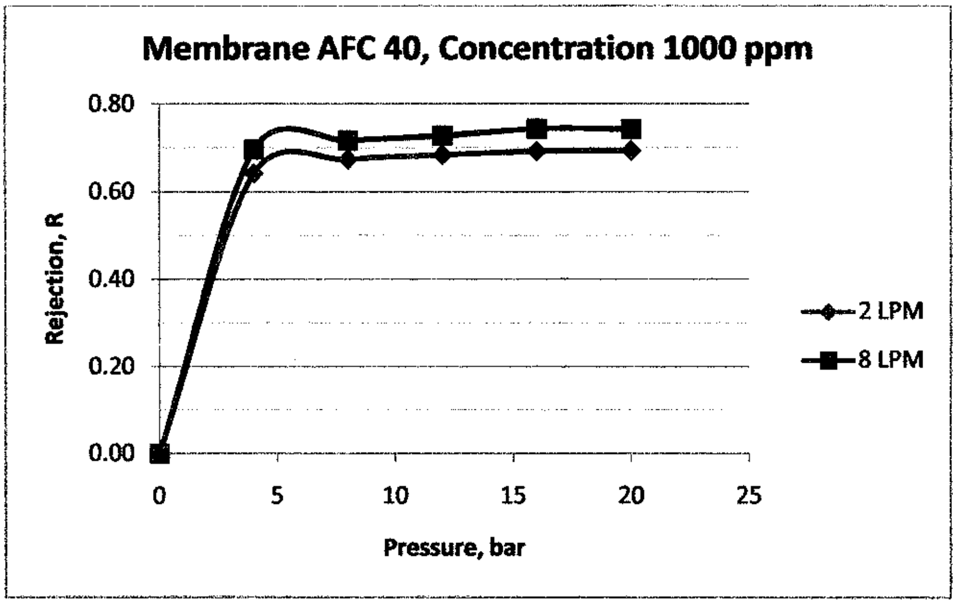


FIGURE 4-17: Rejection vs. Pressure at Variable Velocity with Constant Concentration 1000 ppm and Membrane AFC 40

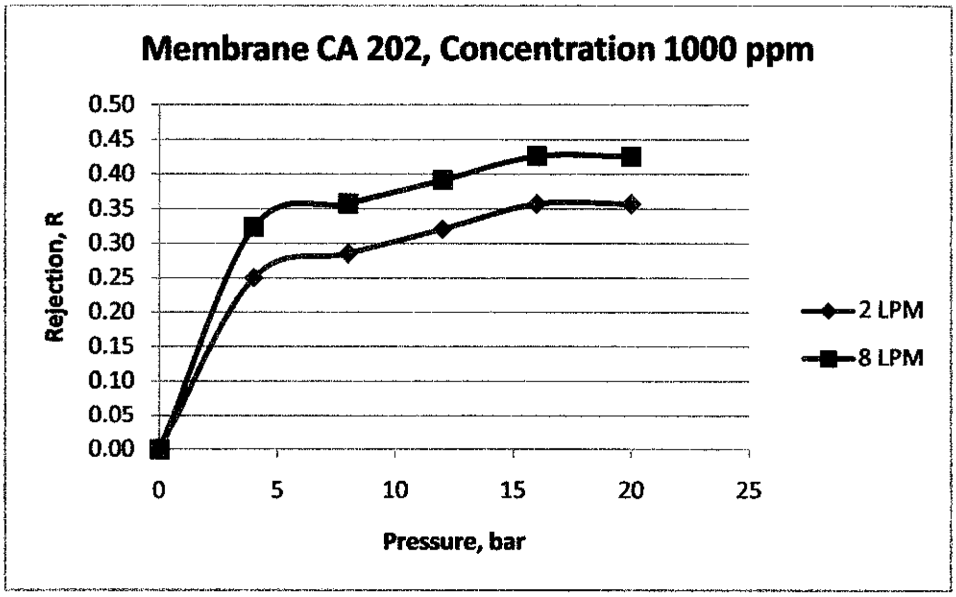


FIGURE 4-18: Rejection vs. Pressure at Variable Velocity with Constant Concentration 1000 ppm and Membrane CA 202

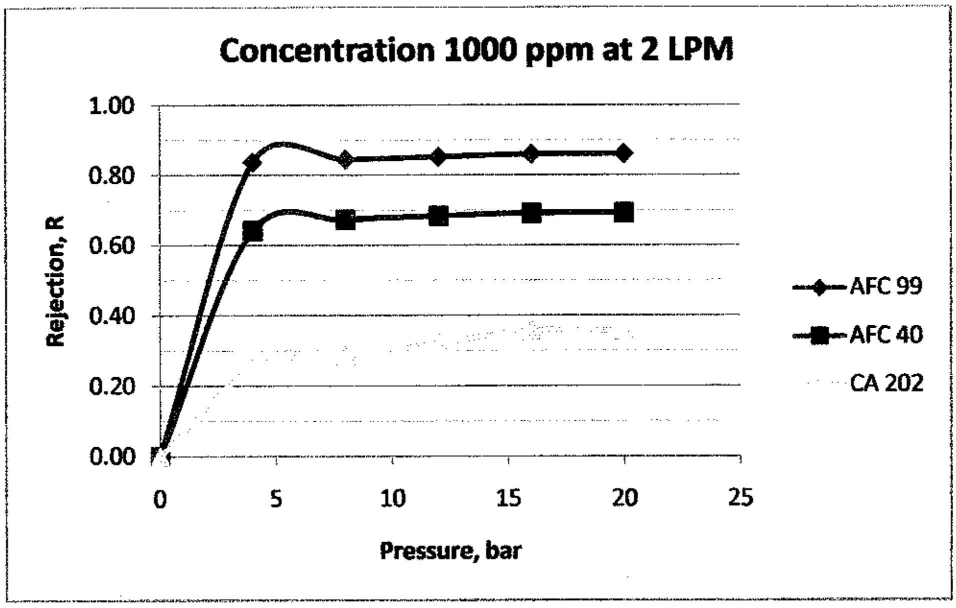


FIGURE 4-19: Rejection vs. Pressure at Velocity 2 LPM with Constant Concentration 1000 ppm and Different Membranes

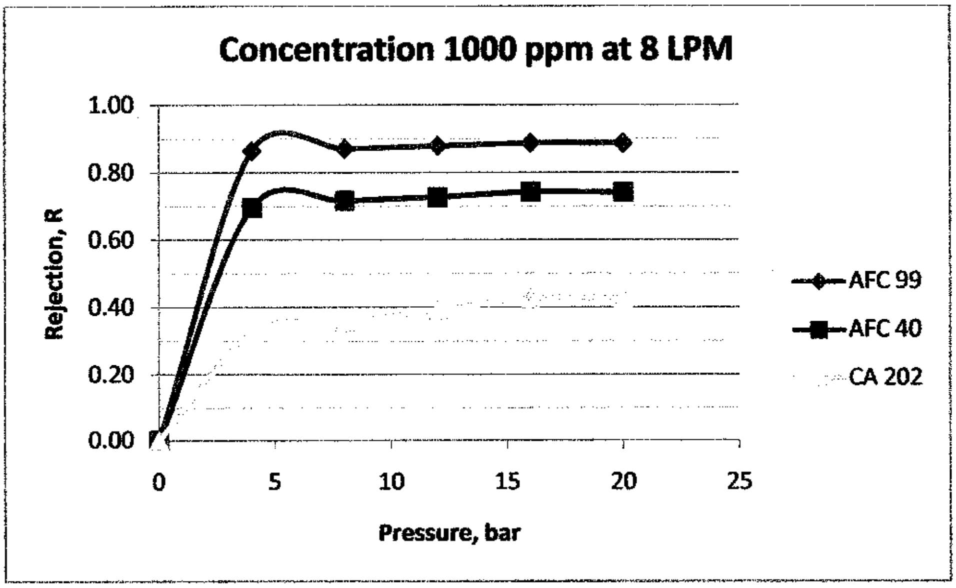


FIGURE 4-20: Rejection vs. Pressure at Velocity 8 LPM with Constant Concentration 1000 ppm and Different Membranes

b) At concentration 100 ppm

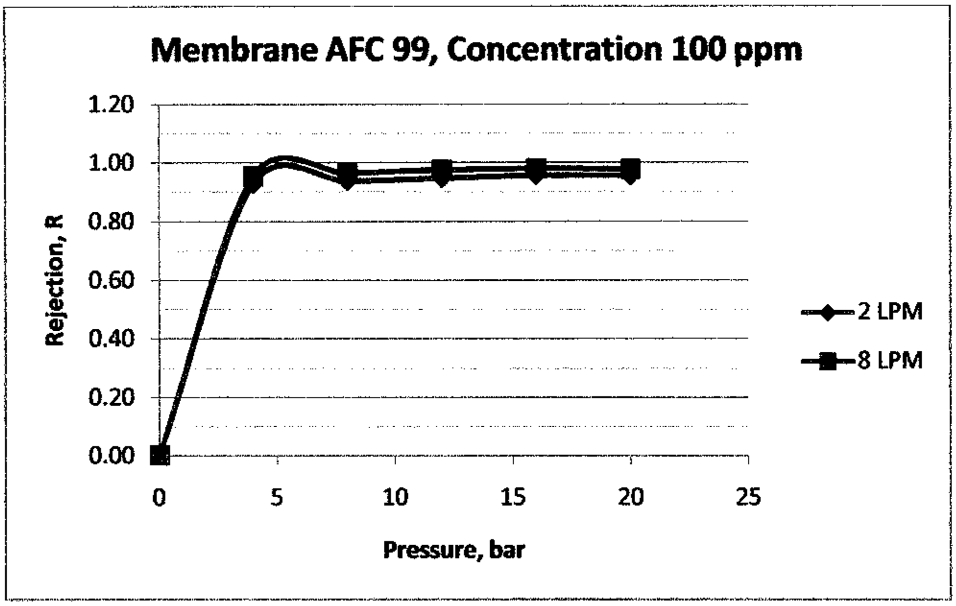


FIGURE 4-21: Rejection vs. Pressure at Variable Velocity with Constant Concentration 100 ppm and Membrane AFC 99

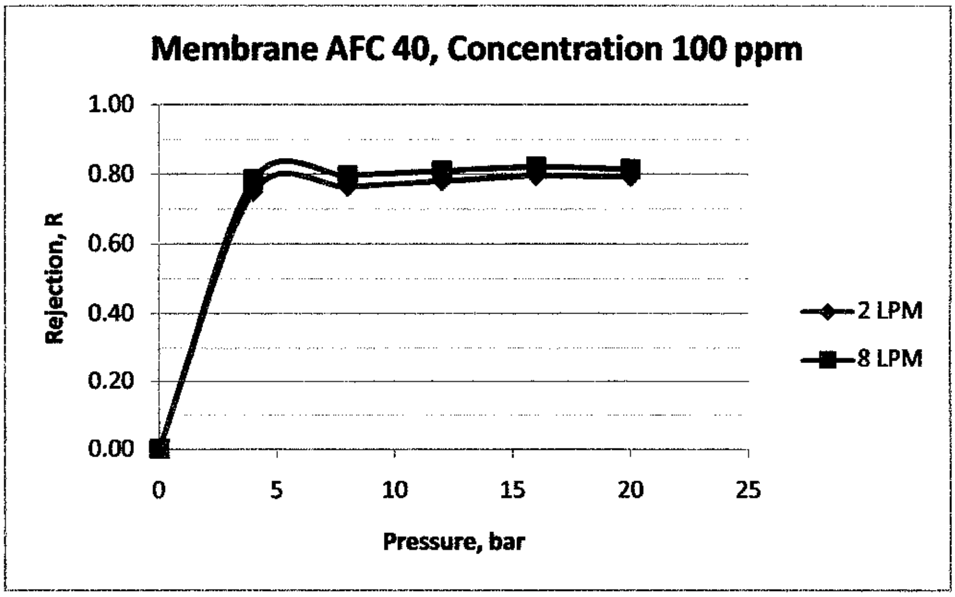


FIGURE 4-22: Rejection vs. Pressure at Variable Velocity with Constant Concentration 100 ppm and Membrane AFC 40

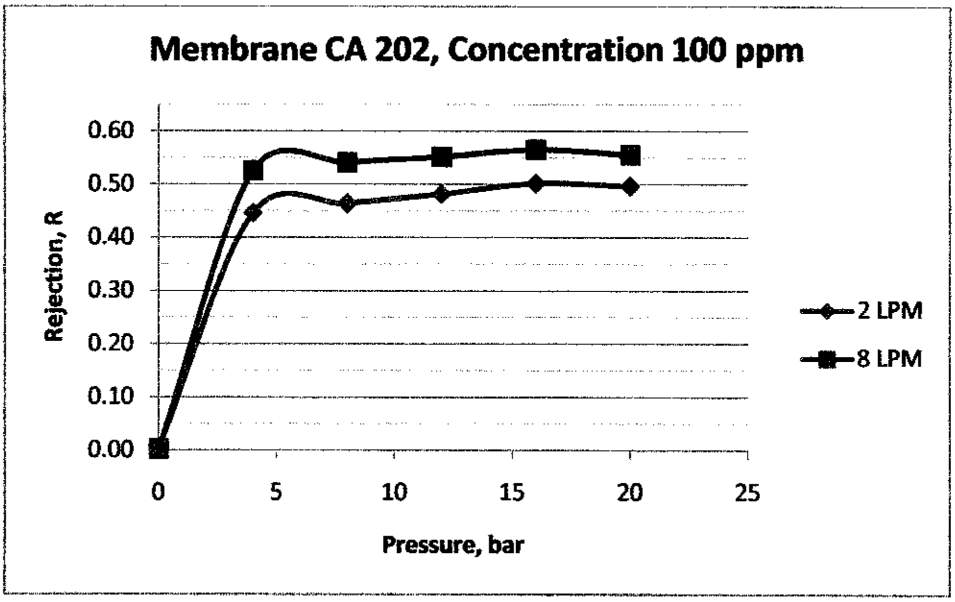


FIGURE 4-23: Rejection vs. Pressure at Variable Velocity with Constant Concentration 100 ppm and Membrane CA 202

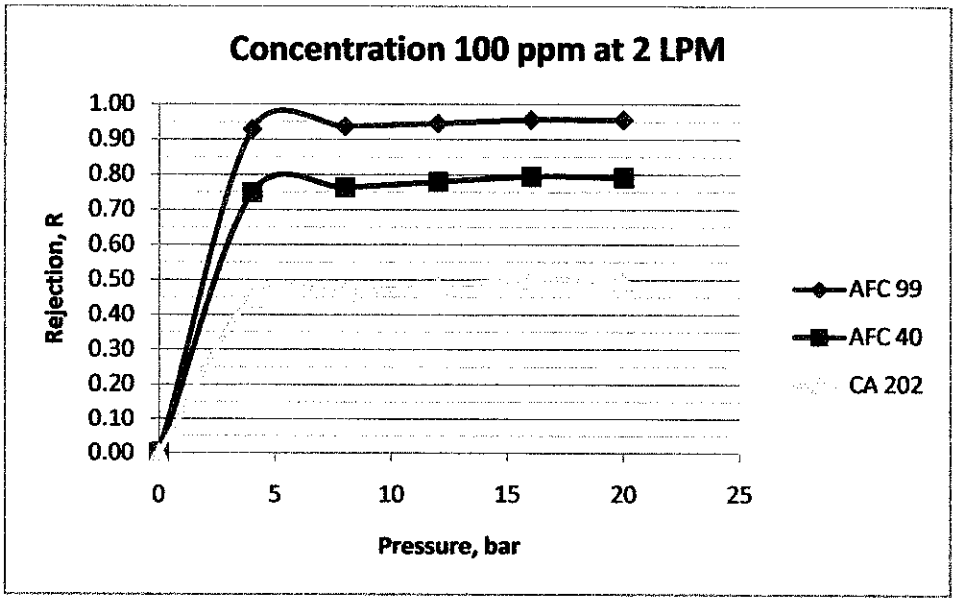


FIGURE 4-24: Rejection vs. Pressure at Velocity 2 LPM with Constant Concentration 100 ppm and Different Membranes

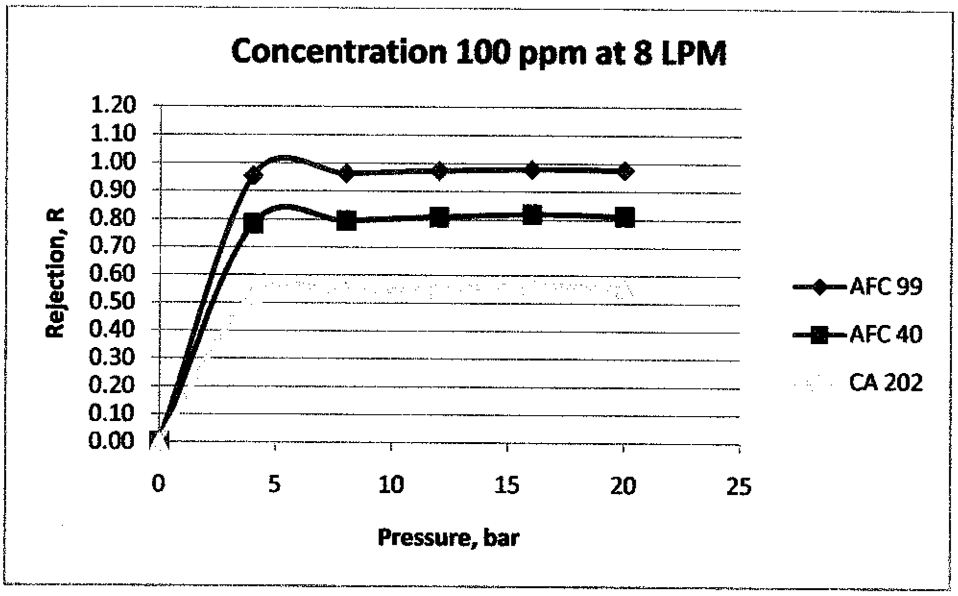


FIGURE4-25: Rejection vs. Pressure at Velocity 8 LPM with Constant Concentration 100 ppm and Different Membranes

CHAPTER 5: CONCLUSION AND RECOMMENDATION

From the experiment data, it was observed that parameters like operating pressure, cross flow velocity, feed concentration and membrane type are important factors in membrane separation and play important role in the membrane performance. From the experimental work, the permeate flux is very dependent to operating pressure, cross flow velocity, membrane type and feed concentration. The flux increases as the operating pressure increases. Similarly, flux increases as the cross flow velocity increases. Highest flux was observed for membrane CA202 (100 $L/m^2.h$) at feed concentration 100 ppm, pressure 20 bar and cross flow velocity, 8 LPM. Lowest flux was observed for membrane AFC 99 (3.5$L/m^2.h$) at feed concentration 1000 ppm, pressure 4 bar and cross flow velocity 2 LPM. At high feed concentration, flux decreases and this was due to concentration polarization at the membrane surface. The lower feed concentration would give the better performance, compare to higher concentration which lead to lower flux. The highest flux recorded was membrane CA 202, which has highest pore size, followed by AFC 40 and AFC 99 respectively.

It was found that the membrane was able to separate ZnCl2 and the separation efficiency depends on operating pressure, cross flow velocity, membrane type and feed concentration. Membrane AFC 99 was found to be best membrane separation, followed by AFC 40 and CA 202, respectively. The separation efficiency of AFC 99 was up to 99%, followed by AFC40 (86%) and CA202 (50%). The AFC 99 has the highest rejection due to smaller size of pore it has compare to the AFC 40 and CA 202 membranes. The rejection increased as the operating pressure is increased. Similarly, the rejection increased as the cross flow velocity is increased. This is because of high concentration polarization on the membrane surface. From the study conducted, it can be concluded that membrane type AFC 99 would give better performance in term of rejection followed by AFC 40 and CA 202. The study of heavy metals salt separation in membrane need to be explored in detail because the use of membrane is very effective in wastewater treatment plant. By revising the result in above section, membrane method is very useful to understand and study the behavior of liquid separation and performance of membrane types.

Few improvements are recommended for this project for better observation and evaluations where further research should be carried out.

- Development of inherently fouling-resistant membranes by changing the membrane surface absorption characteristics.
- By reducing adhesion of the deposited gel layer to the surface, the scrubbing action of the feed solution can be enhanced
- To develop essentially more fouling-resistant modules

REFERENCES

Christie John Geankoplis. *Transport Processes and Separation Process Principle,* Fourth Edition, Pearson Education, Inc. (2003)

Drever, J.I., 1997, *The Geochemistry of Natural Waters: Surface and Groundwater Environments,* Prentice Hall, Upper Saddle River, NJ.

Environmental Quality (Sewage and Industrial Effluent) Regulation, 1979 - Regulation 8. Parameter limits of effluent to be discharged into inland waters

G. Srisuwan and P. Thongchai, 2002, 24(Suppl.), *Removal of heavy metals from electroplating wastewater by membrane*, Songklanakarin J. Sci. Technol.

Hani Abu Qdaisa* , Hassan Moussab, 2003, *Removal of heavy metals from wastewater by membrane processes: a comparative study,* Department of Civil Engineering, Department of Chemical Engineering, Jordan University of Science and Technology.

Ismail Koyuncu, Dincer TopacikStephenson , 2003 *"Effects of operating conditions on the salt rejection of nanofiltration membranes in reactive dye/salt mixtures"*

J. D Seader and Ernest J. Henley, 1998 *Separation Process Principles*
(p 713 to 773), John Wiley & Sons, Inc.

Kangala B. Chipasa*, 2001. *Accumulation and fate of selected heavy metals in a biological wastewater treatment system*
Chemical Faculty, Technical University of Gdansk, Narutowicza 11/12, 80-952 Gdansk, Poland

Matthew M. Matlock, Kevin R. Henke, and David A. Atwood. "*Effectiveness of Commercial Heavy Metal Chelators with New Insights for the Future in Chelate Design*"

McDonald, D.G.; Grandt, A.F. (1981) *Limestone- Lime Treatment of Acid Mine Drainage-Full Scale*. EPA Project Summary (1981).

Metcalf and Eddy, 2004 *Wastewater Engineering: Treatment and Reuse*, 2004, 4th Edition, G. Tchobanoglous, Franklin L. Burton & H. David Stensel

M. Muthukrishnan, B.K. Guha*, 2006, *Heavy metal separation by using surface modified*

nanofiltration membrane, Chemical Engineering Department, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi – 110016, India

P. Moslehi, J. Shayegan and S. Bahrpayma, 2004, Department of Petroleum and Engineering – Sharif University of Technology, Tehran, Iran.

P. S. Sudilovskiy Æ G. G. Kagramanov ÆA. M. Trushin Æ V. A. Kolesnikov, 2007, *Use of membranes for heavy metal cationic wastewater treatment: flotation and membrane filtration.*

Richard W. Baker, 2000, *Membrane Technology and Applications*, McGraw-Hill.

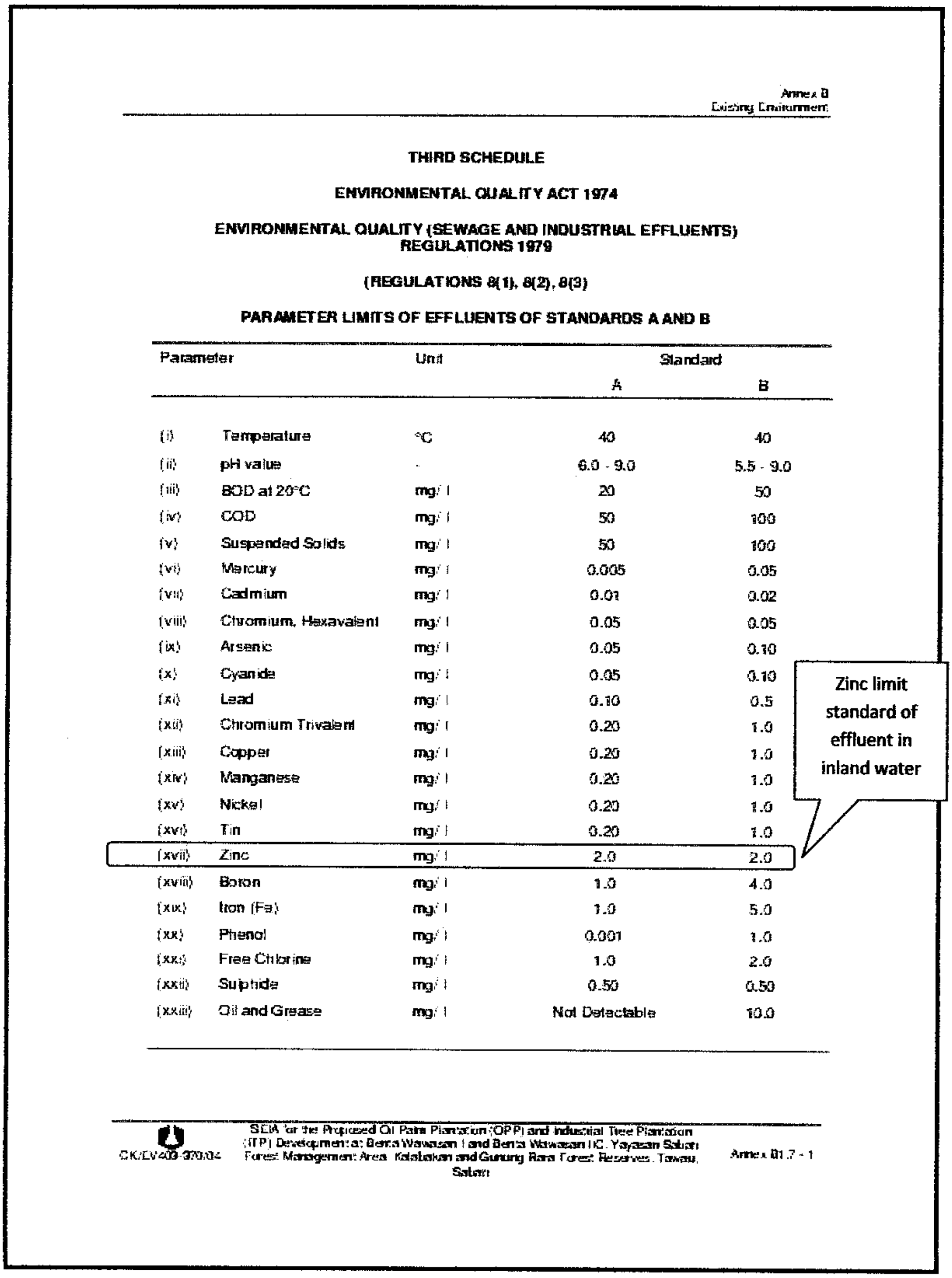
Robert H.Perry, Don W. Green. 1997, *Perry's Chemical Engineers' Handbook (7th Edition)*, (p22-37 to 22-69), McGraw-Hill.

Stephenson Ralph L., Blackburn James W., Blackburn James B., 1998, *The industrial Wastewater Systems Handbook*, CRC Press, United State of America, p350-360

Tom Dauwe*, Ellen Janssens, Marcel Eens, 2004. *Effects of heavy metal exposure on the condition and health of adult great tits (Parus major)*, Department of Biology, Campus Drie Eiken, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Belgium

APPENDIX A

Local Malaysian Standard for Industrial Wastewater Discharge



Annex B
Existing Environment

THIRD SCHEDULE

ENVIRONMENTAL QUALITY ACT 1974

ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS) REGULATIONS 1979

(REGULATIONS 8(1), 8(2), 8(3))

PARAMETER LIMITS OF EFFLUENTS OF STANDARDS A AND B

Parameter		Unit	Standard	
			A	B
(i)	Temperature	°C	40	40
(ii)	pH value	-	6.0 - 9.0	5.5 - 9.0
(iii)	BOD at 20°C	mg/ l	20	50
(iv)	COD	mg/ l	50	100
(v)	Suspended Solids	mg/ l	50	100
(vi)	Mercury	mg/ l	0.005	0.05
(vii)	Cadmium	mg/ l	0.01	0.02
(viii)	Chromium, Hexavalent	mg/ l	0.05	0.05
(ix)	Arsenic	mg/ l	0.05	0.10
(x)	Cyanide	mg/ l	0.05	0.10
(xi)	Lead	mg/ l	0.10	0.5
(xii)	Chromium Trivalent	mg/ l	0.20	1.0
(xiii)	Copper	mg/ l	0.20	1.0
(xiv)	Manganese	mg/ l	0.20	1.0
(xv)	Nickel	mg/ l	0.20	1.0
(xvi)	Tin	mg/ l	0.20	1.0
(xvii)	Zinc	mg/ l	2.0	2.0
(xviii)	Boron	mg/ l	1.0	4.0
(xix)	Iron (Fe)	mg/ l	1.0	5.0
(xx)	Phenol	mg/ l	0.001	1.0
(xxi)	Free Chlorine	mg/ l	1.0	2.0
(xxii)	Sulphide	mg/ l	0.50	0.50
(xxiii)	Oil and Grease	mg/ l	Not Detectable	10.0

Zinc limit standard of effluent in inland water

CK/EV403-370/04
SEIA for the Proposed Oil Palm Plantation (OPP) and Industrial Tree Plantation (ITP) Development at Benta Wawasan I and Benta Wawasan II(C), Yayasan Sabah Forest Management Area Kalabakan and Gunung Rara Forest Reserves, Tawau, Sabah
Annex B1.7 - 1

APPENDIX B

PHYSICAL AND CHEMICAL PROPERTIES

Properties	**$ZnCl_2$**
Appearance:	
Odor:	Odorless
Molecular Weight:	136.28g/moe
Colour:	White
Solubility:	Easily soluble in cold water
Specific Gravity:	2.907 (water = 1)
pH:	Not available
% Volatiles by volume @ 21C (70F):	Not available
Boiling Point:	732°C (1349.6°F)
Melting Point:	290°C (554°F)
Vapor Density (Air=1):	Not available
Vapor Pressure (mm Hg):	Not available
Evaporation Rate (BuAc=1):	Not available

APPENDIX C

MEMBRANE INFORMATION

Table C-1 : Membrane Information

Membrane Material	*Max pH range*	*Recommended max pressure, bar*	*Max Temperature, °C*	*Apparent Retention Character*[1]	*Hydrophylicity*[2]	*Solvent Resistance*[3]
Polyamide Film	*1.5-12*	*64*[4]	*80*	*99%* $NaCl$	*3*	*++*
Polyamide Film	*1.5-9.5*	*60*	*60*	*60%* $CaCl_2$	*4*	*++*
Cellulose Acetate	*2-7.25*	*25*	*30*	*2000 MW*	*5*	*+*
PVDF	*1.5-12*	*10*	*80*	*100 000 MW*	*1*	*+++*

[1] *Retention character depends on several parameters, including nature of the test solution. This information should therefore be used as a guide only.*

[2] *1 low; 5 high*

[3] *+ low; +++ high*

[4] *Maximum pressure limited by module*

In Membrane Test Unit, below are the equipments consist in it. Two pumps are provided with the Membrane Test Unit:

Specification	Lowara Centrifugal Pump	CAT Triple Plunger Pump
Max flow rate (LPM)	80	13
Max head	22	-
Max working pressure (bar)	8	7-5
Max liquid temperature (°C)	110	71
Speed (RPM)	2800	1725
Power (HP)	0.5	3.0

TABLE C-2: Membrane Test Unit Pump Specification

A pressure regulator is installed to regulate the operating pressure of the feed system.

Specifications:

Pressure regulated : 7-70 bar

Allowable flowrates : 3.8-38 L/min

1. Tanks and Heating System

   The Membrane Test unit is supplied with a feed tank and a product tank, both having maximum capacity of 15 L. The feed and the product tanks are made of stainless steel for corrosion and chemical resistance. The retentate line is equipped with a unit of shell and tube heat exchanger.

2. Water Flow Meter

   The Membrane Test unit is supplied with a CT Platon water flow meter.

APPENDIX D

SCHEMATIC DIAGRAM OF MEMBRANE TEST UNIT

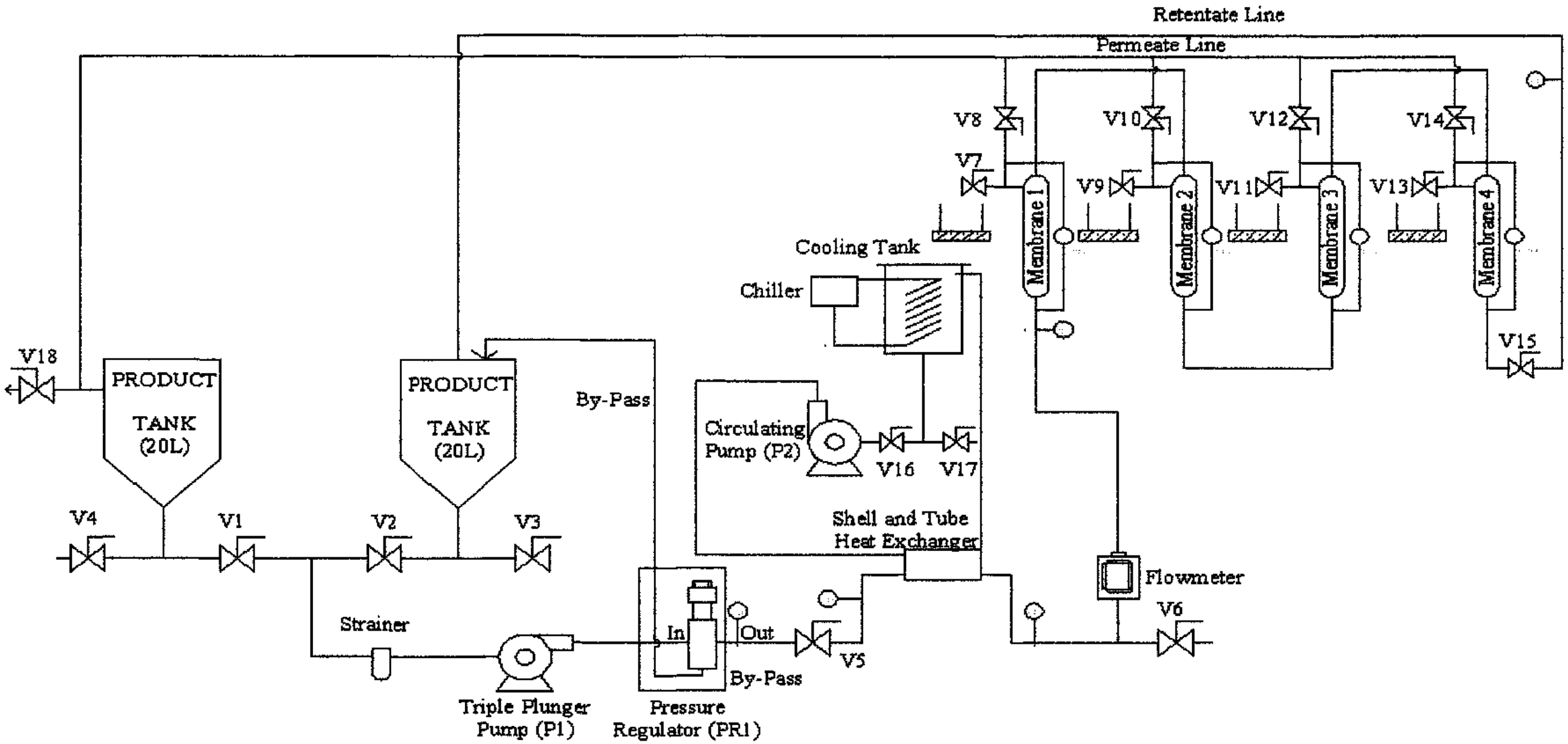


FIGURE D-1: Process Schematic Diagram

APPENDIX E

CALIBRATION CURVE OF ZINC CHLORIDE