REMOVAL OF HEAVY METAL USING MEMBRANE TECHNOLOGY

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REMOVAL OF HEAVY METAL USING MEMBRANE TECHNOLOGY

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A project report submitted in partial fulfilment of the
requirements for the award of the degree of
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DECLARATION

I hereby declares that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declares that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"REMOVAL OF HEAVY METAL USING MEMBRANE TECHNOLOGY"** was prepared by **KOK YAN YIN** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering at Universiti Tunku Abdul Rahman.

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ABSTRACT

Due to the growth of world population and technologies are affecting the water supply demand and its qualities. One of the most serious problems for the environment is water pollution caused by the dissolved of heavy metal into the wastewater. Essentially, toxic metals discharged into the environment are from development industries that manufacturing batteries, metal plating, pesticides, fertilizer and the others. The metal contaminated with water will bring many negatively effects to human health and also the environment. Therefore, many industries paid a major concern for treating wastewater before discharge to the environment. One of the common elements in the Earth's crust is zinc ions. The Baltic Marine Environmental Commission (Helcom) recommended for all industries that the zinc ions contaminated in wastewater are not allowed to exceed 2.0 mg/L. When there is a long term exposure to zinc, which is over or on 40 mg/L, it may cause the serious health hazards like muscular weakness and nausea. The industrial wastewater developed by Rayon Industrial contains about 32 mg/L of zinc ions. Hence, the concentration of zinc ions in the wastewater is over the recommended level. There are a range of methods to treat contaminated metals in wastewater such as chemical precipitation, ion exchanges, coagulation-flocculation, floating, and membrane filtration. Membrane filtration is one of the most frequently study and widely used in the treatment of wastewater for the reduction of toxic metals which has confirmed promise for the removal of heavy metals. This experiment reviewed to investigate the removal efficiency of heavy metal and permeate flux by using cross-flow membrane filtration under different operation conditions. For a better understanding in the operation parameter of the filtration process, central composition design of response surface methodology was used to design and study the responses of the experiment. Besides that, the central composite design was also used to optimize the parameters for maximum the removal efficiency and permeate flux.

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LIST OF SYMBOLS / ABBREVIATIONS

MEUF	micellar-enhance ultrafiltration
CP	concentration polarization
MF	microfiltration
UF	ultrafiltration
NF	nanofiltration
RO	reverse osmosis
TMP	trans-membrane pressure, *kPa*

CHAPTER 1

INTRODUCTION

1.1 Background

The growth in the population and technologies in the world affect the growth demand of water supply (Osman 2014). Nowadays, water pollution has become one of the most serious environmental problems. A major threat to the water quality is the contaminated metal in the wastewater (Fu & Wang 2011). Heavy metal has the atomic weight in between 63 to 200.6 which are very acidic (Fu & Wang 2011). Heavy metals that normally include in wastewater are such as cadmium, arsenic, lead, zinc, copper and nickel (Rudnicki et al. 2014). Basically, the issues of toxic metals discharged into the environment are from development industries that manufacturing batteries, metal plating, pesticides, fertilizer and the others (Fu & Wang 2011). If without adequate treatment of those contaminated metals, high amount of toxic metals in wastewater are a danger to public health and the environment (Polat & Erdogan 2007). Whereas, in every worldwide countries are very concern on the removal of heavy metal from the environment and paid special concern by involving in any advance technologies for the reduction of heavy metal basing on the treatment standard (Barakat 2011).

Among several types of contaminated metals, one of the common elements in the Earth's crust is zinc ions (Lee & Shrestha 2014). According to Baltic Marine Environmental Commission (Helcom), the zinc ions contaminated in the drained out wastewater for all chemical industries are not allowed to exceed 2.0 mg/L (Landaburu-Aguirre et al. 2010) and (Ghosh et al. 2011). When there is the long term exposure to zinc, which is over or on 40 mg/L, it may cause the serious health hazards like muscular weakness and nausea (Channarong et al. 2010). The Korean Water Quality Standard are specifying that the concentration of zinc ions for some rivers, streams and lake areas must be below than 1.0 mg/L; while the zinc ion concentration in drinking water, which are higher than 3 mg/L are not acceptable to consume (Lee & Shrestha 2014). The industrial wastewater in Rayon Industrial contains about 32 mg/L of zinc ions (Ghosh et al. 2011). Hence, the zinc ion concentration in the wastewater is over the recommended level, which is specified not to exceed 2.0 mg/L (Landaburu-Aguirre et al. 2010).

There are various methods to treat the contaminated metals in wastewater such as chemical precipitation, ion exchanges, coagulation-flocculation, floating, absorption and membrane filtration (Polat & Erdogan 2007). Membrane filtration is one of the most frequently study and widely used in the treatment of wastewater for the reduction of toxic metals which has confirmed promise for the removal of heavy metals (Fu & Wang 2011) and (Barakat 2011). Coagulation-flocculation process also known as sedimentation removing settled, bigger and floating solids; while, a coagulant is added into the clarification tank to neutralize the destabilize colloids and flocculation will flocculate the suspended solids size into bigger easier for removal (Osman 2014). Besides that, chemical precipitation usually treated wastewater containing high concentration of metal ions (Fu & Wang 2011). Therefore, adsorption is totally different with chemical precipitation. Absorption is mass transfer bound with the chemical interaction process by transferred a substance from liquid phase into solid surface which is basically used to treat low concentration of metal ions in wastewater (Fu & Wang 2011), (Barakat 2011) and (Kurniawan et al. 2006). Nowadays, flotation can be considered as an alternative method of treating heavy metals from wastewater by dissolved the air flotation using bubble attachment, ions flotation and precipitation flotation (Fu & Wang 2011) and (Polat & Erdogan 2007). Ion exchange is using synthetic or natural solid resin (insoluble substances) to exchange it cations with metal ions contain in wastewater (Fu & Wang 2011), (Rudnicki et al. 2014) and (Kurniawan et al. 2006).

Currently, membrane technologies play an important role in treating wastewater (States et al. 2014). Membrane process turns popular because of it without adding any chemical to disinfect water and this process can prevent the toxic disinfection by-product formation (Ramli et al. 2014). Therefore, there are further discussions of membrane process in chapter 2.

1.2 Problem statement

Due to the growth of word population and technologies are affecting the water supply demand and its qualities. Hence, one of the most serious problems for the environment is the water pollution caused by the dissolved of heavy metal into the wastewater. The metal contaminated in water will bring many negatively effects to human health and also the environment. Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Heavy metals are also harmful to the environment because of their higher toxicity, non-biodegradable and persistent nature. Therefore, many industries paid a major concern for treating wastewater before discharge to the environment. The industrial wastewater in Rayon Industrial contains about 32 mg/L of zinc ions. Hence, the zinc ion concentration dissolved in the wastewater is over the recommended level, which is suggested by the Baltic Marine Environmental Commission (Helcom). The limitation for zinc ions in wastewater is specified not to exceed 2.0 mg/L. So, there is a need to treat the wastewater before its discharge to the environment. There is a range of methods to treat those contaminated metals. Membrane filtration is one of the promising treatments for the last three decades until today. In this experiment, it is important to study the practicality on membrane filtration. Furthermore, is to study on the performance of membrane filtration via the effect of the factors to the membrane. Last of the last, to optimize the parameters for maximizing the removal efficiency and permeate flux using central composite design under response surface methodology.

1.3 Objectives

The objectives of this study are listed as follows:

- To investigate the efficiency of heavy metal removal and permeate flux by using the cross-flow membrane filtration under certain operation condition.
- To study the responses on the design of experiments by using the response surface methodology.
- To optimize the parameters for maximizing the removal efficiency and permeate flux using central composite design under response surface methodology.

1.4 Scope of study

A nanofiltration and reverse osmosis membranes are selected as the membrane separation process. By using a flat-sheet membrane module to evaluate the removal efficiency of heavy metal and develop the permeate flux in this experiment under different operating conditions. Besides that, the experimental study is to investigate the interaction between the differences operating parameters, on the cross-flow membrane filtration system treating on the synthetic wastewater. The zinc concentration in the synthetic wastewater sets out through the experiment representing the zinc concentration in the industrial wastewater from Rayon Industrial. Lastly, study and understanding the statistical analysis of the developed model responses and optimization using response surface methodology.

CHAPTER 2

LITERATURE REVIEW

2.1 General

The rising global demand for water and increasingly of stringent environmental legislation, wastewater treatment have received and reaches the significant attention from the public surround the world (Liu et al. 2013). Nutrients, heavy metal, priority pollutant and suspended solid are those common sources that can be found in wastewater. Heavy metals are one of the most serious environmental contaminant, there are elements which having an atomic weight higher than 63.5 but still in the range of 200.6 (Fu & Wang 2011). There are various types of heavy metal contaminated wastewater, such as copper (Cu), lead (Pb), nickel (Ni), zinc (Zn), chromium (Cr), and cadmium (Cd) (Barakat 2011). It commonly originates from wastewater of mining, electroplating, electrical and batteries manufacturer industrial (Nguyen et al. 2013). Zinc is a toxic and trace element that will bring adverse effect for environmental and human health (Channarong et al. 2010). The adverse effects are including the reduced of muscular growth, depression, increase thirst, nausea, and skin irritation (Channarong et al. 2010; Nguyen et al. 2013; Barakat 2011; Fu & Wang 2011). Therefore, it's necessary to remove those metals dissolved in the wastewater to its discharge to the environment and harm to human being health (Barakat 2011). In order to reduce the contaminated-metal in wastewater, there are several types of methods to treat the wastewater such as chemical precipitation, coagulation, membrane filtration, ion exchange and absorption (Huang et al. 2010). The advantages and disadvantages of those chemical treatments for the heavy metals removal purpose are discussed and summarize in Table 2.1.

Table 2.1 Treatability of Chemical Treatment for Heavy Metals

Type of treatment	Target of removal	Advantages	Disadvantages	References
Chemical precipitation	Heavy metals, divalent metal	Low capital cost, simplicity process	Sludge generation, extra operational cost of sludge disposal, not economical,	(Barakat 2011), (Kurniawan et al. 2006), (Fu & Wang 2011)
Ion exchanges	Dissolved compounds, cations/anions	Less time consuming, no sludge generation, high treatment capacity, fast kinetic	High capital cost, not all ions exchange resin is suitable for metal removal	(Fu & Wang 2011), (Rudnicki et al. 2014), (Kurniawan et al. 2006), (Nguyen et al. 2013)
Flotation	Heavy metals, suspended solids	High metal selectivity, high removal efficiency, high overflow rates, low detention period, low operating cost, increase	High initial capitals cost, high maintenance cost, subsequence treatments are required to improve the removal efficiency	(Fu & Wang 2011), (Polat & Erdogan 2007), (Kurniawan et al. 2006)

		concentration sludge production		
Absorption	Heavy metals	Varieties of low cost absorbent, easy operating conditions, having wide pH range, high metal binding capacities	High cost of AC limits, large surface area	(Fu & Wang 2011), (Barakat 2011), (Kurniawan et al. 2006)
Membrane filtration	Inorganic (heavy metals), organic compounds	High efficiency, space saving, easy operate, low pressure	High cost, membrane fouling	(Fu & Wang 2011) ,(Kurniawan et al. 2006), (Barakat 2011), (Nguyen et al. 2013)
Coagulation-flocculation	Heavy metals, suspended solids	Shorter time to settle suspended solids, improved sludge setting, dewatering characteristic	Cost for sludge disposal, the addition cost for coagulant , increase sludge volume generation	(Kurniawan et al. 2006), (Osman 2014), (Fu & Wang 2011)

However, these techniques are not fully effective and convenient to treat the problem (Chaudhari & Murthy 2010). Membrane filtration has the high efficiency (Zhu et al. 2014) and suitable operation to treat heavy metals contains in wastewater because it can remove the unwanted product without adding in any chemical and direct handling to operate (Barakat 2011) and (Ramli et al. 2014). The advantages and disadvantages of membrane filtration are discussed in Table 2.2. There are four types of membranes are usually used in water and wastewater industries; microfilter, ultrafilter, nanofilter and reverse osmosis membranes (Shirazi et al. 2010). The differences in between the types of membranes are the membrane properties such as the sizing of pores and the operating pressure on the membrane, which are shown in Figure 2.1.

Table 2.2 Advantages and Disadvantages of Membrane Separation

Technology	Membrane separation	References
Advantages	• Suitable across a wide range of industries for their separation processes • retention for all types of particulates • Membrane is positively barrier • No extraneous chemicals are needed • Low energy consumption and low cost • required depending on the size of particles • High selectivity due to the compact and modular	(Osman 2014), (Seo & Vogelpohl 2009), (Ramli et al. 2014), (Barakat 2011), (Seperation process 2014), (Zhu et al. 2014), (Kurniawan et al. 2006), (Giwa & Ogunribido 2012)
Disadvantages	• Membrane fouling • Membrane integrity failure • Production of polluted water during back washing • High operation cost due to membrane fouling	(Ramli et al. 2014), (SSWM 2014), (Nguyen et al. 2013), (Osman 2014), (Van der Bruggen et al. 2008)

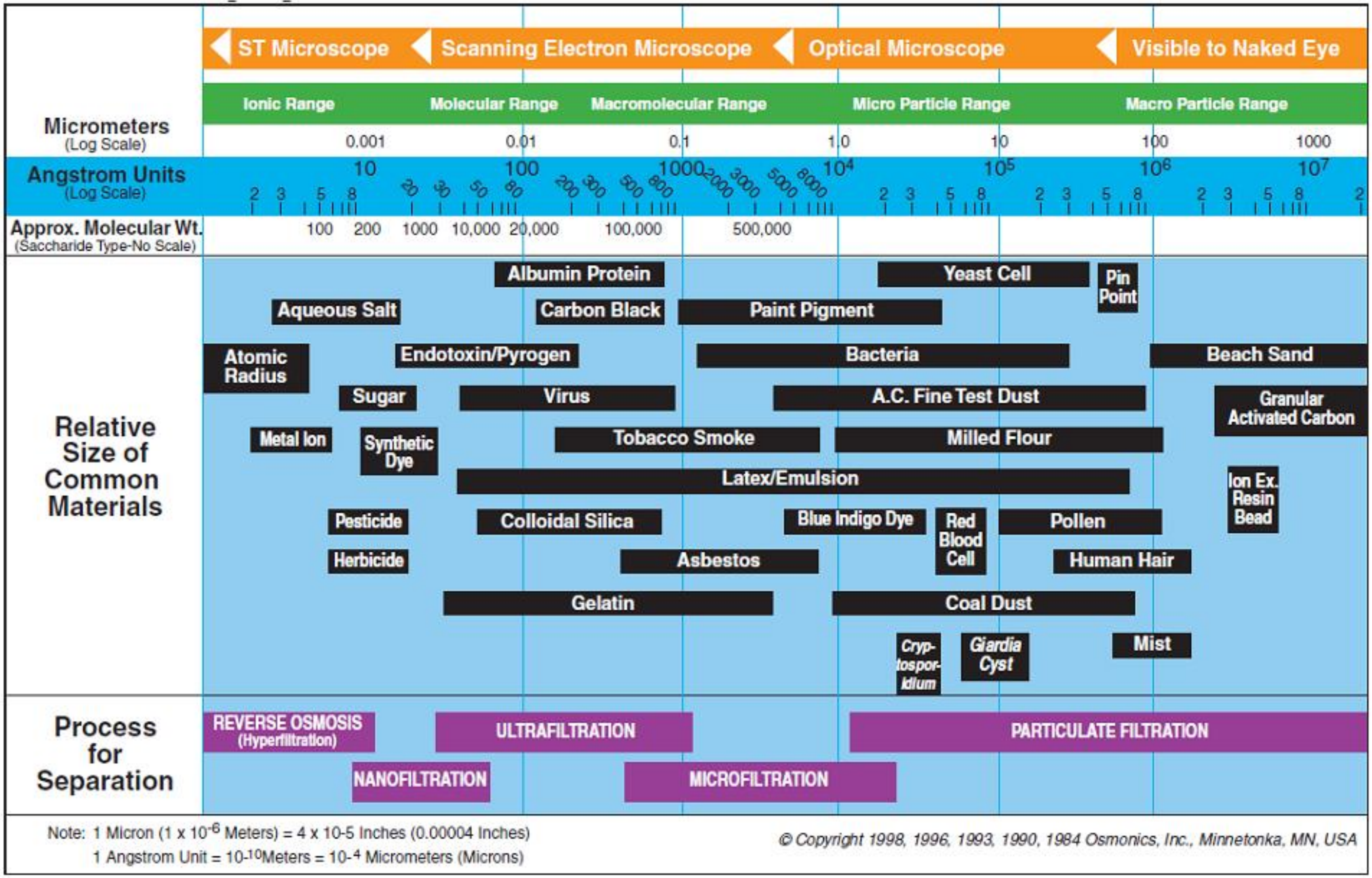


Figure 2.1 Range of Particles Over the Separation Process (SSWM 2014)

2.2 Membranes technology

2.2.1 Microfiltration

Microfiltration (MF) pertains to separate those particles which are bigger than 50 nm and magnitude 200nm (Noble 2014). It operates at low pressure by high permeation flux. (Shirazi et al. 2010) It is widespread in food industry and biotechnology and use to separate particles and bacteria in those products (Shirazi et al. 2010). Microfiltration membranes reduce the turbidity related to the formation of cake layer by particulate materials on the membrane surfaces, but ineffective for the dissolved form of water contaminants like conductivity, heavy metals, metalloids and nutrients (Chon et al. 2014). Dead end flow is classically worked in microfiltration application; only few cross-flow is operating on it (Noble 2014). It depends on the level of the solid to decide with mode should be used (Noble 2014).

2.2.2 Ultrafiltration

Ultrafiltration have the ability to separate soluble macromolecules from other soluble species, including bacteria (Noble 2014) and (Nicholas 2014.). For ultrafiltration (UF) membranes, the pore rating on the basis of the inorganic solution are in between 5nm to 20nm (Kurniawan et al. 2006). Besides that, it often rated by the molecular weight cut off (MWCO) for a measure or rejection (Nicholas 2014). Ultrafiltration is suitable for dissolved particles that are in between 1000 to 300000 MW (Ramli et al. 2014). This membrane process operating at low trans-membrane pressure (Purkayastha et al. 2014)thus it only required less energy for functioning it (Nicholas 2014). Moreover, the cost operating the process is also lower when it only needs less energy (Ramli et al. 2014). Usually, ultrafiltration is done in cross-flow (Noble 2014). Ultrafiltration membrane lifetime can be affected by pH, temperature and fouling (Nicholas 2014).

Once ultrafiltration membranes are selected as the membrane separation process, the dissolved metal ions are smaller than the pore size of ultrafiltration membranes. Therefore, to prevent the zinc ions pass through the membrane easily, the micellar-enhanced ultrafiltration (MEUF) is proposed to achieve high removal of zinc ions (Purkayastha et al. 2014). Based on the analysis (Juang et al. 2003) and Table 2.3, micellar-enhanced ultrafiltration has been successful and obtain high efficiency used in the removal of zinc ions than normal ultrafiltration process (Juang et al. 2003), (Huang et al. 2012), (Hankins et al. 2005) and (Danis & Aydiner 2009).

Table 2.3 Membrane Applications for the Removal of Zinc Ions

Types of membrane filtration system	Initial feed concentration (mg/L)	Removal efficiency (%)	References
UF with hollow fiber module	50-450	>90	(Rahmanian et al. 2010)
MEUF	50	92 - 98	(Fu & Wang 2011)
RO	64-170	98.9	(Fu & Wang 2011)
MEUF	32.7	99	(Fu & Wang 2011)
UF	81.8	95	(Kurniawan et al. 2006)

Micellar-enhanced ultrafiltration is a pressure driven surfactants based membrane separation process (Lee & Shrestha 2014). Therefore, this is a common application used for the separation of heavy metal (Danis & Aydiner 2009) which is also a promising process in removing the heavy metals from wastewater (Li et al. 2009). In order to obtain high removal of small ions, surfactants are added into the wastewater and form micelles (Hankins et al. 2005) and (Yenphan et al. 2010). With the help of anion surfactants, it will aggregates and form larger micellar at the concentration which is higher that its critical micelle concentration (CMC) and used to capture the heavy metals (Juang et al. 2003),(Hankins et al. 2005) and (Li et al. 2009) . Sodium dodecyl sulfate (SDS), an anionic surfactants which has the opposed charge with metal ions that presence in the waste stream to improve the removal efficiency (Purkayastha et al. 2014; Juang et al. 2003; Hankins et al. 2005). Figure 2.2 shows the interaction in between surfactant and metal ions in micellar-enhanced ultrafiltration. The efficiency of zinc removal by micellar-enhanced ultrafiltration depends on the concentration of sodium dodecyl sulfate (SDS), pH value, temperature and etc. The main advantages of micellar-enhanced ultrafiltration (MEUF) are simply operated, high removal efficiency, low energy required for less polluted environment (Danis & Aydiner 2009) and economy (Huang et al. 2014). Micellar-enhanced ultrafiltration has the combination of the high selectivity of reverse osmosis and the high flux of ultrafiltration (Lee & Shrestha 2014).

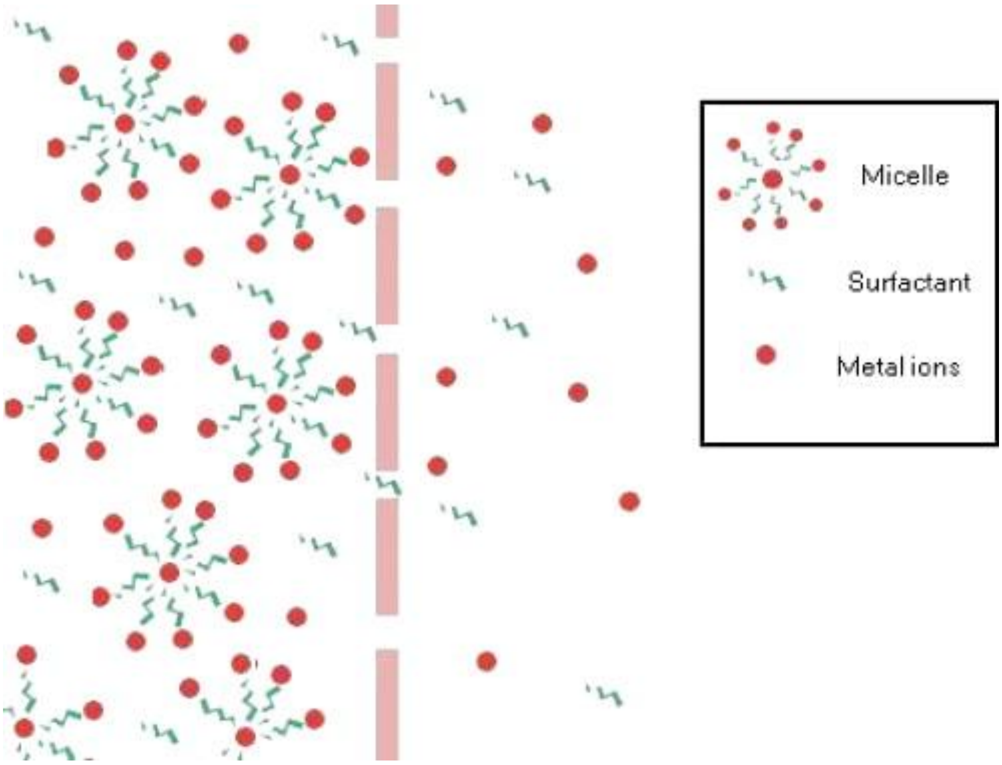


Figure 2.2 A Diagram Illustrate the Surfactant Interact with Metal Ions In Micellar-Enhanced Ultrafiltration (Rahmanian et al. 2010)

2.2.3 Nanofiltration

Nanofiltration (NF) is widely used in drinking water production and wastewater treatment. One of the reason reverse osmosis replaced by nanofiltration in major application because it only required less electrical energy comparatively and it offer higher flux than reverse osmosis (Faridirad et al. 2014) and (Luo & Wan 2013). The characteristics of nanofiltration are in the between ultrafiltration process and reverse osmosis which has high rejection of small molecule compound when compare with ultrafiltration (Wibisono et al. 2014). Nanofiltration easy to operate, reliable and less energy consumption (Purkayastha et al. 2014). Commonly, it used to separate multivalent salt, pesticides, and herbicides from water (Shirazi et al. 2010). Another advantage of nanofiltration in wastewater and water treatment plant is it is able to treat more than one kind of heavy metals in once the process (Maher et al. 2014) and (Mohammad et al. 2014). Nanofiltration used to separate particles based on their size and electrostatic interactions in between particles. Normally, most of the nanofiltration membranes are either positively or negatively charged. Moreover, nanofiltration membranes may cause a slight modification of the membrane charge in some cases from the contacting solution which will lead to have a weak ion-exchange capacity (Mohammad et al. 2014). Nanofiltration has a higher water permeability, but it also operates at low pressure (Zhu et al. 2014). Nanofiltration is a talented technology for the removal heavy metal ions in wastewater industrial (Fu & Wang 2011).

2.2.4 Reverse Osmosis

Reverse osmosis (RO) has the same functions as nanofiltration use in wastewater treatment to purify and separation of water, but it’s commonly used in advanced in the secondary treated wastewater. Both reverse osmosis and nanofiltration is classified as the high pressure membrane filtration process (Motsa et al. 2014). Basically, the operating pressure in reverse osmosis is in between 217.56 psi to 1087 psi (Giwa & Ogunribido 2012). This membrane filtration achieved high removal of constituent such as dissolved solid, metals, inorganic ions and the others, but it required a higher pressure for operation than nanofiltration (Purkayastha et al. 2014). Most of the water contaminants which included seawater, desalt brackish, natural organic matter and synthetic organic and inorganic chemical are purely removed by reverse osmosis (Nicholas P. 2014.). It uses to remove those dissolved particles which larger than 100Da (Chon et al. 2014). Reverse osmosis has a high rejection efficiency than nanofiltration but the flux is not high as nanofiltration due to the smaller pores on the surface (Fu & Wang 2011).

2.3 Parameter affecting the performance of the membrane process

2.3.1 Pressure differential

Pressure related membrane fouling is the transmembrane pressure (TMP). Transmembrane pressure is the driving force for the flux while the permeate flux is the permeate flow rate passing through per membrane area. It is a pressure comes from the top of membrane by pushing those solutes particles towards the membrane pores (Ramli et al. 2014). Transmembrane pressure is linearly with the permeate flux and fouling rate, but there is still an optimum pressure. From the studies summarized that the increase of transmembrane pressure, the fouling rate will increase; while retention of membrane will decrease (Zhao Yan-jun et al. 2014). It increases linearly to constant the pure water flux (Zhao Yan-jun et al. 2014). By increasing the pressure in the membrane, high penetrating of solvent will pass through the membrane (Faridirad et al. 2014). In fact, the increase in transmembrane pressure will cause the permeate flux decline rapidly and increase the rate of membrane fouling formed (Huang et al. 2014). Furthermore, increase the transmembrane pressure lead to the increase of concentration polarization (Huang et al. 2012).

2.3.2 Effect of feed concentration

Through the research report, observed that by increasing the feed concentration, there is the high removal efficiency of heavy metal (Gherasim & Mikulášek 2014). The increase of diffusivity will reduce the membrane fouling on the surface (Zhao Yan-jun et al. 2014). In other side, based on the data in Landaburu-Aguirre et al.2010, the sodium dodecyl sulfate concentration is fixed at 12.5 mM can observe that the higher feed concentration, the retention achieved will drops (Landaburu-Aguirre et al. 2010). Due to the research on Lee & Shrestha 2014, the rejection of zinc ions drop from 84.67 % to 82.42 % when there is the increase of zinc concentration on the feed solution (Lee & Shrestha 2014). The increase of feed concentration will fasten the membrane fouling rate (Zhao Yan-jun et al. 2014).

2.3.3 Effect of flow velocity

The module on the surface of the membrane can be controlled by the wastewater velocity (Hankins et al. 2005). The main transport mechanism for colloids and fine particles includes on the convection, shear induced diffusion, gravitational settling, which depending on the shear rate, size of particles and the particles concentration in the bulk solution (Zhou & Smith 2002). The fouling due to surface crystallization augmented with an increase in operating pressure, but reduced with an increase in flow velocity (Giwa & Ogunribido 2012). The concentration of feed solution and the size of the particle can also be affected the velocity rate (Of et al. 2008). The increase of permeate flux is generally caused by the increase of flow velocity (Zhao Yan-jun et al. 2014). By referring Lin et al. (Lin et al. 2006), described that when the cross-flow velocity reduce, there is an increase on the degree concentration polarization while the flux declined.

2.3.4 Effect of pH

Basically, by increase the feed solution pH will increase the salt rejection from the membrane. Through data analyze, metal rejection will decrease from 3 - 6 % at lower range pH compared to the result at high pH value range (Juang et al. 2003). The rejection by micellar-enhanced ultrafiltration will remain constant at pH range 3 to 12. In the other hand, conclude that at pH 9 will achieved the highest removal efficiency of zinc (Li et al. 2009). The pH value plays the important role with the interaction of metal ions and sodium dodecyl sulfate. The flux and the rejection normally decrease. The fouling potential increases with increasing acidity of the feed solution. (Nanda et al. 2010)

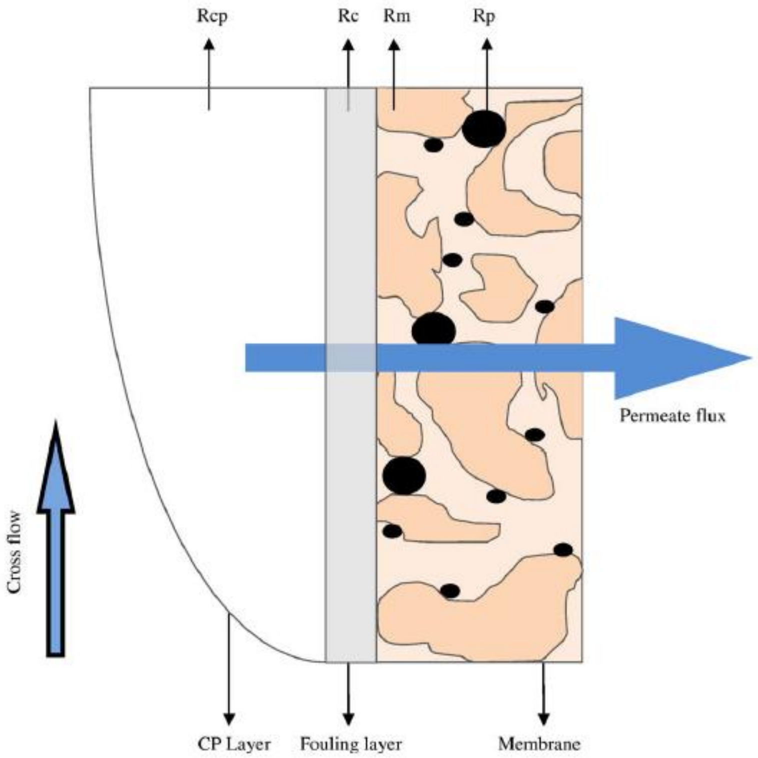
2.3.5 Concentration of sodium dodecyl sulfate

Based on (Lee & Shrestha 2014), the concentration of sodium dodecyl sulfate will affect the percentage of zinc removal from the wastewater. The concentration of surfactant increase, the removal efficiency of zinc will also increase. Concentration of sodium dodecyl sulfate influence the flux (Huang et al. 2014). When the concentration of sodium dodecyl sulfate nearly to the critical micelle concentration, a higher membrane fouling resistance will obtain and has a lower permeate flux (Huang et al. 2014). Besides that, in Landaburu-Aguirre et al.2010 experiment also showed that the when there is the highest concentration of sodium dodecyl in the feed solution, followed by the retention of heavy metal will increase (Landaburu-Aguirre et al. 2010).

2.4 Operating modes for filtration

2.4.1 Cross-flow filtration

Cross-flow filtration is a type of filtration, which allows an incoming feed pass through the surface of cross-flow membrane (Noble 2014). It’s also known as tangential flow filtration because there is a transmembrane pressure comes from the top towards the membrane and presses those soluble or insoluble components passes through the pores of the membrane when there is a feed solution flowing across the membrane (Noble 2014). Cross-flow filtration will generate two exit streams: permeate stream and retentate stream. Permeate stream is the portion of feed solution passes through the membrane and exit the membrane by removing the unwanted big components. The overview of crossflow filtration mode is shown in Figure 2.3. While for those too tiny molecules from the portion of feed solution will follow by passing throughout the pores of the membrane. The rest feed solution which does not pass through the cross-flow filtration will exit as retentate stream. It operates at below the critical flux and there is a dynamic filtration by moving parts (Wibisono et al. 2014). In higher suspended solid, cross-flow mode required high pumping energy for operation (Osmosis 2014). There is the limited growth of cake build up in cross-flow filtration (Daniel et al. 2010).



Where,

R_m, resistance on the membrane or filter cloth

R_c, cake resistance or boundary layer resistance

R_p, resistance on the blocking of pores by solutes

R_{cp}, resistance of concentration polarization

Figure 2.3 Overview of the Cross-Flow Mode During Filtration (Shirazi et al. 2010)

Table 2.4 Characteristics of the Polymer in Membrane

Membrane materials	Channel diameter	Thermal Limit (˚C)	pH	Rejection	References
Cellulose acetate (CA)	Not stated	30	4-8	>90%	(Vijayalakshmi et al. 2008), (Wibisono et al. 2014), (Shi et al. 2014), (Li et al. 2009)
Polysulfone (PS)	3mm	75	1-13	98-99%	(Kurniawan et al. 2006), (Shi et al. 2014), (Li et al. 2009)
Polyvinylidene fluoride (PVDF)	0.8-2mm, 40mm	40	2-10.5	>99%	(Hou et al. 2013), (Wibisono et al. 2014), (Shi et al. 2014), (Li et al. 2009)
Polyamide	Not stated	45	4-11	98-99%	(Kurniawan et al. 2006)
Polysulfone fluoride (PSF)	2mm	35	4	70-97%	(Tanhaei et al. 2014), (Shi et al. 2014), (Li et al. 2009)

2.4.2 Dead-end mode

Dead-filtration is the second technique in the membrane filtration process. In dead-end filtration, the inlet solution is flow perpendicularly through the membrane which are different from cross-flow that are tangentially flow across the membrane surface (Daniel et al. 2010) and (Of et al. 2008). Pressure is pushing the feed solution to pass through dead-end filtration (Spring & Hashsham 2006). A diagrammatically of cross-flow and dead-end filtration are shown in Figure 2.4. A thick layer of retentate is deposited and formed filter cake on the membrane surface (Daniel et al. 2010). The thickness of the filter cake depends on the volume of permeate pass through the membrane. Therefore, filter cake growth proportion when there is an increase in the volume of permeates and the time (Daniel et al. 2010) and (Spring & Hashsham 2006). The filtration rate will decrease due to the hydraulic resistance of the filter cake (Of et al. 2008). Table 2.4 are the material normally used in the membrane process. The comparable of cross-flow filtration and dead-end filtration were summarized in Table 2.5.

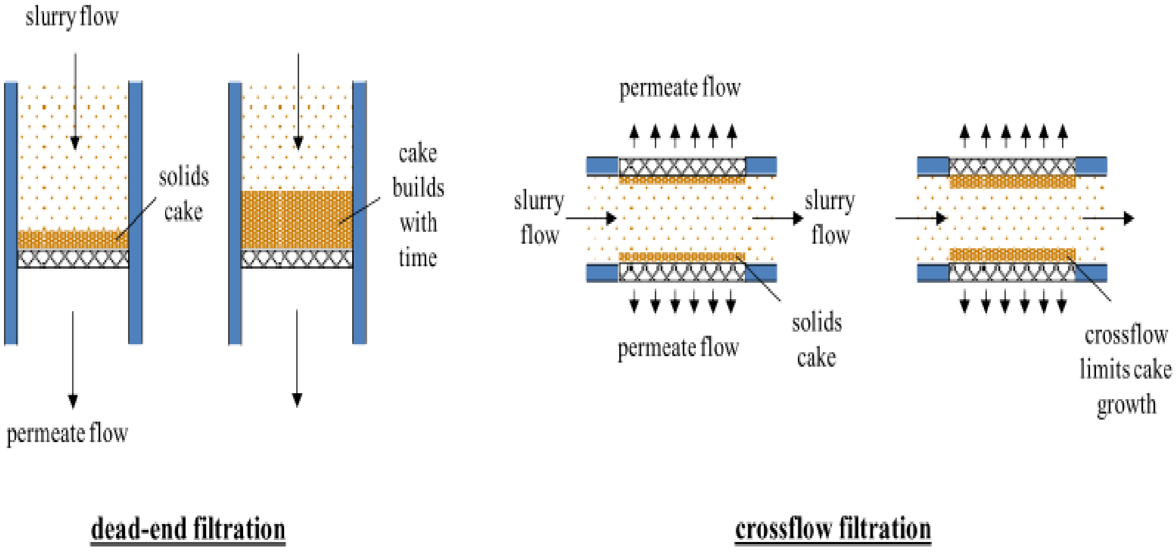


Figure 2.4 Diagrammatic Representation of Cross-Flow and Dead-End Configuration (Daniel et al. 2010)

Table 2.5 Disadvantages and Advantages Of Cross-Flow And Dead End Filtration

Techniques	Advantages	Disadvantages	References
Cross-flow filtration	• High permeate flux • Thickness of the filter cake can be limited • Better condition for reduced fouling • Better hydrodynamic condition	• High loading feed • Required higher pumping energy for bigger size solid suspension	(Of et al. 2008), (Tsibranska & Tylkowski 2013)
Dead-end filtration	• Simpler configuration • Require less capital outlay and maintenance cost • Low feed loading • Useful technique for concentrating compound	• Poor filtration performance • High resistance of filtrate flow • No limitation on the thickness of filter cake	(Of et al. 2008), (Spring & Hashsham 2006)

2.5 Membrane fouling

One of the greatest problems in micellar-enhanced ultrafiltration is membrane fouling which is mainly caused by concentration polarization (Huang et al. 2014). An increase in transmembrane pressure and the decrease of water flux will cause the occurs of membrane fouling (Nicholas 2011) . Membrane contaminated is usually known as fouling. Fouling must be good control in micellar-enhance ultrafiltration to prevent the decreasing of removal efficiency and the performance during in the filtration process (Huang et al. 2012) and (Ramli et al. 2014). Therefore, fouling will cause the increase in operating cost (Hankins et al. 2005). Membrane fouling is a process where the particles, solid suspension and contaminated solids deposit or trapping on the surface of the membrane and on or within the membrane pores (Performed 2009). This process occurs when there is a material stream flow through the membrane and form flux towards the surface of the membrane (Giwa & Ogunribido 2012). Fouling can be characterized by the mechanism and location which is whether foul on, above or within the membrane pores (Nicholas 2011). The location and how the membranes foul are show in Figure 2.5. There are several factors that can affect the efficiency of membrane fouling such as concentration of feed solution, membrane pores sizes, operation conditions (pH, temperature, pressure and flowrate) and the others (Performed 2009). By decreasing down the concentration gradient in between then membrane surface and the bulk fluid is one of the strategies of the control the membrane fouling (Zhou & Smith 2002). Backwashing is one of the methods performed in several studies to control fouling by lessening the amount of accumulate particles on and in the membrane and enhance the membrane fluxing (Huang et al. 2012) and (Shi et al. 2014). While, permeate flux decline defined as the reduce of the permeation through a membrane by a retention time (Performed 2009). By increasing the frequency of backwashing can reduce the fouling rate (Nicholas 2011). Otherwise, keep preserve the velocity of the feed side of the membrane under high condition (Giwa & Ogunribido 2012).

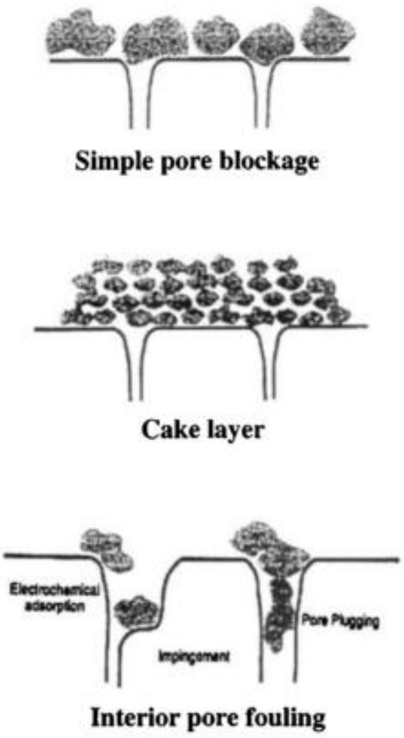


Figure 2.5 A Diagram Showing Where and How The Membrane Fouls
(Nicholas P et al. 2011)

2.6 Concentration polarization

Other major factors hinder on the membrane is concentration polarization. Concentration polarization is considered to be a hydrodynamic or diffusion phenomena which are inherent in all types of membrane filtration process (Shirazi et al. 2010). It has special characteristic in all membrane separation process (Lee & Shrestha 2014). Generally, concentration polarization (CP) is causing the flux decline due to the high level concentration of solutes or particles at the upstream surface of the membranes than the bulk fluid (Performed 2009). The fewest number of factors that an effect concentration polarization; there are the filtration flux, mass transfer coefficient, retention and concentration of solutes (Performed 2009). In fact, to minimize the concentration polarization, increase the flow rates and temperature of the solution (Shirazi et al. 2010). Another way, the increase of concentration polarization is caused by the increase of permeate flux and the operating pressure; therefore also the decrease in retention (Al-Rashdi et al. 2013). When there is a formation of surface cake and the existence of concentration polarization, the interaction force will become significant near the membrane wall (Zhou & Smith 2002). Table 2.6 is the summary of developed quantitative models to describe concentration polarization during membrane filtration (Shirazi et al. 2010).

Table 2.6 Application and limitation of different concentration polarization models (Shirazi et al. 2010) and (States et al. 2014)

Concentration Polarization model	Application	Limitation
Film theory	The model determines permeate flux based on chemical potential gradient.	It assumes a constant mass transfer coefficient for all cases.
Spiegler-Kedem model	Similar to solution diffusion theory but incorporates reflection coefficient as an additional term.	It neglects the phenomenon that concentration polarization increase along the membrane surface.
Gel layer model	The model determines permeate flux based on the constant gel layer resistance (developed by gels of macromolecules) and membrane resistance.	It assumes a fixed surface gel concentration and adapts a mass transfer coefficient from theories of convection heat transfer to impermeable surface.
Osmotic pressure model	The model determines the osmotic pressure near membrane surface that reduce transmembrane pressure and permeates flux.	It cannot be applied to microfiltration and ultrafiltration since osmotic pressure is negligible in these cases.

Resistance in series model	The model estimates permeate flux during different fouling stage.	It only predicts the fouling behaviour of colloids and mono-disperses particles.
Theory of non-interacting particles	The model determines the average permeate velocity of uniform non-interacting spherical particles.	It cannot be used for multi-component system.
Cake-enhanced concentration polarization	The model is a conceptual analysis of the solute transport and concentration polarization in cross-flow membrane filtration.	Its performance in the multi-component system is unknown.

2.7 Cleaning membrane

When there is a membrane fouling occurs, membrane cleaning is the necessity requirement to clear the particles absorbed on the surface of membrane to maintain the membrane lifetime (Motsa et al. 2014). There are several ways to clean the fouled membrane. Two major categories cleaning methods are physical and chemical cleaning methods.

2.7.1 Physical cleaning method

Mechanical action is a physical way to clean the absorbent particle away from the surface of the membrane (Huang et al. 2014). There are several physical cleaning method shows in Table 2.7.

Table 2.7 Physical Cleaning Methods (Shi et al. 2014)**,** (Zhao Yan-jun et al. 2014) and (Van der Bruggen et al. 2008)

Methods	Function
Backwashing	Carried out by reverse flow on the direction of permeate water flow and push the precipitate to the feed side on the membrane.
Hydraulic and mechanical cleaning	Shear forces on the membrane surface, in order to loosen and dislodge the reversing TMP , increasing turbulence or applying mechanical scouring
Compressed air to a filtration system	Inject or incorporating air into a membrane module, either intermittently or continuously, through the retentate side or permeate side, for capillary or flat-sheet membranes.
Membrane relaxation	Allow concentrated foulants at the membrane surface to diffuse away via the concentration gradient
Sponge balls	Effectively scrape deposits off the membrane modules, but the method is time-consuming and may cause scratches on the membrane surface

2.7.2 Chemical cleaning method

Chemical cleaning method is applied of chemical reagent to the membrane by removing the deposits remain on the surface of membrane for cleaning after membrane fouling. Soak the membrane into the chemical solution to get the higher cleaning efficiency. The usages of the chemical reagent are to dissolve, soften and remove the deposits on the surface and pores of the membrane. Besides that, is to avoid the formation of new fouling on the membrane surface (Zhao Yan-jun et al. 2014). There have various types of cleaning agents are normally used for chemical cleaning method is shown in Table 2.8. The cleaning agents are separate into six categories; there are alkaline and acid group, oxidant, surfactant, chelants and enzyme cleaning reagent.

Table 2.8 Common Cleaning Agents and Possible Interaction Between Cleaning Agents and Fouling Layer (Shi et al. 2014), (Al-Amoudi & Lovitt 2007), (Ang et al. 2006), (Regula et al. 2014)

Family	Functions	Advantages	Disadvantages
Acid	Use on inorganic salts and metals oxide and remove and dissolve organic solvents	• For strong acids, can clean many organic and biological foulants by nitration • Less corrosive	• High cost • May cause re-decomposition
Alkaline	pH regulation, alteration of surface charges, alkaline hydrolysis of proteins, catalyzing saponification of fats	• Less caustic • Additional chelating capability	• may form insoluble salts with divalent metal ions
Oxidants	Sterilization purposed, used to eliminate the entire pathogenic microorganism and reduce their growth rate on the membrane	• strong cleaner	• oxidizing capability which will shortening the membrane lifetime
Surfactant	Dispersion or suspension of deposits which help in lower down the interface tension in between two particles	• reduce the rinsing time and water consumption	• surfactants will adsorb onto the available membrane surface eventually cause a more

			hydrophilic membrane surface • flux decline
Chelants	Complexion with metals, removal of mineral deposits by destroying the cross-linked in between fouling layer	• effective in destroying cross-linked	• Cleaning efficiency of is depends on pH
Enzyme	Catalyzing lysis of specific substrates	• prolongs membrane life • very efficient and require less rinsing • do not require high temperature	• Enzymes are selective catalysts, designed for specific targets • cost efficiency is difficult to control

CHAPTER 3

METHODOLOGY

3.1 Membranes

Flat sheet types of nanofiltration membranes (NF and NF90) and reverse osmosis (UTC-80LB) membranes were used in the experiment. All the membranes were soaked for overnight before the day used to remove the preservative on the membranes (Mah et al. 2014). The details properties of the membranes were listed in Table 3.1.

Table 3.1 The Properties of NF and RO Membranes used in this study.

Membrane	Composition on top layer	MWCO (Da)	Salt rejection (%)	Contact angle (˚)	Mean pore radius (nm)	References
NF (Dow FilmTec)	Poly-piperazin NF	200-400	99% MgSO$_4^3$	30	-	(Xu et al. 2010), (Sterlitech 2015)
NF90 (DowFilm Tec)	Polyamide Thin-film composite	200-400	>97CaCl 2 85-89% NaCl	63	5.9	(Hilal et al. 2015), (Mohammad et al. 2014),

						(Xu et al. 2010),(Cathie Lee et al. 2014)
UTC-80LB (Toray)	Proprietary polyamide	0	99.7	88.47	1.17	(Mah et al. 2014)

3.2 Experimental Setup

The concentration of zinc in the synthetic wastewater is set at 32 mg/L, representing the wastewater in Rayon Industry. 13 L of synthetic wastewater was prepared by dissolved 1.898 g of zinc nitrate hexahydrate with a molecular weight of 297.47 g/mol ($Zn(NO_3)_2.6H_2O$) into ultrapure water. All the membranes used in this study are immersed overnight in deionized water for 24 hours to remove the preservative which are some chemicals originated from manufacture and act as a wetting process to stabilize the inner and outer surface parts of the membrane. Flat sheet types of membranes were used in this experiment.

3.2.1 Cross-flow filtration

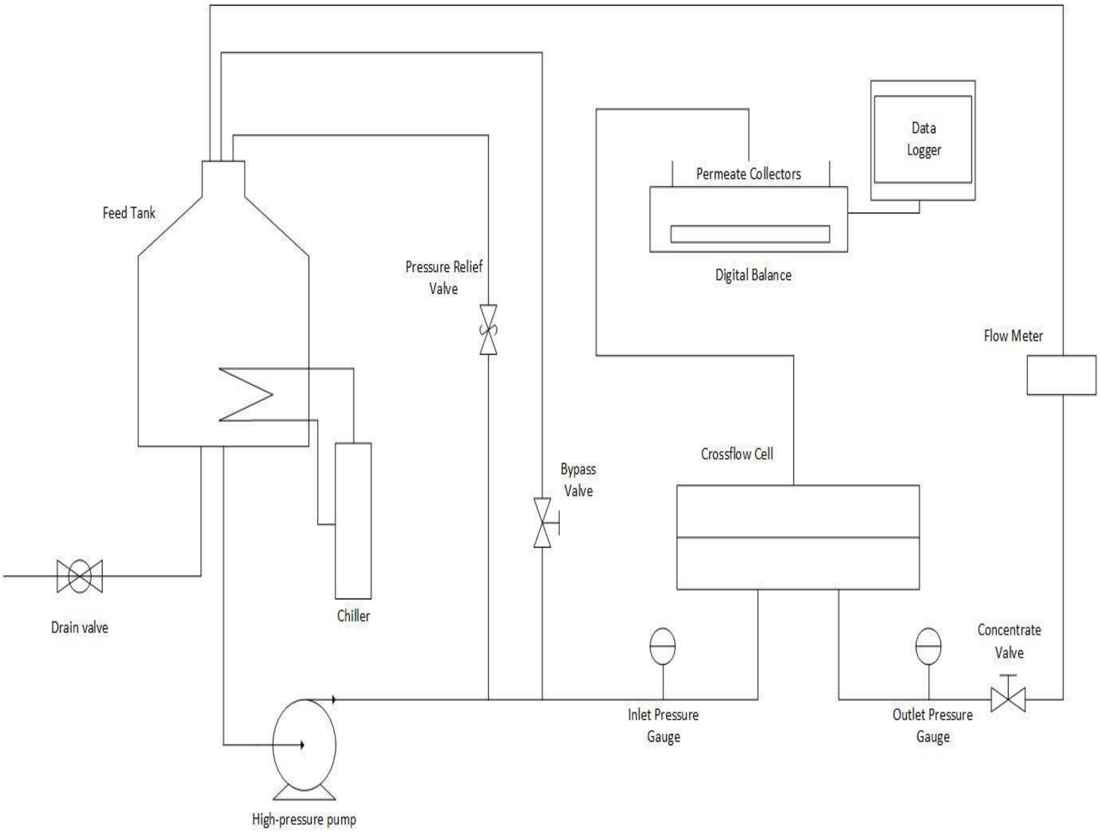


Figure 3.1Schematic diagram of cross-flow filtration experimental set up. Redraw from (Mah et al. 2014)

Figure 3.1 schematize the flat sheet cross-flow membrane module sets up employed in this experiment. The experiments were conducted using Sterlitech stainless steel cross-flow filtration cell, CF042 with effective surface area of 0.0042 m^2. The active surface of the membrane was faced on the feed side by placing it on the middle of cell. Therefore, the opposite surface of membrane was placed facing to the permeate side. Prior to the filtration experiments, those membranes were compacted under 60bar operating pressure, 25 ˚C and 3 L/min for 60 minutes by using deionized water which is to improve the membrane’s permeability to water purpose (Cathie Lee et al. 2014). The prepared synthetic wastewater was poured into the feed tank and pumped to the membrane cell by using a high pressure pump. The cross-flow filtration rig with the compacted membrane twice to stabilize the concentration of the feed solution in this experiment. A chiller was used to control the temperature of synthetic water contain in the feed tank. On the other hand, adjusting the bypass valve and concentrate valve were the purposed to manipulate the parameter of flow rate and the filtration pressure. Each run of the experiment was conducted for one hour experiment under the design range of parameter. The reading of permeate flux was recorded by a data logger for every 1 minute to 60 minutes. The membrane was rinsed with deionized water once after each run of the experiment.

3.2.2 Measurement and analytical method

The amount of permeate collected at the end was recorded by a data logger connected to the cross-flow rig. The permeate flux, J was calculated by the following Equation 3.1:

$$\mathrm{J} = \frac{\Delta \mathrm{W}}{\Delta \mathrm{t} \times \mathrm{A}} \qquad \textbf{(3.1)}$$

Where J is the permeate flux (kg/m^2.hr), $\Delta \mathrm{W}$ is the quantity of permeate (kg). The area of the membrane on the cell module, A (m^2) and $\Delta \mathrm{t}$ is the sampling time (hr). While, the percentage of zinc rejection on the membrane can be determined from Equation 3.2 showed below:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \qquad \textbf{(3.2)}$$

C_p, is the permeate concentration measured from the permeate collector tank in mg/L; while, C_f is the concentration of the feed solution in mg/L. The feed concentration and the permeate concentration were measured by using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) at 213.85 nm spectral lines. The samples introduced into the cyclonic nebuliser chamber by using a meinhard concentric pneumatic nebuliser which was attached on a peristaltic pump (Vanini et al. 2015). The samples were then introduced into the plasma formed in the quartz torch by an alumina injector (Vogt et al. 2014). All measurements were performed in triplicate, and the intensity peak areas were integrated in the respective wavelengths of each element. The peak area value of each sample detected by Inductively Coupled Plasma was referred to the calibrated standard curve to determine the concentration of zinc in the samples. The a standard curve shown in figure was generated by using standard zinc solution from the range 1 mg/L to 40 mg/L to acquire corresponding intensity value.

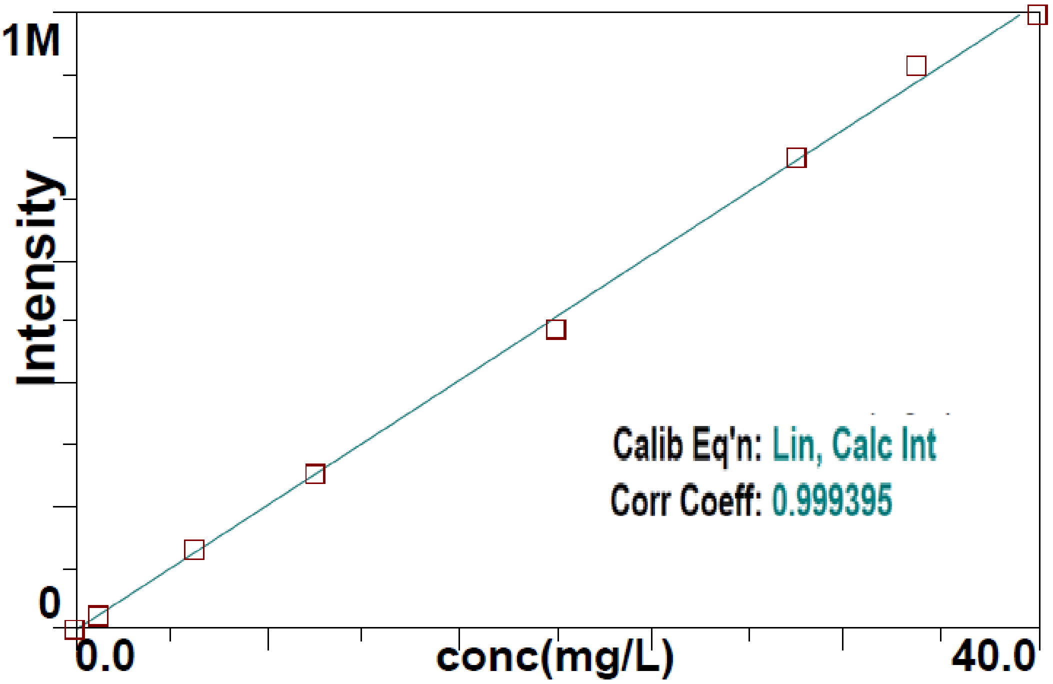


Figure 3.2: Calibration Curve for Zinc Standard Concentration.

3.3 Statistical Analysis

A statistical method is used in this study to analyze and collect appropriate data in the process of planning the experiments by resulting in valid and objective conclusions. Basically, statistical method is used in quantitative data from appropriate experimental designs to determine and solve multivariate equations simultaneously (Statisticalanalysis 2014). There are three stages of experimentation in experiment design: screening, optimizing and verification. Screening experiments purpose is to identify the important factors by focus on the main effect of important variables and find out more about the best settings (Evangelaras & Koukouvinos 2003). The optimization experiment is to build a mathematical model which can be predict the behaviour of the process being investigated and produce specific optimal value for the experiments factors. The experiment is design to estimate interaction and quadratic effects, and therefore present shape of the response surface which is termed as response surface method (RSM) design (Dasgupta et al. 2015). Lastly, is the verification experiment which to include the investigation by verify over a given range.

3.3.1 Response Surface Method (RSM)

Response surface method is a collection of mathematical and statistical techniques useful for modelling and analysis of problems, and hence to describe how the test variables affect the response. Central composite design is one of the response surface design method that is widely used to design the experiment because they do not require an excessive number of experimental runs (Saeed et al. 2014). Therefore, a central composite design was hence employed in the present study to optimize the parameter of the cross-flow filtration process runs statistically configured by RSM through Design Expert software. This method will also analyze and predicting the best experiments data results by optimizing it.

3.3.2 Design of Experiment

Central composite rotatable design (CCRD) is one of the response surface method design with less than 6 selected factors. Central composite rotatable design was selected in the design expert software to evaluate three factors which were pressure, temperature and flowrate. There have 5 levels-2-factorial designs in central composite design. Three factors in 2^3 full factorial CCRD with five levels resulted in 20 runs of experiments ($=2^k + 2k + 6$), k represented the number of independent variables or factors selected. There were 6 runs of center point experiments that evaluated the pure error augmented with 6 axial and 8 factorial experimental runs (Kraber 2014). Therefore, a total of 20 runs of experiment were used in this study. Before beginning with the optimizing process, a screening process was carried manually under pressure 30 bar, 25 ˚C and with the flow rate of 3 L/min. The operating parameters in this experiment were set in between the range: pressure (20 - 40 bar), flowrate (1 - 3 L/min) and temperature (20 - 35 ˚C) and design by central composite design as shown in below Table 3.2.

Table 3.2 Operating Conditions for Optimizing Of Zinc Removal Based On Central Composite Design

Run	Factor 1 A:Pressure (bar)	Factor 2 A:Flowrate (L/min)	Factor 3 A:Temperature (˚C)
1	30.00	3.68	27.50
2	20.00	1.00	20.00
3	30.00	2.00	27.50
4	30.00	2.00	27.50
5	30.00	2.00	27.50
6	30.00	0.40	27.50
7	20.00	3.00	20.00
8	30.00	2.00	14.89
9	40.00	3.00	35.00
10	40.00	1.00	35.00
11	13.18	2.00	27.50
12	20.00	1.00	35.00
13	30.00	2.00	27.50
14	20.00	3.00	35.00
15	30.00	2.00	39.00
16	30.00	2.00	27.50
17	40.00	3.00	20.00
18	30.00	2.00	27.50
19	46.82	2.00	27.50
20	40.00	1.00	20.00

The responses in this experiment are the permeate flux and the rejection of zinc removal in the synthetic wastewater.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Water permeation flux

Water permeate flux analysis was carried out during the compaction on the membrane. The temperature and pressure stay under 25 ˚C and 60 bar which is operating at 3 L/min flow rate. The result of water permeate fluxes was recorded for the membranes were shown in Table 4.1.

Table 4.1Steady Water Permeate Flux at 25˚Cand 60bar

Membranes	Permeate Flux (kg/m^2·hr)
UTC-80LB	86.57
NF	383.01
NF90	423.72

According to Table 4.1, NF and NF90 membranes have a higher water permeate flux than UTC-80LB which is a reverse osmosis membrane. As can be seen in Table 3.1, the mean surface pore radius for nanofiltration membranes was bigger than the reverse osmosis membrane. Same case in Hilal et al. 2015, the flux for RO membrane was lower than the flux for nanofiltration membranes. Therefore, this case might indicate that nanofiltration membrane has the better flux rate than reverse osmosis membrane due to the UTC-80LB membrane has a smaller pore size than the NF and NF90. In fact, nanofiltration membrane has advanced production rate than reverse osmosis membrane (Mohammad et al. 2014). They found that the hydrophobic fraction was the major factor effect the permeate flux declined (Al-Amoudi & Lovitt 2007). From Table 3.1 we knew that UTC-80LB is more hydrophobic than NF90. Therefore, UTC-80LB had the lowest permeate flux rate.

4.2 Membranes screening

In fact, the comparison of the three membranes shown in table 3.1 was carried out to determine the most suitable for removing zinc ions from the synthetic water. The permeate flux and rejection efficiency are the criteria for selecting a suitable membrane. Both are the most important criteria because it indicates which of the membranes have the highest performance by removing the zinc ions which undergo on a short period. A manually screening method was used in this experiment to investigate the responses of permeate flux for the respective membranes under a reference of temperature and flow rate which are 25 ˚C and 3 L/min. The operating pressure of the membrane cell maintains under 30 bar. The permeate flux analysis was recorded down and shown in Figure 4.1 and compared in between the deionized water and synthetic wastewater permeate fluxes results.

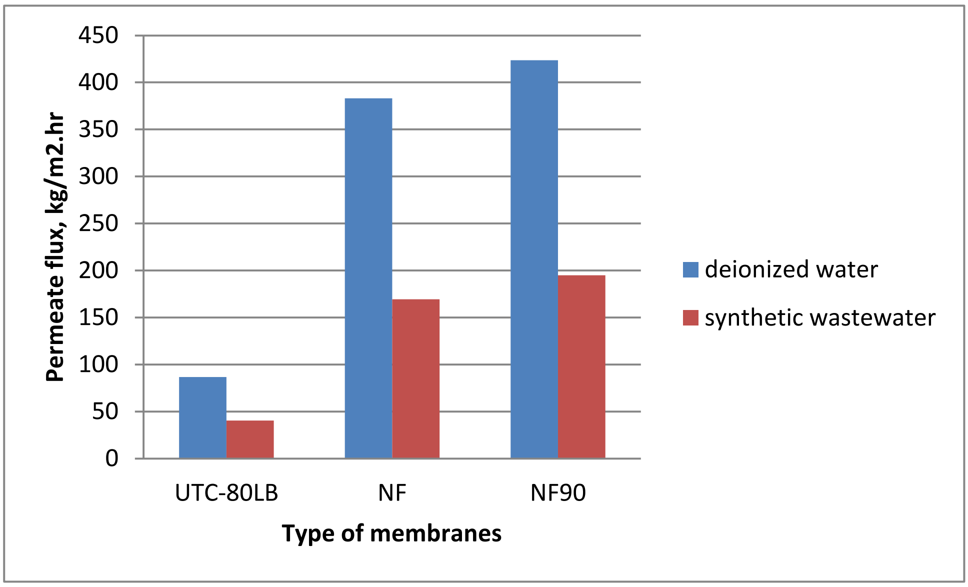


Figure 4.1 Comparison between Water and Synthetic Water Permeate Flux

Based on Figure 4.1, UTC-80LB has the lowest permeate flux in water and synthetic water. This is because it is a reverse osmosis membrane which has a smaller radius of pores than the nanofiltration membrane which was shown in Table 3.1. Therefore, NF membrane has higher permeate flux than UTC-80LB. From the observation on Figure 4.1, the permeate flux in between the synthetic water and deionised water havs a big difference on it. On the contrary, the permeate flux for the synthetic water are lower than the deionised water. This can be indicates that membrane fouling might be taken up or due to the osmotic pressure build up caused by the organic and inorganic salts (Al-Rashdi et al. 2013). According to Mohammad et al. 2014 , both indication from above are the two phenomena related to the fouling mechanism which will lead the reduction of permeate flux.

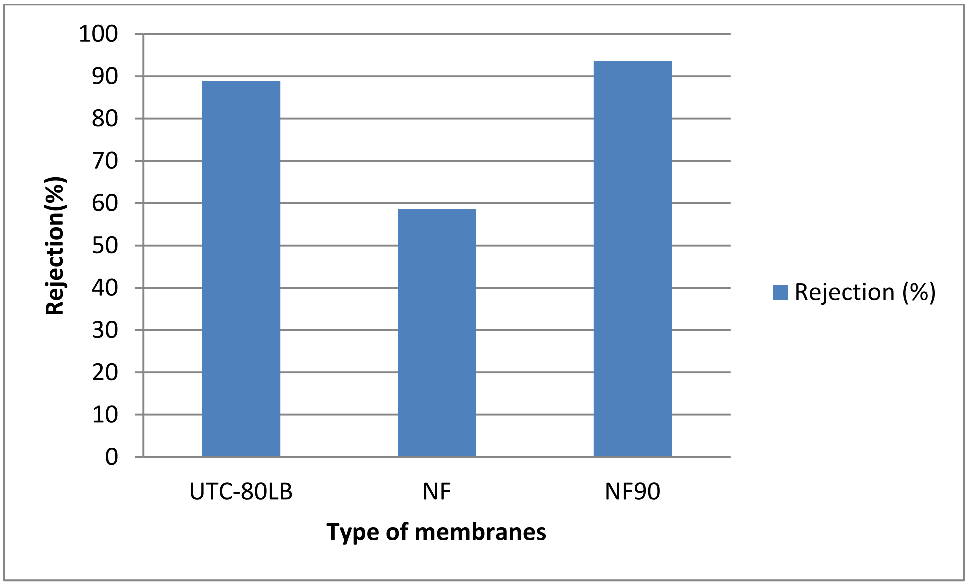


Figure 4.2 The Rejection of Zinc Removal from Synthetic Wastewater

NF90 membrane has the highest permeate flux, while the rejection efficiency is also the highest among the three membranes. The rejection rate of the three membranes during the screening process was shown in Figure 4.1. Although UTC-80LB has a smallest radius pore among the three membranes, the rejection rate is not high as NF90. This is because of nanofiltration membrane have charged which is good in removal divalent ions and low molecular weight organic materials (Mehdipour et al. 2015) and (Gao et al. 2014) which needed low operating pressure than RO and reasonably high salt rejection. The NF membrane has the lowest rejection among those three membranes, which might be indicate that NF is not effective as NF90, although both of its are nanofiltration membranes. Besides that, NF90 has more sensitivity on ion transport, which had worked synergistic on the size exclusion and electrostatic interaction (Mohammad et al. 2014). Lastly, a NF 90 was selected in the screening process and proceeds to the optimization part.

4.3 Design of experimental and response surface modelling

The experimental design used for modelling of the cross-flow filtration by using NF90 membrane was carried out with differences range of the three factors shown in Table 3.2. In this study, Central Composite Design (CCD) was used to optimize the significant factor and study the performance of the three factors on the responses on the cross-flow filtration by using NF90 membrane. The results of the permeate flux and the rejection was recorded and shown in Figure 4.1 and 4.2. The range of the permeate flux are within 72.57 kg/m^2·hr to 170 kg/m^2·hr. While, for the rejection efficiency was reached to the highest 98.67 % from 92.83 %.

Table 4.2 Permeate Flux and Rejection Result by NF90 Membrane Of The CCD Analysis

Run	Factor 1 A:Pressure (bar)	Factor 2 A:Flowrate (L/min)	Factor 3 A:Temperature (˚C)	Response 1 Permeate flux ($kg/m^2 \cdot hr$)	Response 2 Rejection (%)
1	30	3.68	27.5	163.43	95.88
2	20	1	20	110.43	92.83
3	30	2	27.5	142.86	95.83
4	30	2	27.5	141.43	96.88
5	30	2	27.5	136.15	96.79
6	30	0.4	27.5	128.29	95.1
7	20	3	20	105.57	94.71
8	30	2	14.9	72.57	97.58
9	40	3	35	170	96.99
10	40	1	35	151.57	96.33
11	13.2	2	27.5	73.14	95.73
12	20	1	35	85.72	95.78
13	30	2	27.5	132.72	98.08
14	20	3	35	89.72	97.03
15	30	2	39	110.57	97.03
16	30	2	27.5	124.57	98.67
17	40	3	20	116	96.16
18	30	2	27.5	123.72	95.97
19	46.8	2	27.5	163.29	97.33
20	40	1	20	109.29	96.99

4.3.1 Statistical model

Table 4.3 and 4.4 show that the quadratic response surface model was suggested for permeate flux and the rejection efficiency by the software dictated model summary statistics analysis based on it has the lowest standard deviation among other models. Due to model summary statistics, there is a big distance in between the predicted R-squared and adjusted R-squared value. Therefore, the Statistical adequacy of the quadratic response surface model was further analyzed for analysis of variance (ANOVA) and selecting model which focuses on maximizing the predicted R-squared value and the adjusted R-squared value. By pulling nearer the predicted and adjusted R-squared value, reducing the predicted residual sum of squares (PRESS) value is also important in selecting the model. PRESS is a measure of how this particular model fits each point in the design. The coefficients are calculated without the first point. This model is then used to estimate the first point and calculate the residual for point one. This is done for each data point and the squared residuals are summed. According to the model summary statistics for both responses, the full cubic model is aliased which is not good.

Table 4.3 Model Summary Statistics for Permeate Flux

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	21.10293	0.5459076	0.460765312	0.2114428	12373.56	
2FI	18.90716	0.7038344	0.56714252	0.3394869	10364.37	
Quadratic	8.318004	0.9559063	0.916221931	0.7949552	3217.438	Suggested
Cubic	8.166823	0.9787473	0.919239622		+	Aliased

Table 4.4 Model Summary Statistic for Rejection

Source	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**	
Linear	1.18991	0.270803435	0.1340791	-0.1438437	35.53613	
2FI	1.175036	0.42224726	0.1555921	-0.6444903	51.089865	
Quadratic	1.012939	0.66973431	0.3724952	-0.299829	40.382171	Suggested
Cubic	1.134507	0.792851829	0.212837		+	Aliased

4.3.1.1 Analysis of variance (ANOVA)

According to the model summary statistic table for both responses, a full quadratic model was suggested. To obtain and checked the significance of the factors on the models, analysis of variance (ANOVA) has been employed to test with minimizing the PRESS value and improving the adjustable R-squared and predicted R-squared value in the ANOVA analysis. Besides that, it used in determined the corresponding interaction terms to be use for fitting the response surface model. Through the analysis to develop a good model, reduced cubic model was selected by obtaining a larger F-value and a significant p-value which is lesser than 0.05 for permeate flux and rejection in the ANOVA which will pull up the R-squared value and minimize the PRESS value (Kraber 2014).

F-value and *p*-value of the model was generated on ANOVA to determine the statistically significant parameters that were affecting the rejection efficiency and permeate flux. The F-value is also known as the Fisher variation ratio to test for comparing model variance with residual variance (Dasgupta et al. 2015). The *p*-value is the probability of the statistical test in evidential studies and calculated by having the F-value and degree of freedom. If the p-value is low and less than a predefined limit is considered as “statistically significant to the response” (Cojocaru et al. 2009). In this study, the limit for significant parameters is set to $p < 0.05$ which means that the confidence level of this study is more than 95 %. The F statistics and *p*-values for the response were listed in the ANOVA table.

4.3.1.1.1 Permeate flux

Accordingly, the final regression model Equation 4.1 which obtained from the sinplified model that was fitted to the experimental data was represented in terms of actual factors as:

$$\text{Permeate flux} = 204.17 - (12.59 \times \text{pressure}) - (180.38 \times \text{flowrate}) + (9.10 \times \text{temperature}) + 7.57(\text{pressure} \times \text{flowrate}) + 0.23\,(\text{pressure} \times \text{temperature}) + 0.34(\text{flowrate} \times \text{temperature}) + 0.09\,(\text{pressure}^2) + 26.76\,(\text{flowrate}^2) - 0.28(\text{temperature}^2) - 0.07(\text{pressure}^2 \times \text{flowrate}) - 0.74\,(\text{pressure} \times \text{flowrate}^2) \qquad \mathbf{(4.1)}$$

The pressure, temperature and flowrate are the actual value terms which have an interaction relationship in the final equation of permeate flux. The corresponding significant coefficients were estimated and tabulated in Table 4.5.

Table 4.5 ANOVA Summary for Permeate Flux Response Surface Reduce Cubic Model

Source	Sum of squares	df	Mean square	F value	p-value Prob > F	
Model	15336.0296	11	1394.1845	31.3861	< 0.0001	significant
A-Pressure	4063.5113	1	4063.5113	91.4785	< 0.0001	
B-Flowrate	513.4262	1	513.4262	11.5583	0.0094	
C-Temperature	826.3174	1	826.3174	18.6022	0.0026	
AB	84.5000	1	84.5000	1.9023	0.2052	
AC	2340.6482	1	2340.6482	52.6931	< 0.0001	
BC	52.9420	1	52.9420	1.1918	0.3067	
A^2	408.0443	1	408.0443	9.1860	0.0163	
B^2	260.2499	1	260.2499	5.8588	0.0418	
C^2	3208.4261	1	3208.4261	72.2287	< 0.0001	
A^2B	156.3305	1	156.3305	3.5193	0.0975	
AB^2	180.1983	1	180.1983	4.0567	0.0788	
Residual	355.3631	8	44.4204			
Lack of Fit	21.8782	3	7.2927	0.1093	0.9510	not significant
Pure Error	333.4850	5	66.6970			
Cor Total	15691.3927	19				

PRESS	809.8276
R-Squared	0.9774

Adeq Precision	18.7534

Based on Table 4.5, variables A, B, C, AC, A^2, B^2 and C^2 are significant model terms in this case. For those values of "Prob > F" less than 0.0500, can consider indicate model terms are significant. While, values greater than 0.1000 indicate the model terms are not significant but if the value in between 0.05 and 0.1 still under consideration(Dasgupta et al. 2015). In this case, variable AB, BC, A^2B, and AB^2 are insignificant terms but still counting in the analysis was required to support the model reduction which may improve the model. The R-squared in the permeate flux respnse surface reduced cubic model is 0.9774 which is close to 1, which is desirable can be acceptable (Cojocaru et al. 2009). While, the adequate precission which is greather than 4 and the lact of fit is 0.9510 which implies that it is not significant to the model and the model fits the data.

From the analysis, pressure is the most significant factor that affected the permeate flux response followed by tempearature and flow rate. Figure 4.3 show the corresponding in between the three parameters and the response. The interaction in between the pressure and flowrate at tempearture 35 ˚C is illustrated in Figure 4.3 (a) the . From the figure and analysis, pressure showing the superior result on effecting the permeate flux. According to Landaburu-Aguirre et al. 2010, pressure has the dominant effect to the permeate flux. This is because of permeate flux is pressure driven (Ajao et al. 2015). As it can be observed, when the pressure increase, the increasing on driven pressure will lead the permeate flux turn higher.

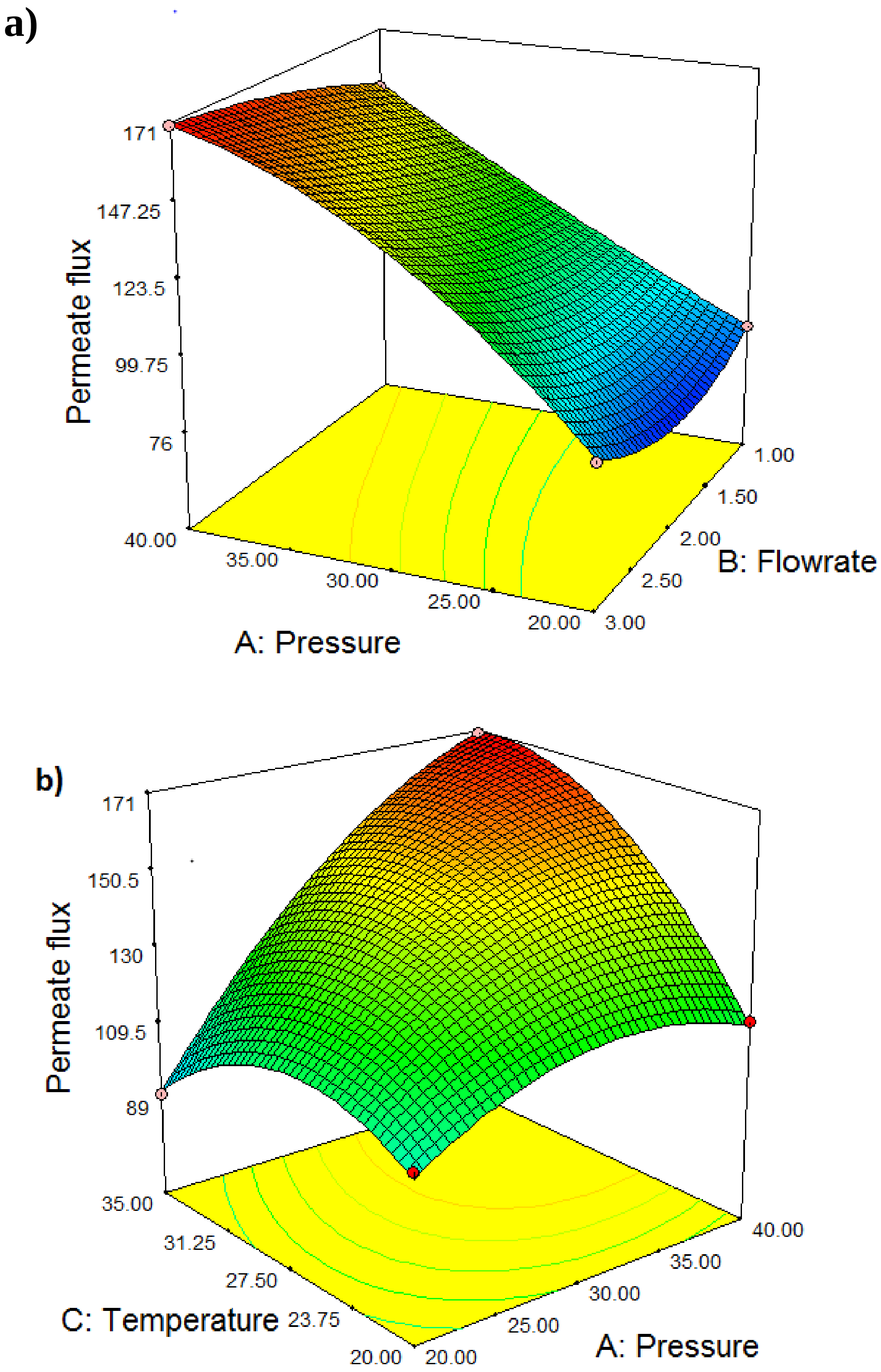


Figure 4.3 Response Surface Of Combined Effects of a) Flowrate and Pressure b) Temperature and Pressure on Permeate Flux

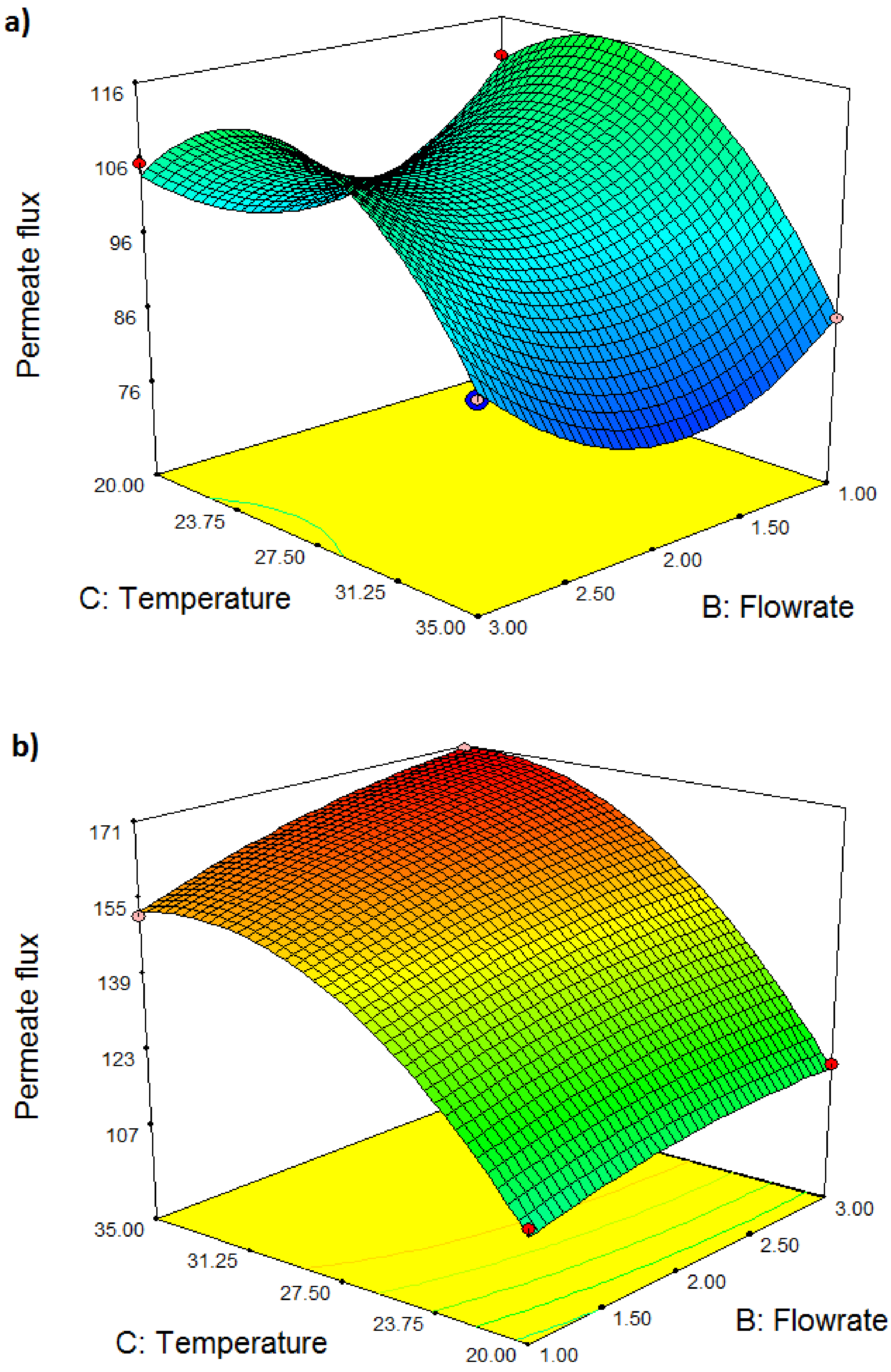


Figure 4.4 Model Graph of Combined Effects Of Temperature and Flowrate under a) 20bar and b) 40 bar.

According to Figure 4.3 (b), pressure is the dominant parameter to the response to the temperature. In fact to achieve high performance of permeate flux, increase the pressure and temperature will do. Based on figure 4.4 is the model graph of permeate flux corresponding with temperature and flowrate, which under 20 bar and 40 bar. It can be observed that when there is at a low pressure, by maximizing the temperature and flowrate, it only can get 89.72 $kg/m^2h{\cdot}r$ permeate rate which is still unable to reach the maximum response. Therefore, it gets highest permeate flux when increases the pressure to 40 bar while the temperature and flow rate increase at the same time.

4.3.1.1.2 Rejection

The final regression model equation for the rejection response (Equation 4.2) that obtained from the simplified model that was fitted to the experimental data was represented in terms of actual factors as:

$$\text{Rejection} = 51.76 + (2.43 \times \text{pressure}) + (4.59 \times \text{flowrate}) + (1.26 \times \text{temperature}) - 0.04\ (\text{pressure} \times \text{flowrate}) - 0.08\ (\text{pressure} \times \text{temperature}) - 0.034\ (\text{pressure}^2) - 0.74\ (\text{flowrate}^2) + 0.0011\ (\text{pressure}^2 \times \text{temperature}) \qquad \textbf{(4.2)}$$

The ANOVA was performed on the statistical model and it is concluded that the model is significant with a *p*-value that is less than 0.05 (Cojocaru et al. 2009). Another important parameter to determine the usefulness of the model is the lack of fit. Based on Table 4.6, the model F-value of 3.93 implies the model is significant. It means that there is only a 1.96 % chance that a "Model F-Value" this large could occur due to noise. In this case A, B^2 are only variances lower than 0.05 which are the significant factors would affect the model terms. The "Lack of Fit F-value" of 0.21 implies the Lack of Fit is not significant relative to the pure error. There is a 95.87 % chance that a "Lack of Fit F-value" this large could occur due to noise. Therefore, non-significant lack of fit is good. For a good model, the diifferences in between the preddicted R-squared and adjustable R-squared should be less than 0.2 which still can consider as a good agreement in between that (Kraber 2014). The preddicted R-squared of 0.4195 for rejection effieciency is in reasonable agreement with the adjustable R-squared of 0.5526. Adequate precision measures the signal to noise ratio. Whereas, a ratio greater than 4 is desirable. A ratio of 7.3477 indicates an adequate signal is shown in Table 4.6.

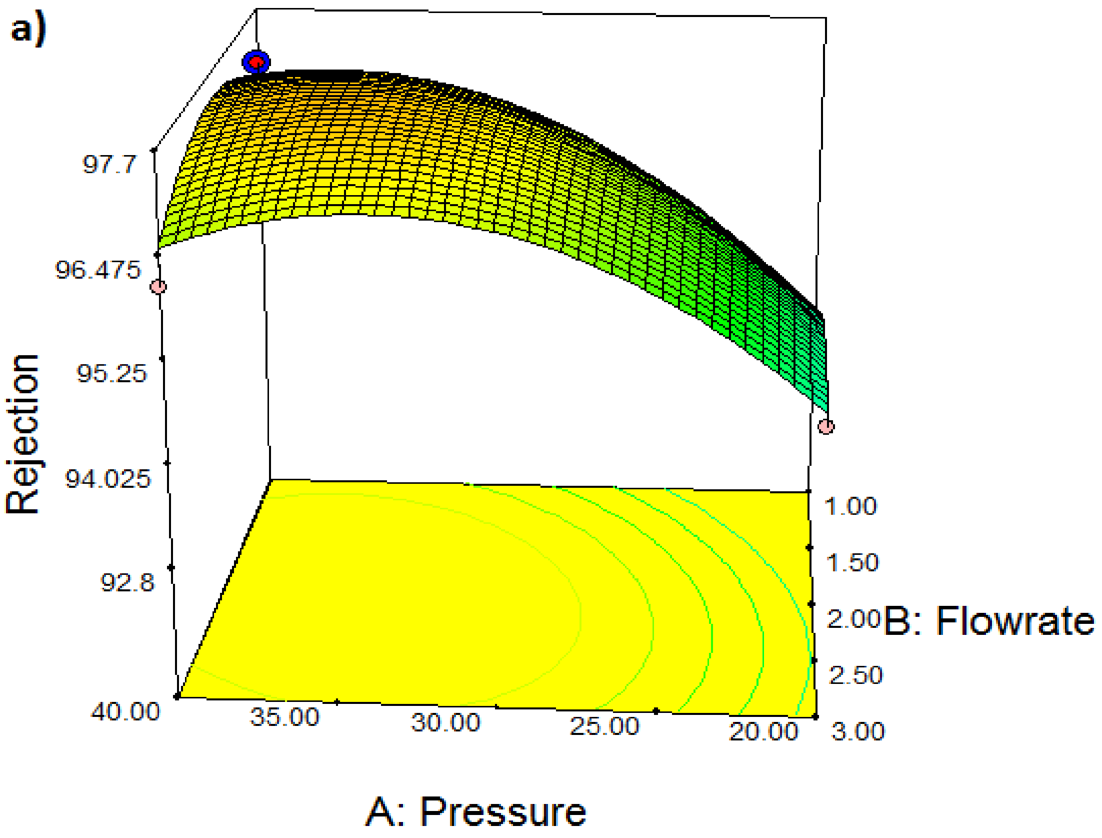
Table 4.6 ANOVA Summary for Rejection Response Surface Reduce Cubic Model

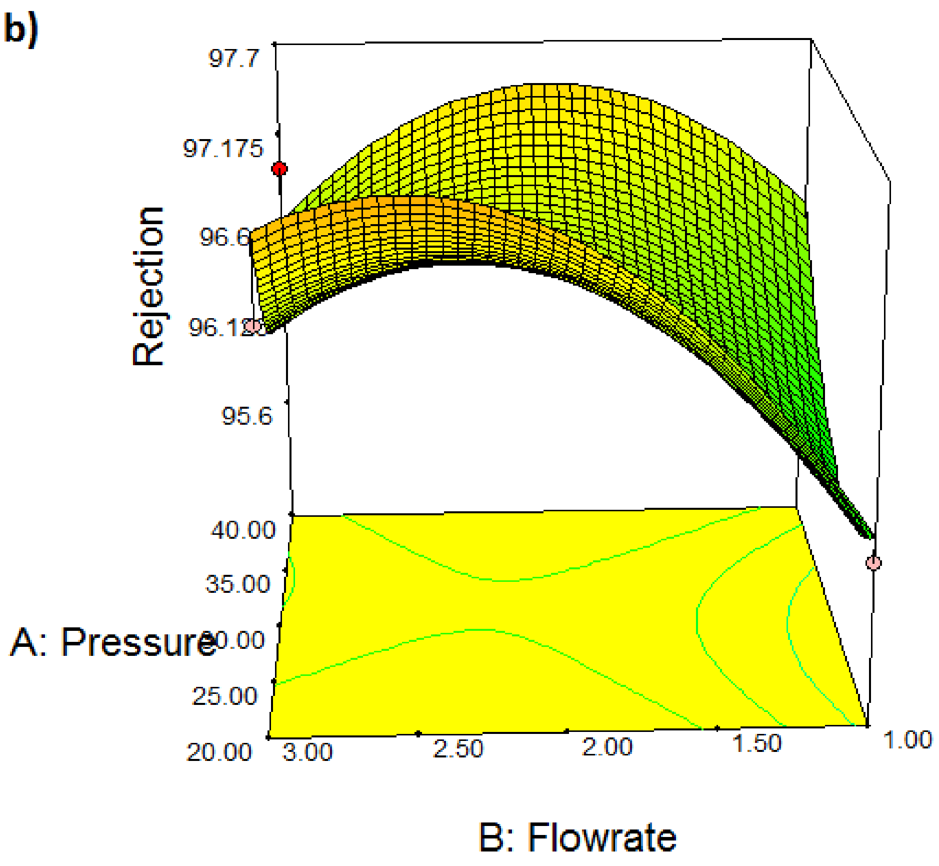
Source	Sum of squares	df	Mean square	F value	p-value Prob > F	
Model	23.0201	8	2.8775	3.9334	0.0196	significant
A-Pressure	5.6844	1	5.6844	7.7702	0.0177	
B-Flow rate	1.8495	1	1.8495	2.5282	0.1401	
C-Temperature	0.1638	1	0.1638	0.2239	0.6453	
AB	1.3613	1	1.3613	1.8607	0.1998	
AC	3.2513	1	3.2513	4.4442	0.0588	
A^2	1.1173	1	1.1173	1.5272	0.2423	
B^2	6.7993	1	6.7993	9.2942	0.0111	
A^2C	2.3132	1	2.3132	3.1620	0.1030	
Residual	8.0472	11	0.7316			
Lack of Fit	1.6117	6	0.2686	0.2087	0.9587	not significant
Pure Error	6.4355	5	1.2871			
Cor Total	31.0673	19				
PRESS	18.0359					
R-Squared	0.7410					
Adeq Precision	7.3477					

According to the ANOVA analysis shown in Table 4.6, only pressure is significant to this response among the three parameters. Variables B^2 and AC have p-value in between the range lower than 0.05 or in the middle range of 0.05 to 0.1

which is still under consideration and acceptable. Therefore, the main and important factor which will affect the rejection of the experiment is mainly on pressure. Referring to Figure 4.5 (a), at low temperature 20 ˚C, the rejection achievement is only 97.58 %, while the rejection started to drop when the pressure and flowrate keep increasing. On the other hand, Figure 4.5 (b) explain that the retention rate is decreasing after the flowrate at 2 L/min and pressure, 30 bar in the mean time while increasing the temperature to 40 ˚C. Based on the theory of Al-Rashdi et al. , concentration polarization occurred and increase with the increasing of pressure which will cause the reduction of retention. However, the convective transport act as the opposite role with concentration polarization which will help to improve the retention rate.

Therefore, the increased in convective transport in the same time the concentration polarization also increasing, it will have a nearly constant rejection value in the experiment In this case, the rejection of zinc removal starts dropping in the meantime of increased the operation pressure which implies that the concentration polarization had occurred followed by the convective transport and concentration polarization. However, the changes in between that are too tiny which will overcome and nearly turn into constant value. This means that, a high pressure needed to obtain a high rejection efficiency, but due to the problem of concentration polarization, increase the flow rates and temperature of the solution is needed to reach an high achievement on the rejection efficiency (Shirazi et al. 2010). While, Figure 4.5 (c) shows that there is not much changes in the rejection by maximizing and minimize the flowrate.


a)
Rejection
97.7
96.475
95.25
94.025
92.8
40.00
35.00
30.00
25.00
20.00
A: Pressure
1.00
1.50
2.00
2.50
3.00
B: Flowrate


b)
Rejection
97.7
97.175
96.6
96.12
95.6
40.00
35.00
0.00
25.00
20.00
A: Pressure
3.00
2.50
2.00
1.50
1.00
B: Flowrate

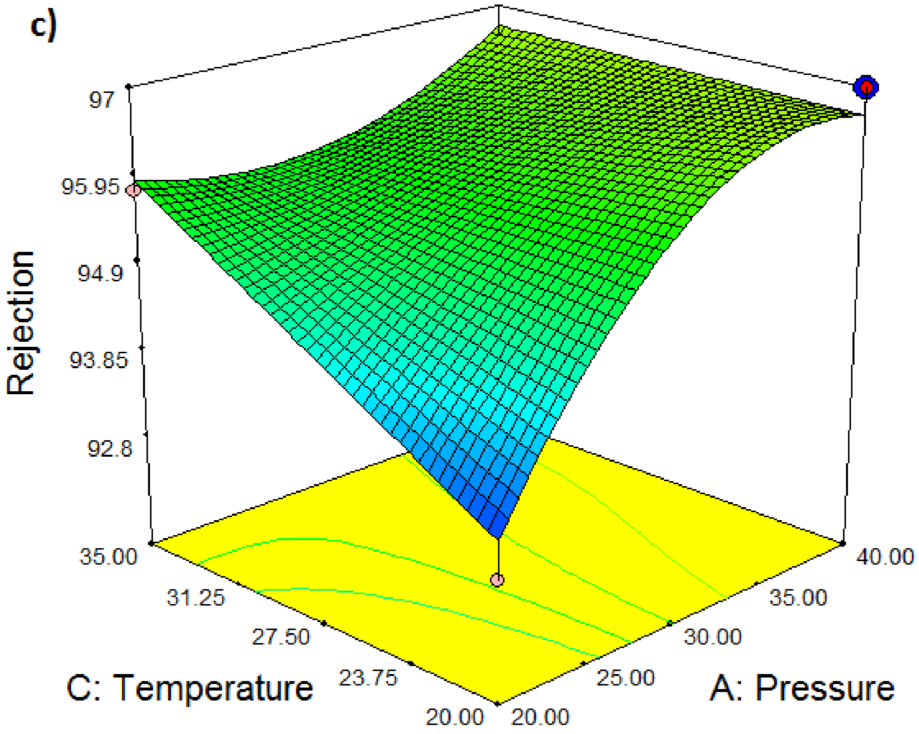


Figure4.5 Model Graph for Interaction of Pressure and Flowrate Under Temperature a) 20˚C and b) 40˚C and c) Pressure and Temperature

4.3.1.2 Diagnostic plots

Diagnostic plots of the case statistics are used to validate the selected model. In order to further investigate the validity of the model, the normality plot of residuals is used to confirm the normality assumption. Figure 4.6 shown plots as normal % probability versus internally studentized residuals. If all the residuals are following a straight line means that the model is normal. When some scatter is expected, a definite pattern "S" shape will be shown (Kraber 2013). By referring Figure 4.6, all the residuals with the repeated points are close to the straight line. This shows that the reduced cubic model chosen in the ANOVA analysis is suitable.

Another validation method is examining the residual plot versus the predicted response by confirm the constant variance assumption (Cathie Lee et al. 2014). When there is a random scattered point which is showing good fitting on the plots, it can be considered as a good model. So, the variance (scatter) should be approximately constant over the range of predictions. Both plots showed in Figure 4.7 have corresponding scattered points above and below the horizontal axis.

The last validation can be done by using the predicted against an actual plot to see how the model predicts over the range of data by verifying the model that generated. The plot shown in Figure 4.8 is used to check the coefficient of determination in the ANOVA analysis for the permeate flux and rejection efficiency. Permeate flux and rejection in Figure 4.8 show reasonably good fit to the experimental values obtained. Somehow, the predicted against actual for rejection plots is shown in Figure 4.8 (b) more or less along the straight line in between range 92.83 % to 98.67 %. All the scatters are concentrated on a certain area except the lowest and highest rejection point which still consider as a good fit model to the experiment. Due to this reason able to cause the degradation of the correlation coefficient.

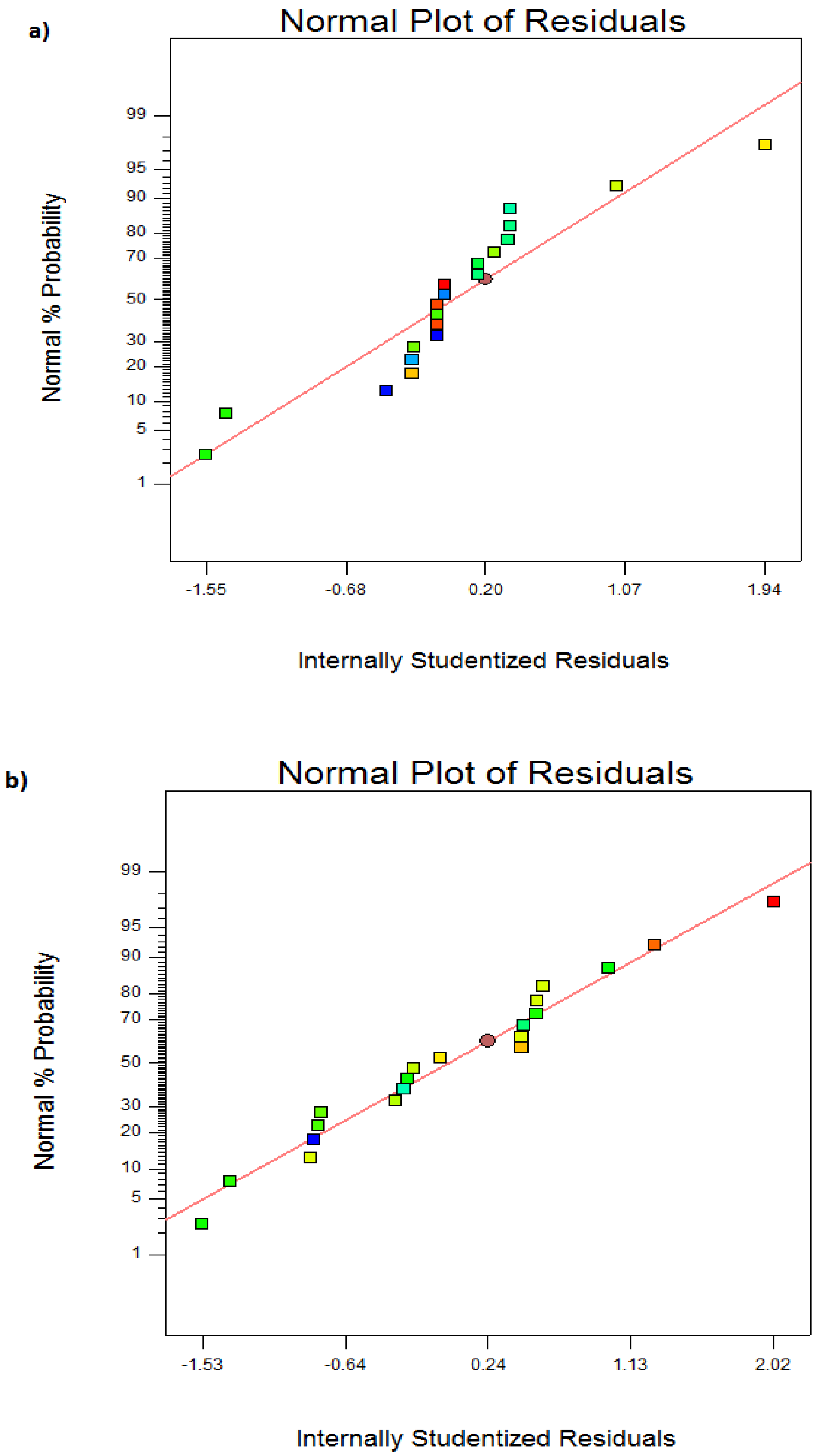


Figure 4.6 Normal Plot of Residuals a) Permeate Flux and b) Rejection

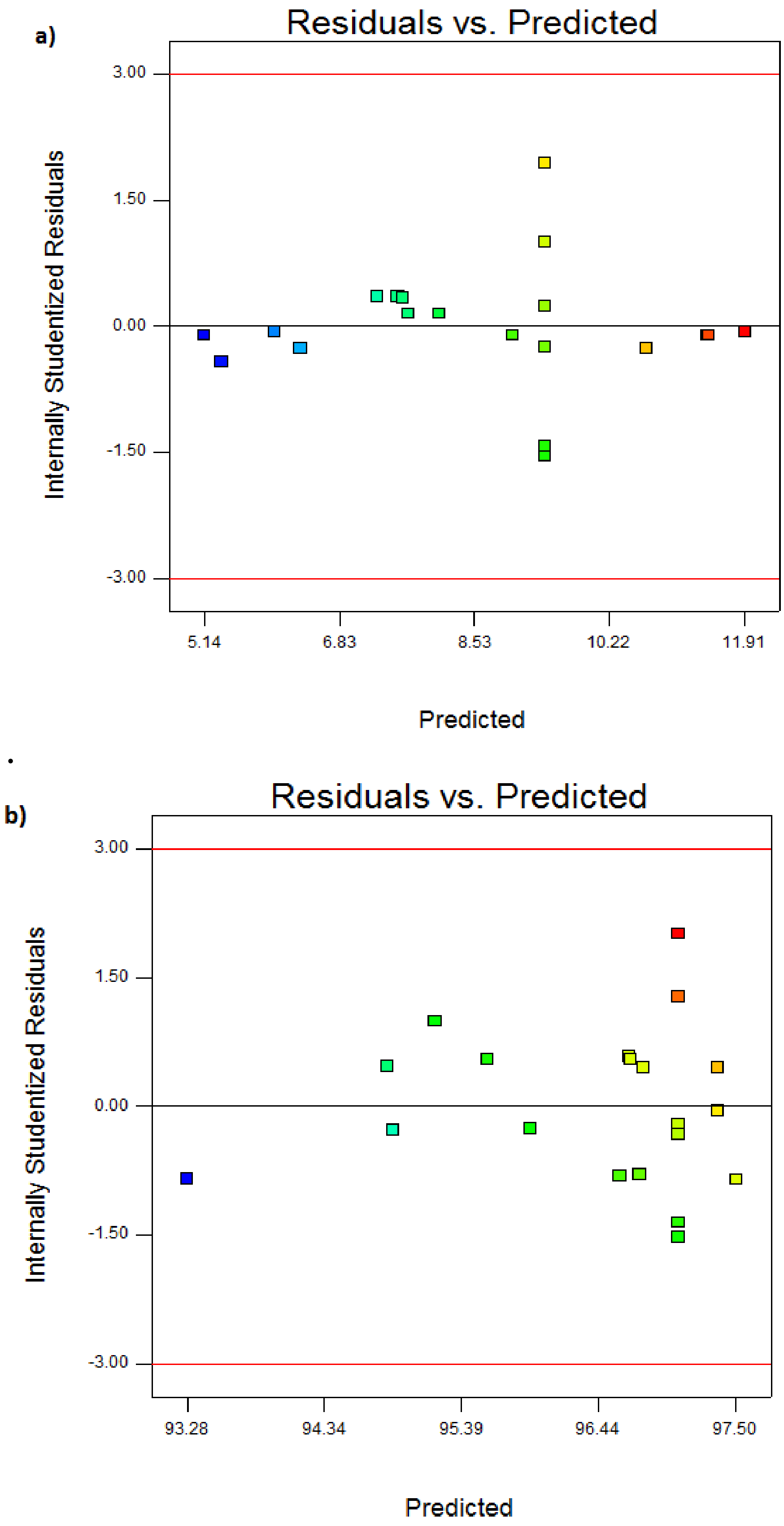


Figure 4.7 Plots of Residuals Versus Predicted a) Permeate Flux and b) Rejection

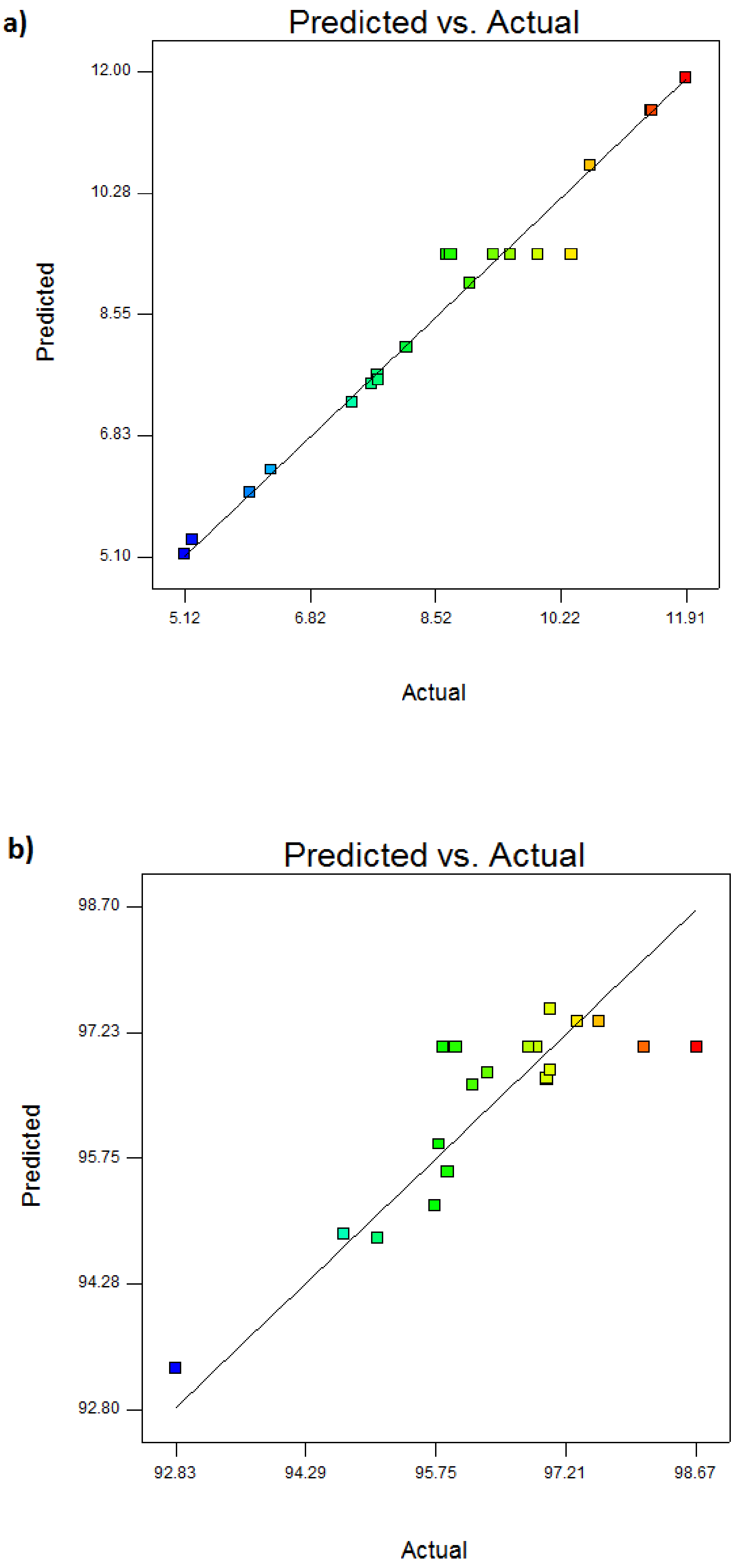


Figure 4.8 Plots of Predicted Against Actual a) Permeate Flux and b) Rejectio

4.4 Optimization of process parameter

The optimization method in this study is to maximize the retention of zinc ions and get the highest permeate flux as possible under reasonable range those three parameters. The predicted rejection and permeate flux were determined by using the model equation generated from ANOVA analysis. Therefore, the optimum parameters approximated from this statistic model based on the highest desirability, 0.871 were 40 bar, 2.2 L/min and 34 ˚C. In fact, the estimated permeate flux and the rejections were 166.60 $kg/m^2 \cdot hr$ and 97.42 %, respectively is shown in Table 4.7. One run of the experiment had been run based on the optimum parameter to calculate the error percentage and validation of the response at the optimum conditions.

Table 4.7 Validation of response under optimum parameter

Rejection (%)		**Error (%)**	**Permeate flux($kg/m^2 \cdot hr$)**		**Error (%)**
Predicted	**Experimental**		**Predicted**	**Experimental**	
97.42	96	1.45	166.60	157.86	5.25

The mean of error from predicted and rejection are 1.45 % and 5.25 %, respectively. This indicates good agreement in between permeate flux and rejection.

4.5 Relationship between permeate flux and rejection

According to the Table 4.2, there were actually consist of 6 runs of center point experiments that evaluated the pure error augmented with 6 axial and 8 factorial experimental runs. In the total 20 runs, there are actually a 6 runs were repeated with the same value of parameter. Based on the observation on those 6 repeated center points, there all had the different value of permeate flux and rejection, although there were operating under the same value of parameter. The only thing consistence is when the permeate flux rate increase, the rejection was low. Well, when there is an improvement in the rejection efficiency, at the same time the permeate flux started to drop. The indication on this situation is membrane fouling occurred (Performed 2009). Based on Figure 2.6, gel layer formed on the surface of the membrane when the concentration polarization keeps increasing (Shirazi et al. 2010). The metal particles will across the membrane and stick on the membrane in this case which blocked by the pores of the membrane (Zhao et al. 2014). In fact, the metal particles will accumulate more and more which are blocked by the pores and form a gel layer on the surface of the membranes. Therefore, it causes the permeate flux decline, whereas the flowrate of solute diffuse into the membrane decrease. Other than that, it wills harder the particle molecules move harder through the membrane which will increase the rejection percentage.

CHAPTER 5

CONCLUSION

5.1 Conclusion

The central composite rotatable design was used in optimizing and study the responses of parameter in this experiment. The experimental design optimized the range of operating conditions: presssure, flowrate and temperature shown in Table 3.2. The permeate flux and rejection result were investigated and listed in Table 4.2. The highest permeate flux was 170 kg/m^2.hr, which was achieved using the experimental design for Run 9. According to the ANOVA, the significant variables affecting the permeate flux were pressure followed by temperature and flowrate. All of the significant factors contributed positive effects on permeate flux response. This shows that pressure, flowrate and temperature are significant in this model with the *p*-value lesser than 0.005 and R^2 value of 0.9774 which is near to 1. The model fits with the data with the *p*-value of less than 0.001.

On the other hand, the significant variable affecting the rejection of zinc ion removal was only pressure. The mathematical model of rejection is significant with *p*-value 0.0177 and R^2 value of 0.7410. The model fits with the data with the *p*-value of 0.0196, which is significant. The maximum rejection (98.67 %) was achieved by the experimental run 16. Lastly, the optimum parameter generated to get the highest rejection and permeate flux were under an operating pressure and temperature, 40 bar and 34 ˚C at flowrate 2.2 L/min. Based on the model, the predicted permeate flux and rejection were 166.6 kg/m^2 ·hr and 97.42 %.

5.2 Recommendation

Membrane fouling had been indicated in this study during the experiment. Therefore, the study of fouling should be investigate as a future study to have a better understanding on the interactive effects of the investigated process parameters on the performance of membrane fouling. Due to the limitation of time, further membrane characterization can be carried out to investigate the effects of membrane characteristics on the membrane fouling.

Fouling may result in an increase in operational costs. Therefore, a cost analysis is recommended due to an increased energy demand, additional labor for maintenance, cleaning chemical costs, and shorter membrane life. Besides that, the study of membrane cleaning techniques is recommended to prevent fouling and improve the anti-fouling properties of the membranes.

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