# OPTIMIZATION OF ADDITIVE CONCENTRATION IN POLYMERIC MEMBRANE FABRICATION (HIGH POLYMER CONCENTRATION)

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**A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Environmental Engineering**

**Faculty of Engineering and Green Technology**
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# DECLARATION

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

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# APRROVAL FOR SUBMISSION

I certify that this project report entitled "**OPTIMIZATION OF ADDITIVE CONCENTRATION IN POLYMERIC MEMBRANE FABRICATION (HIGH POLYMER CONCENTRATION)**" was prepared by **LIM YI SIN** has met the requirements for the award of Bachelor of Engineering (Hons.) Environmental Engineering at Universiti Tunku Abdul Rahman.

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## Abstract

As technology become more and more advance, it causes water pollution and newly contaminants found in water resources (Hogan, 2014). Membrane technology is one of the diversity of water treatment technologies have been employed in order to meet the water quality standards and water demand. Membranes are classify into microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. In this study, Polyethersulfone (PES) as polymer, N-methyl-2-pyrrolidinone (NMP) as solvent and Powdered Activated Carbon (PAC) as additive were used to fabricate high performance of membranes. Five types of membrane (0% PES-PAC, 1% PES-PAC, 7% PES-PAC, 9% PES-PAC, and 11% PES-PAC) were tested with pure water flux, salt solution flux, and salt rejection to determine the membrane performance in term of permeation rate. The results showed that 11% PES-PAC has the highest flux which is in range of $6.403 \times 10^{-5} – 1.3098 \times 10^{-4}$ $m^3/m^2s$ and 0% PES-PAC has the lowest flux which is $8.300 \times 10^{-6} – 1.413 \times 10^{-5}$ $m^3/m^2s$. Meanwhile, highest salt rejection was obtained by 11% PES-PAC which is in range of 56.67 – 79.62 % and lowest salt rejection was obtained by 1% PES-PAC which is 26.94 – 30.12 %. Scanning Electron Microscopy (SEM) was used to study the morphology of each membranes. It showed that membranes with PAC will enhance marcovoid formation of the membrane and increase the porosity. However, addition of PAC in casting solution will decrease the tensile strength. Generally, the overall performances of membrane improved with the increase of PAC concentrations except tensile strength.

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# LIST OF SYMBOLS / ABBREVIATIONS

| | |
|---|---|
| BAC | Biologically Activated Carbon |
| BOD | Biochemical Oxygen Demand |
| CA | Cellulose Acetate |
| CAS | Conventional Activated Sludge Treatment |
| DMAc | Dimethylacetamide |
| DMF | Dimethylformamide |
| DMSO | Dimethylsulfoxide |
| DOE | Department of Environment |
| EMBR | External Membrane Bioreactors |
| GAC | Granular Activated Carbon |
| MBR | Membrane Bioreactors |
| MF | Microfiltration |
| NF | Nanofiltration |
| NMP | N-methyl-2-pyrrolidinone |
| PAC | Powdered Activated Carbon |
| PE | Polyethylene |
| PES | Polyethersulfone |
| PP | Polypropylene |
| PTFE | Polytetrafluoroethylene |
| PVP | Polyvinylpyrrolidone |
| RO | Reverse Osmosis |
| SEM | Scanning Electron Microscopy |
| SMBR | Submerged Membrane Bioreactors |
| SOC | Synthetic Organic Chemical |
| SRT | Sludge Retention Time |
| TMP | Trans Membrane Pressure |
| TMU | Tetramethylurea |

| | |
|---|---|
| TSS | Total Suspended Solids |
| UF | Ultrafiltration |
| UV | Ultraviolet Light |
| VOC | Volatile Organic Compound |

# CHAPTER 1

# INTRODUCTION AND OBJECTIVES

## 1.1 Introduction

Water is an important element in maintenance of all the living organisms like humans, plants, and animals. For humans, we need to drink clean water to maintain our body temperature, lubricate and cushions organs, metabolize body fat, transport nutrients to the cells, flush toxins out of organs, offer a moist environment to regions like the throat, and play a role in digestion (Carr and Neary, 2008). Besides, we need clean water for daily activities like cooking, washing, and bathing.

Domestic wastewater is the sewage that generated by residents, commercial or industries. According to Hogan (2014), as the technologies become more and more advance, it causes water pollution due to inadequate of proper wastewater treatment before discharge to environment.

The wastewater treatment plant can involve in few levels of treatment such as preliminary treatment, primary treatment, secondary treatment, and tertiary treatment (Pescod, 1992; Environmental Protection Agency, EPA, 2004). Preliminary treatment is to remove coarse materials that often found in raw wastewater by screening; primary treatment is to remove larger suspended matter by sedimentation and remove materials that will float by skimming; secondary treatment is further treatment of wastewater to reduce residual organic matter and suspended solids; and tertiary treatment is used to address different pollutants using different treatment processes (disinfection processes use ultraviolet light (UV) or chlorine before the treated sewage effluent are released from plants) (Hendricks and Pool, 2012).

A membrane is any material that, in the form of thin films, have the property of selectively opposing the transfer of different components found in a liquid or gas fluid (Andriamirado et al, 2007). Membrane allows certain elements making up this fluid to be separated out into particles, solutes or solvents. Particles that can pass through the membrane is determined by the material being filtered, as well as the pore size, and the chemical characteristics of the membrane.

Membranes can be made from organic, and inorganic materials. There are few types of membrane such as flat sheet membrane, hollow membrane, and tubular membrane. Normally, membranes used for wastewater treatment are typically organic which includes Polypropylene (PP), Cellulose Acetate (CA), Polyethylene (PE), Polytetrafluoroethylene (PTFE), and Polyethersulfone (PES) (Andriamirado et al, 2007). Almost all membranes are made of polymeric material because they are much less expensive than membranes constructed of other materials.

This research focus on fabrication of hybrid membrane with different concentration of additive (PAC). Membranes are usually use with bio-reactor and formed Membrane Bio-reactor (MBR). The benefits of using MBR compared to conventional activated sludge treatment (CAS) are less sludge is produced, lower space requirements and produce excellent and high quality effluent (Torretta et al, 2013). However, MBR requires higher operation and maintenance costs, and capital costs due to energy consumption, pretreatment, and membrane replacement caused by membrane fouling. Research showed that a low Powdered Activated Carbon (PAC) dosage combined with long sludge retention time (SRT) can reduce the membrane fouling in pilot-scale MBR (Remy et al, 2010).

## 1.2 Problem Statement

Growth of population and technologies has increment to water pollution (Hogan, 2014). This is because industries need water in their production for cleaning, washing, and rinsing purpose. Humans use water for daily activities like bathing, cooking and so on. These activities will produce wastewater and cause more and more water resources are polluted due to inadequate of proper wastewater treatment.

When water resources like rivers are being contaminated, it may cause water-borne diseases such as *Cholera*, *E-coli*, *Typhoid*, *Shigellosis*, *Leptospirosis*, *Giardia Lamblia*, and *hepatitis A* to human (Hogan, 2014). Pollutants like Lead, Fluoride, Mercury, Cadmium, Zinc, Iron, and Chromium originating from various sources may finally reach surface soil from rivers. (Hogan, 2014; Easa & Abou-Rayan, 2010) Consumption of fish, prawn or vegetables that have contaminated by pollutants will affect human reproduction rates and life spans.

MBR has the problem of membrane fouling which caused by the particles in wastewater that will choke the pore of membranes and this require membrane replacement. Directly, it will cause the capital cost and operation and maintenance cost increased. Thus, this study will focus on fabrication of hybrid membrane with different concentration of additive (PAC) to reduce the fouling rate.

## 1.3 Objectives

- To fabricate membrane with different concentration of additive (PAC)
- To study the effect of additive (PAC) in membrane fabrication in terms of flux production, salt rejection, and tensile strength
- To characterize the membrane structure and membrane properties of produced membrane

## 1.4 Research Scopes

The scopes of this research are listed below:

i. To fabricate membranes with formulation: PES / NMP / PAC
ii. To fabricate membrane with different concentration of additive (PAC) by using membrane auto casting machine
iii. To determine the performance of produced membrane in terms of flux production and salt rejection by using Dead End Membrane Test Rig
iv. To determine the tensile strength of produced membrane by using Light Weight Tensile Testing Machine
v. To characterize the membrane structure and membrane properties of produced membrane using SEM

# CHAPTER 2

# LITERITURE REVIEW

## 2.1 Domestic Wastewater

Domestic wastewater is the water used by community. It consists of water from toilets and grey water. The examples for water from toilets are feces and urine (human waste) together with the water used to flush toilets while the grey water consist of wastewater come from kitchens, bathrooms, laundries / washing machine and other appliances in household (Mara, 2004). According to Government of Western Australia Department of Water (2010), each person in a household produces 150 to 200 liters of wastewater every day. Inadequate of proper wastewater treatment before discharge to environment will harm the environment and human health. Therefore, wastewater must be treated to reduce water pollution, reduce transmission of water-borne disease and to provide a clean environment for future generations.

## 2.2 Wastewater Treatment Plant

The wastewater treatment plant can involve in few levels of treatment such as preliminary treatment, primary treatment, secondary treatment, and tertiary treatment in order of increasing treatment level.

Preliminary treatment is to remove coarse materials that often found in raw wastewater by screening, grit removal, flow equalization, as well as oil and grease removal (Pescod, 1992). The main purpose of having preliminary treatment is to prevent coarse materials from entering subsequent treatment units and affect their operation.

Primary treatment is to remove larger suspended matter (organic and inorganic) by sedimentation and remove materials that will float by skimming. Primary treatment remove about 25 – 50 % of Biochemical Oxygen Demand ($BOD_5$), 50 – 70 & of total suspended solids (TSS), and 65% of the oil and grease (Pescod, 1992).

Secondary treatment is further treatment of wastewater to reduce residual organic matter and suspended solids. There are many methods used in secondary treatment such as activated sludge, aerated lagoon, aerobic granulation, constructed wetland, membrane bioreactor, rotating biological contactor, and trickling filter (Pescod, 1992). Some secondary treatment methods include a clarifier to settle out the floc in the secondary treatment bioreactor.

Tertiary treatment (which also known as advanced treatment) is used to address different pollutants using different treatment processes which cannot be removed in secondary treatment such as nitrogen, phosphorus, additional suspended solids, refractory organics, heavy metals, and dissolved solids (Pescod, 1992). For example, disinfection process used ultraviolet light (UV) or chlorine to kill bacteria before treated sewage effluent are released to environment (Hendricks and Pool, 2012).

## 2.3 Membrane Technology

As technology become more and more advance, it causes water pollution and newly contaminants found in water resources (Hogan, 2014). This has give rise to concern of the people about their health and the cleanliness of the water. Membrane technology is one of the diversity of water treatment technologies have been employed in order to meet the water quality standards and water demand. According to Baker (2004), philosopher scientists such as Abbe Nolet started to study membrane at eighteenth century. At nineteenth century, membrane technology was used in laboratory, soon it has developed in industrial or commercial applications in 1960. Membranes are used to produce portable water, desalinate water, treat industrial wastewater, as well as reuse and reclaim wastewater. Besides that, membranes also used in the manufacture of food and pharmaceutical products, production of base chemicals, energy conversion devices such as fuel cells, and in medical devices such as haemodialysis, blood oxygenators, and controlled drug delivery products (Singh, 2015).

## 2.4 Membrane Classification

A membrane is a material that, in the form of thin films, has the property of selectively opposing the transfer of different components found in a liquid or gas fluid (Andriamirado et al, 2007). Membrane allows certain elements making up this fluid to be separated out into particles, solutes or solvents. Particles that can pass through the membrane is determined by the material being filtered, as well as the pore size and the chemical characteristics of the membrane. Membrane processes are classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Below is the filtration spectrum (Baker, 2004).

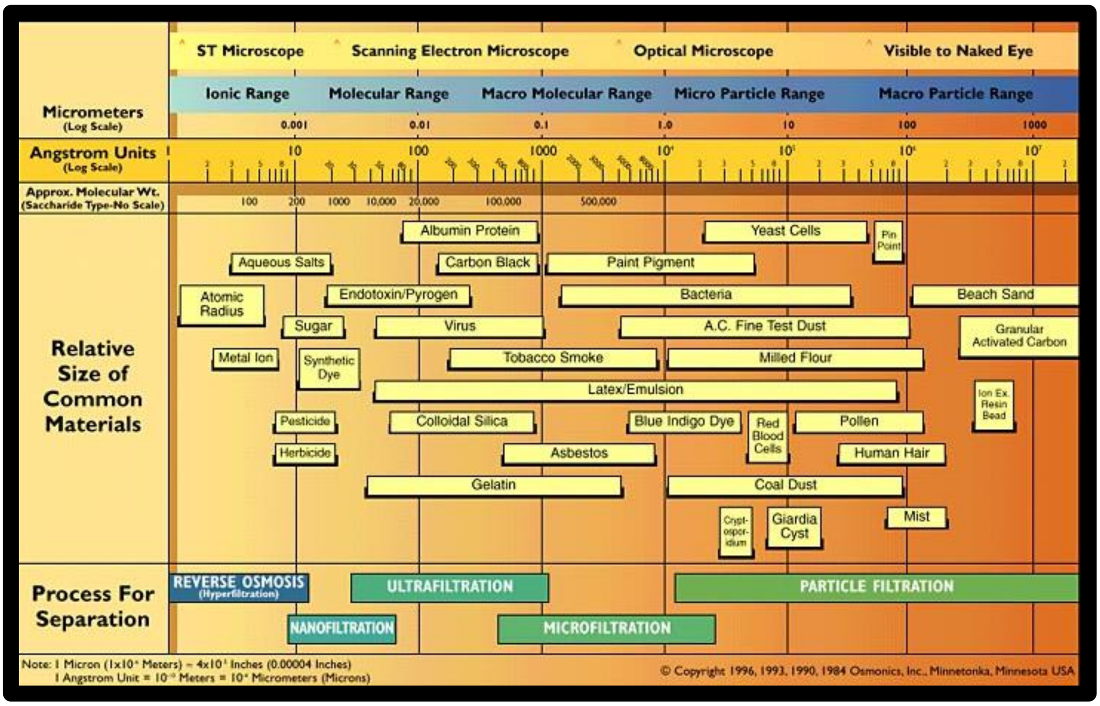


Figure 2.1: The filtration Spectrum (Osmonics)

### 2.4.1 Microfiltration (MF)

Microfiltration is a membrane separation process using membranes with a pore size in range of about 0.1 to 10 μm. MF used to filter large suspended solids, bacteria or large colloids such as sand, silt, clays, and some bacterial species but not viruses. It is the loosest of the membrane process due to its large pore size and can be operated under ultralow pressure which is 0.1 – 2 bar. MF can be used as pre-filter to ensure the downstream membrane has a longer lifetime. In primary market, MF is used to sterile the filtration of water for the pharmaceutical industry and polish the ultrapure water for the electronics industry. Besides that, in another emerging market area, MF is used to remove bacteria and yeast from cold sterilization of beer, wine, and other beverages (Baker, 2004).

### 2.4.2 Ultrafiltration (UF)

Ultrafiltration is a pressure-driven membrane separation process using membranes with a pore size in range of approximately 0.002 to 0.1 μm. UF can remove all microbiological species, proteins, polysaccharide, as well as some viruses. It operates at the pressure of approximately 1 – 5 bar. Ultrafiltration membranes were originally used in laboratory market. Later, UF also ideally used for desalting of protein solutions, removal or exchange of sugars, and change of ionic (Baker, 2004).

### 2.4.3 Nanofiltration (NF)

Nanofiltration is the process of removing virtually small particles such as cysts, viruses, bacteria, and humic materials by using membranes with a pore size of approximately 0.001 μm. Due to its smaller pores of membrane, it requires higher operating pressure compared to MF and UF. The operating pressure are in range of 5 bar and can go as high as 20 bar. NF membranes operate based on the principle of diffusion rather than sieving as with MF and UF membranes (Baker, 2004).

### 2.4.4 Reverse Osmosis (RO)

Reverse osmosis is defined as the movement of solvent from a concentrated solute to a dilute solute through a semipermeable membrane by exerting a pressure higher than the osmotic pressure on the concentrated solute (10 – 100 bar), thus reversing the direction of flow cross the membrane. It can separate nearly all impurities from water and produce nearly zero effluent contaminant concentrations by passing through the multiple units. RO system are compact, simple to operate and primarily used to purify tap water. In some country, they used RO system to desalinate brackish water or seawater. Besides that, some company also used RO system to produce ultrapure water for electronics, pharmaceuticals, and power generation. The remainder are used in small niche applications such as pollution control and food processing (Baker, 2004).

## 2.5 Membrane Transport Mechanism

Membrane is a thin films that allows certain elements to pass through the membrane depend on the material being filtered, and the size and the chemical characteristics of the membrane. Membrane process required two different concentration of solvent, separated by a membrane. The movement of solvents in the membrane process will be controlled by the pressure applied, thus it is called pressure-driven membrane.

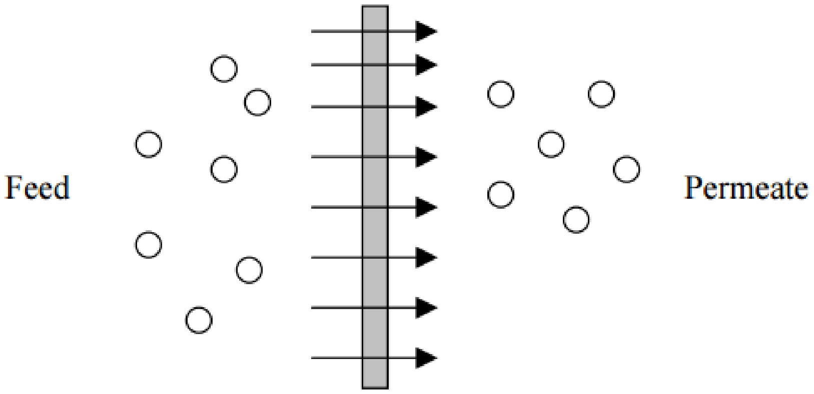
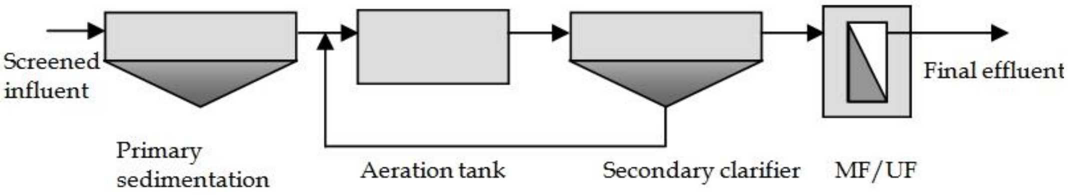


Figure 2.2: Schematic representation of the different concentration of solvent on membrane separation (Ahsan Munir, 2006).

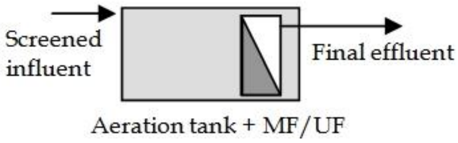
## 2.6 Membrane Bioreactor (MBR)

The MBR is a treatment system that combines both conventional activated sludge treatment and membrane filtration process (Le-Clech, Jefferson and Judd, 2003). MBR systems are characterized into two configuration: submerged / immersed MBRs (SMBR) and external / side-stream) MBRs (EMBR) as shown in Figure 2.3 below. For submerged MBRs, membrane is immerged in biological reactor for solid / liquid separation. Vacuum pump is used to suck the effluent pass through the membrane and leave solids behind. For side-stream MBRs, it consists of 2 units which are biological reactor and membrane separation tank. The influent will first flow through the biological reactor for a period of time and then flows through the membrane separation tank. SMBRs require much lesser power than EMBRs due to the absence of a high-flow recirculation pump (Wang et al., 2008).

a) Conventional activated sludge process



b) Submerged MBR (SMBR)



c) External MBR (EMBR)

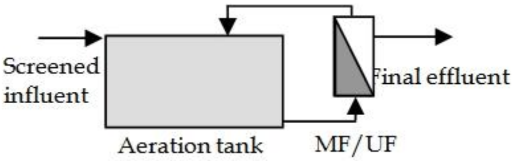


Figure 2.3: (a) Conventional activated sludge process (b) Submerged MBR (SMBR) and (c) External MBR (EMBR) (Delgado et al., 2011)

The advantages of MBR include smaller plant footprint (secondary and tertiary filtration processes are eliminated), achieve good and stable effluent quality, and low sludge production (Ng et al, 2013). On the other hand, the drawbacks of MBR include higher operation and maintenance cost, and capital cost (due to backwashing and energy consumption for pumps), frequent membrane replacements (due to membrane fouling), and short membrane lifespan (due to membrane pore clogging) (Li et al., 2005; Jamal Khan, Visvanathan and Jegatheesan, 2012).

## 2.7 Membrane Fouling

Basically, membranes can made up by two types of material such as organic and inorganic. Organic polymer membrane material includes Polypropylene (PP), Cellulose Acetate (CA), Polyethylene (PE), Polytetrafluoroethylene (PTFE), and Polyethersulfone (PES) (Andriamirado et al, 2007). Inorganic membrane is semi-permeable film made by inorganic material such as ceramics, metal oxides, metals, and porous glass zeolite. Currently, membranes used for MBRs are typically organic because they are significantly less expensive than membranes constructed of other materials, convenience of control and small aperture size (Gao et al., 2009).

Membrane fouling is the main cause that affect the development of membrane filtration resulted from accumulation of solid concentration on the surface of membrane or in the membrane pores (Ng et al., 2013). According to Remy et al. (2010) and Torretta et al. (2013), there are many factors that can cause membrane fouling in MBRs such as membrane properties, biomass characteristics, extracellular polymers, module design, the concentration of the mixed liquor suspended solid, colloids, and operation conditions. Membrane fouling in MBRs can be divided into membrane pore clogging and sludge cake deposition on membranes as shown in Figure 2.2 below (Meng et al., 2009).

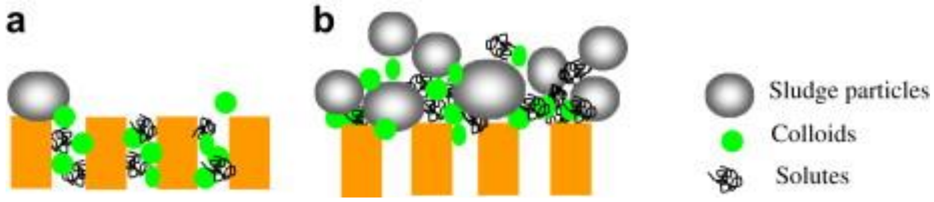


Figure 2.4: Membrane fouling process in MBRs: (a) pore blocking and (b) cake layer (Meng et al., 2009)

Due to the fact that membrane fouling in filtration processes decreases membrane performance, increases the trans membrane pressure (TMP), shortens membrane lifespan, MBR system energy demand and requires membrane replacement frequently as well as increases the operation and maintenance cost (Meng et al., 2009). Therefore, few researches had been carried out to solve this problem. Remy et al., 2010 reported that addition of low PAC can increase the membrane flux by 10% and improve the performance of membrane filtration. This is because of the adsorption effect that will enhance scouring effect on the membrane surface. Besides that, Yang, Cicek and Ilg (2006) had proposed few techniques to control membrane fouling which are optimize the packing density of hollow fibers or flat sheets by modify the membrane module design, control the filtration process below the critical flux, by air-sparging and by operating in intermittent mode to reduce formation of fouling material on membrane surfaces, add PAC to improve the mixed liquor filtration characteristics, and backwashing / chemical cleaning to remove cake formation on membrane surface.

## 2.8 Powdered Activated Carbon (PAC)

Activated carbon which also known as activated charcoal or activated coal is commonly used to remove taste and odor compounds, synthetic organic chemicals (SOCs), and volatile organic compounds (VOCs) in water treatment by using adsorption (Tennant and Mazyck, 2007). Activated carbon is an effective adsorbent because of its porosity which provides a large surface area for adsorption. Basically, activated carbon are divided into two types such as Powdered Activated Carbon (PAC) and Granular Activated Carbon (GAC) (Tennant and Mazyck, 2007).

PAC is produced from organic materials like coal and wood. PAC typically has a diameter less than 0.1 mm. 1 g of Pac has a surface area of 500 $m^2$ (Tennant and Mazyck, 2007). PAC is commonly used in wastewater treatment plants as it removes organic compounds, taste and odor effectively. PAC is used more often than GAC, as PAC can be added in varying amounts depending on water conditions and the degree of the odor episode. PAC is more effective than other treatment processes such as chlorination, aeration, biodegradation, and filtration (Tennant and Mazyck, 2007).

PAC is normally added early in the treatment process and is subsequently removed either by sedimentation or by the filter beds during backwashing. PAC should not be added concurrently with chlorine or potassium permanganate as these chemicals will adsorb to the PAC (Environmental Protection Agency, EPA, 2015). Numerous researchers have found that addition of PAC into MBR would develop biologically Activated Carbon (BAC) which could enhance filtration performance of a conventional MBR (Ng et al., 2013) and reduce membrane fouling (Satyawali and Balakrishnan, 2009).

## 2.9 Polyethersulfone (PES)

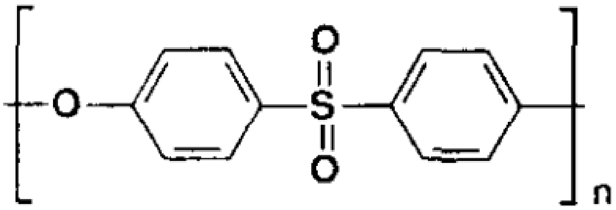


Figure 2.5: Molecular structure for Polyethersulfone (Lau, Guiver and Matsuura, 1991)

PES is one type of easy handling polymeric material that used to fabricate membrane (Basri, Ismail and Aziz, 2011). PES is extensively used in fabrication of microfiltration and ultrafiltration due to its good mechanical and film-forming properties, resistance to chemical attack such as hydrocarbons, alcohols and acids, excellent pH, and thermal tolerance ($T_g$ = 225 ℃), high strength, oxidation resistance, and high dimensional stability (Zhao et al., 2014). PES membrane are usually made by the phase inversion technique by precipitating a cast polymer solution with a non-solvent, normally water (Lau, Guiver and Matsuura, 1991).

Many researches have reported that the main drawback of using PES membrane is its hydrophobic characteristic (Zhao et al., 2014; Li et al., 2009; Razmjou, Mansouri and Chen, 2011) which often cause membrane fouling in the treatment system and suggested some methods to make some changes to the PES membrane. The methods are hydrophilic coating, surface grafting polymerization, blending, and change bulk materials of membrane which have shown a good result to enhance the membrane fouling resistance. According to Li et al. (2009); Razmjou, Mansouri and Chen (2011), they have found that the addition of TiO2 could produce membranes with higher hydrophilicity, better thermal and mechanical stability as well as better permeation performance. Besides that, Marchese et al. (2003) has reported that a hydrophilic polymeric additive, polyvinylpyrrolidone (PVP) is often blended with PES to form a hydrophilic membrane. In addition, Zhou et al. (2010) also found that with addition of PVP, a lower porosity, lower rejection, and higher permeability of membrane will be formed by increasing PES molecular weight. In this case, dead-end filtration is used to measure the permeability of membrane. In this research, PES is used as polymer, and PAC as additive to fabricate the membranes.

## 2.10 N-methyl-2-pyrrolidinone (NMP)

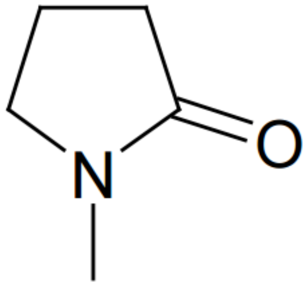


Figure 2.6: Chemical Structure of NMP (Environmental Protection Agency, EPA, 2012)

N-methyl-2-pyrrolidinone is a colorless solvent used to dissolve a wide range of polymers such as PES. PES is more soluble in NMP/$H_20$ mixture. The width of these miscibility regions indicate that the solvent dissolution power for PES ranks N-methyl-2-pyrrolidinone (NMP) > tetramethylurea (TMU) > dimethylacetamide (DMAc) > dimethylsulfoxide (DMSO) > dimethylformamide (DMF) (Lau, Guiver and Matsuura, 1991). The polymer dissolving power of the solvent will reduce when a non-solvent (water) is added to a polymer solution. Table 2.1 below showed the summary of physical chemical properties of NMP.

Table 2.1: Physical-Chemical Properties of NMP (Environmental Protection Agency, EPA, 2012)

| | |
|---|---|
| Molecular formula | $C_5H_9ON$ |
| Molecular weight | 99.13 g/mol |
| Physical form | Colorless to slightly yellow liquid; slight amine odor |
| Melting point | -24.4 ℃ |
| Boiling point | 202 ℃ |
| Vapor pressure | 0.190 mmHg at 25 ℃ |
| Water solubility | 1000 g/L at 25 ℃ |

## 2.11 Trans Membrane Pressure (TMP)

TMP is the change in the pressure of the water as it passes through the membrane. Membrane resistance that created by the fluid undergoing filtration affects the membrane filtration performance. The permeation flux can be determined by using flow resistance equation as shown in Equation 2.1.

$$J = \frac{\Delta P}{\mu R_t} \qquad \text{(Eq. 2.1)}$$

Where

J = permeate flux ($m^3/m^2.s$)

μ = viscosity of the permeate (Pa.s)

$R_t$ = total resistance for filtration (l/m)

$\Delta P$ = transmembrane pressure (Pa)

## 2.12 Scanning Electron Microscopy (SEM)

SEM is a type of microscope that generates images of a sample by using a focused beam of high-energy electrons. Information about the sample's surface topography, composition and crystalline structure, and orientation of materials making up the sample are generated through the electron-sample interaction at the surface of sample. Thus, it plays a major role in the characterization of membrane structure. (Reingruber et al., 2012).

## 2.13 Cross Flow Filtration

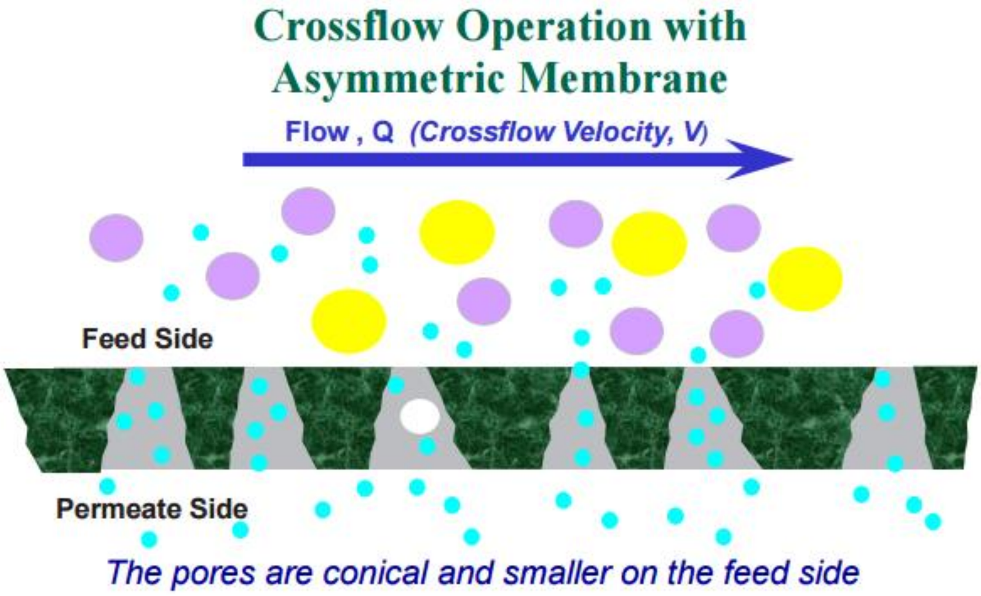


Figure 2.7: Cross flow filter operation (Koch Membrane Systems, Inc., 2012)

Cross flow filtration means that the feed water is pumped tangential to the membrane, feed water that does not pass through the membrane is recirculated as concentrate with additional feed water or to a storage reservoir (Tchobanoglous, Burton and Stensel, 2003). The use of tangential flow will prevent the formation of cake on the membrane surface compared to dead-end filtration technique which means it can last for longer operational periods and less membrane backwashing or cleaning are needed (Ahsan Munir, 2006). Cross flow required more energy compared to dead end flow because some of the particle that being pumped into the module only flow across the membrane. The critical flux is depends on the permeate flux and cross flow velocity. Cross-flow filtration is an excellent way to filter feed water with a high concentration of filterable matter or if pretreatment with Powdered Activated Carbon is being used (Ahsan Munir, 2006).

## 2.14 Dead End Filtration

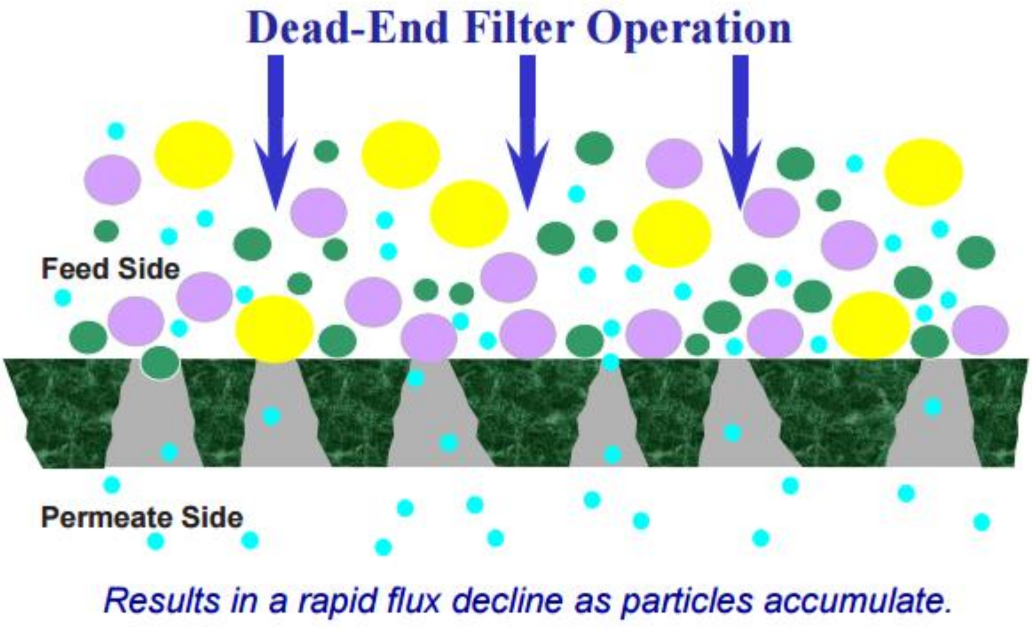


Figure 2.8: Dead end filter operation (Koch Membrane Systems, Inc., 2012)

A dead end filtration means that the feed water is pumped perpendicular to the membrane (Ahsan Munir, 2006). It does not recirculate the feed water which means there is no rejected water, the water that passes through the membrane is called as permeate. The main problem of this filtration is the particles will accumulate on the membrane surface and caused membrane fouling, result in decreasing of permeate flux and need membrane replacement or membrane backwashing/cleaning.

Basically, dead end filtration is divided into dead end microfiltration with constant flux and dead end microfiltration with constant pressure drop. For the dead end microfiltration with constant flux, it uses positive displacement pump to make sure the permeate flux remains constant throughout the filter. The pressure must be increased to maintain the constant flux if cake formation occurs. On the other hand, cake formation with time will cause the permeate flux to decrease in dead end microfiltration with constant pressure.

# CHAPTER 3

# METHODOLOGY

## 3.1 Membrane Fabrication and Casting

Materials that required for membrane fabrication are PES which used as polymer, NMP which used as solvent and PAC which used as additive. The ratio of polymer (PES) to solvent (NMP) is 16:84 and the percentage of PAC was varied during membrane fabrication as shown in Table 3.1. The calculation was shown in Appendix A.

Table 3.1: Amount of PES, PAC and NMP needed in membrane fabrication.

| Membrane | Additive, PAC (%) | Additive, PAC (g) | Polymer, PES (g) | Solvent, NMP (g) |
|---|---|---|---|---|
| 0% PES-PAC | 0 | 0.00 | 16.00 | 84.00 |
| 1% PES-PAC | 1 | 0.16 | 15.84 | 84.00 |
| 7% PES-PAC | 7 | 1.12 | 14.88 | 84.00 |
| 9% PES-PAC | 9 | 1.44 | 14.56 | 84.00 |
| 11% PES-PAC | 11 | 1.76 | 14.24 | 84.00 |

### 3.1.1 Dope Preparation

Before process of producing dope starts, polymer (PES as shown in Figure 3.1) and 250 mL 3-neck flask needed to put into oven (Brand: Memmert) at 60 ℃ for 24 hours to remove the moisture content. First, the apparatus and equipment were set up in fume hood as shown in Figure 3.2. This is to make sure the user safety purpose. After that, solvent (NMP) was measured and poured into the 3-neck flask. The magnetic stirrer was put into the 3-neck flask too. The condenser was filled with water and let it to run off before starting to heat the solvent. The condenser is used to cold down the water vapor in the 3-neck flask when heating and prevent condensed water drop back into the dope. Then, the solvent was heated by heating mantle (Brand: Favorit) and stirred using magnetic stirrer for at least 10 to 15 minutes with medium speed. When the temperature is stable which is in between 50 ℃ and 60 ℃, one spatula of polymer was added into the solvent slowly. It is important to make sure that the previously added polymer is completely dissolved and continue to add another one spatula of polymer into the solvent. This step was repeated until all the needed polymer had completely dissolved in the solvent. Heat was turned off and kept stirring until the dope cool down to room temperature. After the dope was cool down into room temperature, the dope was poured into reagent bottle. Be careful when pouring the dope and make sure the magnetic stirrer did not drop into the reagent bottle. Lastly, additive (PAC) was added to the dope and put into sonicator bath for 8 hours until it became homogeneous mixture as shown in Figure 3.3.

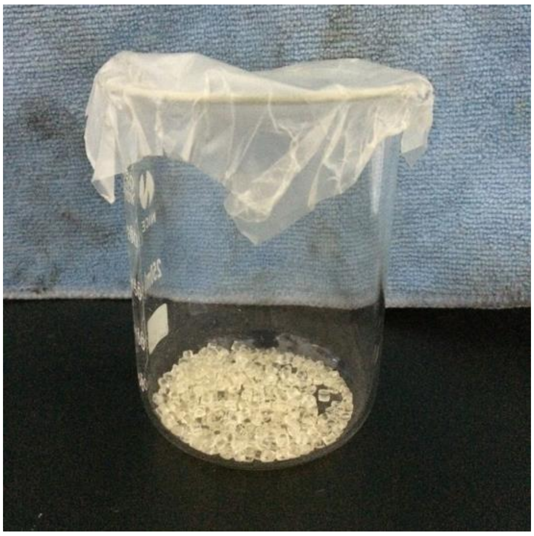


Figure 3.1: Polymer, Polyethersulfone (PES)

Figure 3.2: Dope preparation apparatus set up

Figure 3.3: Dope in reagent bottle

### 3.1.2 Membrane Casting

The membranes were casted by using membrane auto casting machine (Brand: Autonics) as shown in Figure 3.4. Then, the dope was poured slowly onto a smooth glass plate. The thickness of the membrane which also called membrane spacing was set as 10 micrometer and checked beforehand using a knife gap. The membrane was immediately submerged in a water bath for at least 10 minutes after the membrane has been cast. A thin layer of polymeric film will be formed and it will separate itself from the glass plate. After that, the formed membrane was then transferred into container filled with water for 24 hours as shown in Figure 3.5.

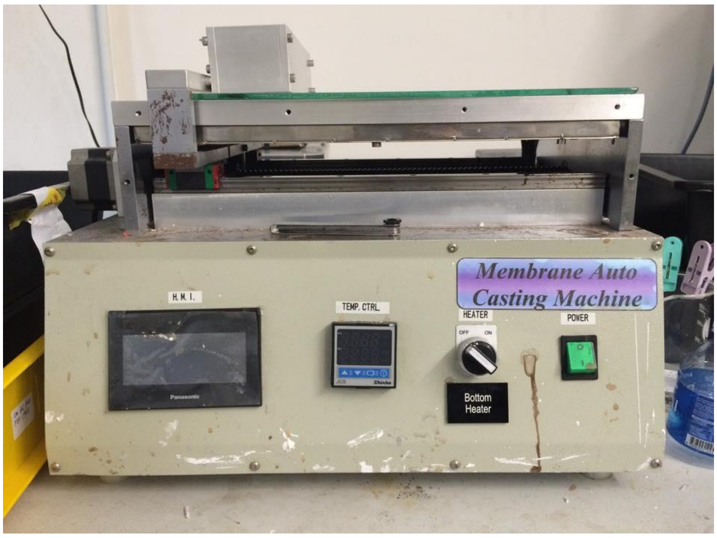


Figure 3.4: Membrane auto casting machine

Figure 3.5: Membrane sheet in water bath

### 3.1.3 Post Treatment

The membrane was placed in another container filled with methanol for 8 hours and hanged to dry at room temperature for 24 hours. Figure 3.6 showed the membrane was cut into circular shape of 47 mm diameter and it is ready for testing.

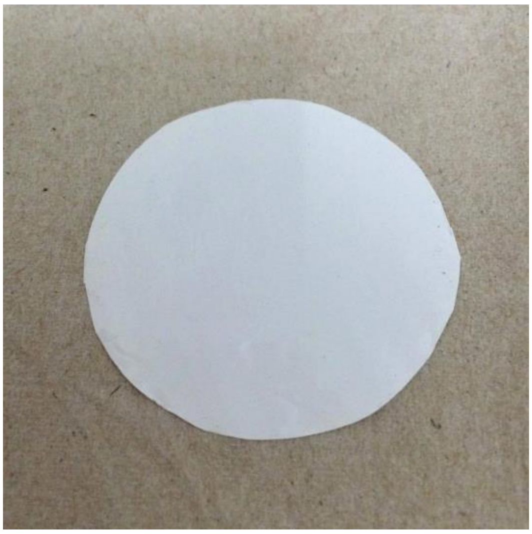


Figure 3.6: Membrane ready for testing

## 3.2 Membrane Performance Test

In this study, pure water flux, salt water flux and salt rejection were carried out to evaluate the membrane performance by using Dead End Membrane Test Rig. Membranes must submerge into distilled water for 1 hour before started to run the tests to prevent impurities stick on the surface of water.

### 3.2.1 Pure Water Flux

Dead End Membrane Test Rig was used to test the permeation rate of the membranes. Distilled water was used as the feed. 5 mL of permeate solution that passed through the membrane was collected in measuring cylinder. The time taken to get 5 mL of permeate was recorded and used to calculate the pure water flux by using the Equation 3.1 as shown below. The pure water flux was measured at different pressure which is 0.1 bar, 0.2 bar, and 0.3 bar to determine water permeability.

$$\text{Flux, J} = \frac{\text{Volume of permeate that passed through membrane (v)}}{\text{Membrane area (A)} \times \text{time (T)}} \qquad \text{(Eq. 3.1)}$$

Where

J = pure water flux or salt rejection flux ($m^3/m^2s$)
V = volume of permeate solution collected ($m^3$)
A = effective area of the membrane ($m^2$)
T = time needed to the 5 mL of permeate (s)

### 3.2.2 Salt Solution Flux

Same as pure water flux, Dead End Membrane Test Rig was used to carry out the test. 0.01 M of NaCl solution was used as the feed. 10 mL of permeate solution that passed through the membrane was collected in measuring cylinder. The time taken to get 10 mL of permeate was recorded and used to calculate the salt rejection flux by using the Equation 3.1 as shown above. The salt rejection flux was measured at different pressure which is 0.1 bar, 0.2 bar and 0.3 bar to determine the permeability of salt solution.

### 3.2.3 Salt Rejection

After the salt rejection flux was carried out, the collected 10 mL of permeate solution at different pressure was used to measure the conductivity by using conductivity meter. The rejection characteristics of a membrane are described by observed rejection, $R_{obs}$ and real rejection, $R_{real}$. In the membrane separation processes, the concentration on the membrane surface is always higher than in the bulk due to concentration polarization. A concentration on the membrane surface is not directly obtained from experiment thus the following equation was applied (Schirg and Widmer, 1992).

$$\mathrm{In}\left(\frac{1-R_{obs}}{R_{obs}}\right) = \left(\frac{1-R_{real}}{R_{real}}\right) + \frac{J}{k} \qquad \text{(Eq. 3.2)}$$

$$R_{obs} = \left[1 - \frac{C_p}{C_b}\right] \qquad \text{(Eq. 3.3)}$$

$$R_{real} = \left[1 - \frac{C_p}{C_w}\right] \qquad \text{(Eq. 3.4)}$$

Where

$C_p$ = salt rejection in permeate
$C_b$ = salt concentration in bulk
$C_w$ = salt concentration in wall

## 3.3 Preparation of NaCl Stock Solution

In order to prepare 1 L of 0.1 M NaCl stock solution, 5.845 g of NaCl was dissolved in 1 L of distilled water by using volumetric flask. The grams of the NaCl required can be calculated by using the Equation 3.5. The calculation for preparation of 0.1 M NaCl stock solution was shown in Appendix B.

$$g_s = MW \times M \times V \qquad \text{(Eq. 3.5)}$$

Where

$g_s$ = grams of the NaCl required
MW = molecular weight of NaCl, 58.45 g/mol
M = molarity of solution required, M
V = volume of solution required, L

### 3.4 Stock Solution Dilution

After preparing the 0.1 M of NaCl stock solution, a series of different concentration of salt solution were prepared. The required concentration of salt solutions were 0.08 M, 0.06 M, 0.04 M, 0.02 M, 0.01 M, 0.008 M, 0.006 M, 0.004 M, and 0.002 M. The dilution of each salt solution can be obtained through the Equation 3.6. The calculation for stock solution dilution was shown in Appendix C.

$$M_1V_1 = M_2V_2 \qquad \text{(Eq. 3.6)}$$

Where

$M_1$ = molarity of NaCl stock solution, 0.1 M
$V_1$ = volume of NaCl stock solution to be pipette into the volumetric flask, L
$M_2$ = wanted molarity of salt solution, M
$V_2$ = wanted volume of salt solution, 0.05 L

Table 3.2: Dilution table for Salt Solution

| Concentration, M | Volume of NaCl stock solution to be pipette into the volumetric flask, mL |
|---|---|
| 0.08 | 40 |
| 0.06 | 30 |
| 0.04 | 20 |
| 0.02 | 10 |
| 0.01 | 5 |
| 0.008 | 4 |
| 0.006 | 3 |
| 0.004 | 2 |
| 0.002 | 1 |

## 3.5 Preparation of Conductivity-Concentration Curve

NaCl solution was used as feed solution or inorganic electrolytes. It is important to prepare the different range of calibration curve which was 0 – 0.01 M and 0.01 M – 0.1 M of salt solution respectively to meets the required range of the concentration of permeate and retentate. Thus, the different concentration of prepared salt solution was measured by using conductivity meter and used to plot the calibration graph. The unit of conductivity is expressed in millisiemens (mS). Calibration curve for salt solutions for conductivity versus concentration was shown in Appendix D.

## 3.6 Observation of Membrane Morphology by SEM

SEM will be used to study the surface topography and composition of PES membranes. Data are collected over a selected area of the surface of the sample, and a 2-dimensional (2D) image is generated that displays spatial variations in these properties Areas ranging from approximately 1 cm to 5 microns in width can be displayed in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm) (Techniques, 2013). In this study, FESEM- JEOL 6701-F is used as the equipment to identify the morphology of the membranes.

## 3.7 Tensile Property Testing of Membranes

Before tensile testing was started, membranes were machined from stock shapes or injection molded into the standard shape of tensile specimen as shown in Figure 3.7 below. Then, the flat grip section was griped with serrated grips of the Light Weight Tensile Testing Machine. The testing machine pulls the sample from both ends and measures the force required to pull the specimen apart and how much the specimen stretches before breaking. This main purpose of having this tensile testing was to determine the ability of produced membrane to resist breaking under stress condition and find the ultimate tensile strength. Some of the testing parameters were fixed throughout the testing as shown in Table 3.3. The only parameter that needed to key in into the system was thickness of the specimens.

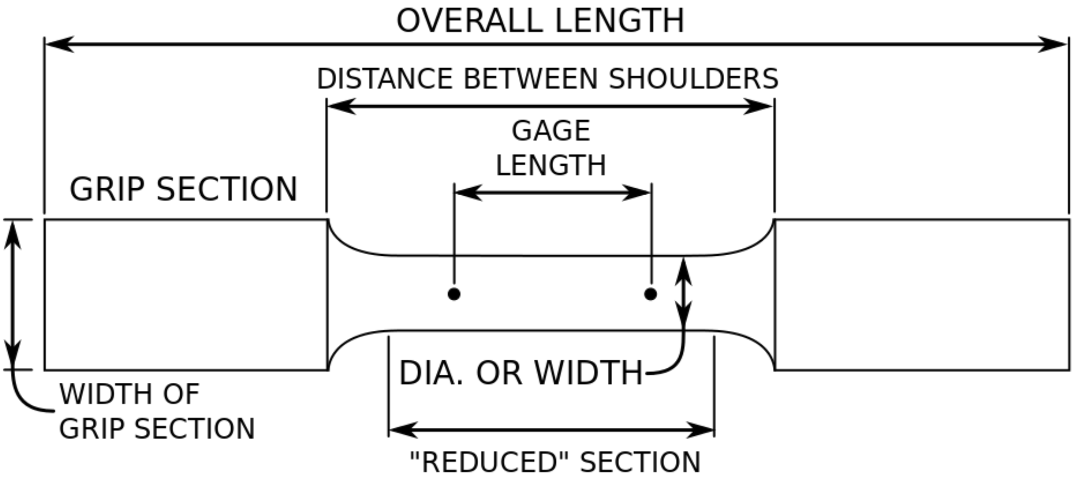


Figure 3.7: Standard tensile specimens

Table 3.3: Parameters that were fixed throughout the testing

| Parameters | Value |
|---|---|
| Load range, N | 500 |
| Extension range, mm | 2000 |
| Gauge length, mm | 10 |
| Width, mm | 3 |
| Speed, mm/min | 5 |

# CHAPTER 4

# RESULT AND DISCUSSION

In this study, five asymmetric PES-PAC membranes with 0%, 1%, 7%, 9%, and 11% of PAC were successfully fabricated. The membrane performance had been tested using pure water and 0.01 M NaCl permeation test. The SEM image of surface topography PES-PAC membranes were obtained from the Faculty of Science, Universiti Tunku Abudul Rahman. The tensile strength of the PES-PAC membranes also tested by using Light Weight Tensile Testing Machine in Faculty of Engineering and Green Technology, Universiti Tunku Abudul Rahman. All the results will be discussed in detail in the following section.

## 4.1 Pure Water Flux

Each PES-PAC membrane was casted under the same condition such as thickness, temperature, casting solution and shear rate. The diameter of the membrane was fixed at 47 mm with an effective area of $1.7349 \times 10^{-3}$ m$^2$. The flux was measured at different pressure which is 0.1 bar, 0.2 bar, and 0.3 bar by using dead-end filtration. Distilled water was used as the feed in this testing. The time taken to collect 5 mL of permeate was recorded and used to calculate the pure water flux as shown in Table 4.1. The purpose of having this pure water flux test is to ensure the stability of the membranes (Abdul Aziz and Mojiri, 2014) and as a reference flux for comparison. From Table 4.1, 11% PES-PAC has the highest flux which is in range of $6.403 \times 10^{-5}$ – $1.3098 \times 10^{-4}$ m$^3$/m$^2$s. 9% PES-PAC has the second highest flux which is in range of $4.502 \times 10^{-5}$ –

$9.295\times10^{-5}$ $m^3/m^2s$, followed by 7% PES-PAC and 1% PES-PAC which is in range of $2.596\times10^{-5}$ – $5.541\times10^{-5}$ $m^3/m^2s$ and $1.237\times10^{-5}$ – $2.620\times10^{-5}$ $m^3/m^2s$. Lastly, 0% PES-PAC has the lowest flux which is $8.300\times10^{-5}$ – $1.413\times10^{-5}$ $m^3/m^2s$.

Table 4.1: Pure water flux produced by different membrane at different pressure

| Pressure (bar) | Pure water flux produced by membrane ($m^3/m^2s$) | | | | |
|---|---|---|---|---|---|
| | 0% PES-PAC | 1% PES-PAC | 7% PES-PAC | 9% PES-PAC | 11% PES-PAC |
| 0.1 | $8.300\times10^{-6}$ | $1.237\times10^{-5}$ | $2.596\times10^{-5}$ | $4.502\times10^{-5}$ | $6.403\times10^{-5}$ |
| 0.2 | $1.048\times10^{-5}$ | $1.883\times10^{-5}$ | $4.117\times10^{-5}$ | $6.701\times10^{-5}$ | $9.936\times10^{-5}$ |
| 0.3 | $1.413\times10^{-5}$ | $2.620\times10^{-5}$ | $5.541\times10^{-5}$ | $9.295\times10^{-5}$ | $1.3098\times10^{-4}$ |

Based on Figure 4.1, the pure water flux of all PES-PAC membranes is directly proportional to the applied pressure. It was found that 11% PES-PAC has the best pure water flux, followed by 9% PES-PAC, 7% PES-PAC, 1% PES-PAC and 0% PES-PAC. Besides that, it is also clearly showed that addition of PAC during membrane fabrication will increase the pure water flux. The higher the amount of PAC added during membrane fabrication, the higher the pure water flux. In other word, the pure water flux increased as the concentration of polymer decreased in membrane fabrication. It might be caused by the porosity of the membrane. Permeate can pass through membrane faster if the membrane has higher porosity. Although 11% PES-PAC has a great pure water flux among all the produced membranes, it does not indicate that it has the best rejection. Thus, another permeation test with 0.01 M NaCl solution was carried out to determine the membrane performance. The results will be explained in the following section.

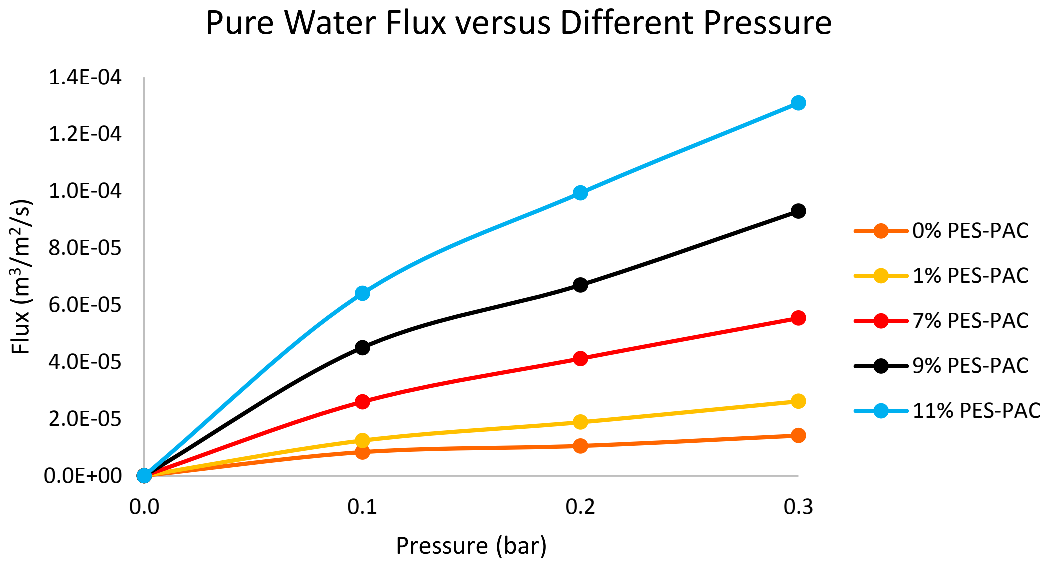


Figure 4.1: Comparison of pure water flux produced by different membrane at different pressure

## 4.2 Salt Solution Flux

In this testing, 0.01 M NaCl solution was used as the feed. Time taken to collect 10 mL of permeate was recorded and used to calculate the salt solution flux as shown in Table 4.2. 11% PES-PAC showed the highest flux ranging from $4.059 \times 10^{-5} – 8.602 \times 10^{-5}$ $m^3/m^2s$. Meanwhile, 9% PES-PAC has the second highest flux which is in range of $2.495 \times 10^{-5} – 4.803 \times 10^{-5}$ $m^3/m^2s$, followed by 7% PES-PAC and 1% PES-PAC ranging from $1.562 \times 10^{-5} – 2.940 \times 10^{-5}$ $m^3/m^2s$ and $8.320 \times 10^{-6} – 1.614 \times 10^{-5}$ $m^3/m^2s$. Lastly, 0% PES-PAC showed the lowest flux of $4.070 \times 10^{-6} – 1.313 \times 10^{-5}$ $m^3/m^2s$.

Table 4.2: Salt solution flux produced by different membrane at different pressure

| Pressure (bar) | Salt solution flux produced by membrane (m$^3$/m$^2$s) | | | | |
|---|---|---|---|---|---|
| | 0% PES-PAC | 1% PES-PAC | 7% PES-PAC | 9% PES-PAC | 11% PES-PAC |
| 0.1 | $4.070 \times 10^{-6}$ | $8.320 \times 10^{-6}$ | $1.562 \times 10^{-5}$ | $2.495 \times 10^{-5}$ | $4.059 \times 10^{-5}$ |
| 0.2 | $7.700 \times 10^{-6}$ | $1.253 \times 10^{-5}$ | $2.200 \times 10^{-5}$ | $3.514 \times 10^{-5}$ | $6.197 \times 10^{-5}$ |
| 0.3 | $1.313 \times 10^{-5}$ | $1.614 \times 10^{-5}$ | $2.940 \times 10^{-5}$ | $4.803 \times 10^{-5}$ | $8.602 \times 10^{-5}$ |

From Figure 4.2, it can be clearly observed that the salt solution flux of all PES-PAC membranes is directly proportional to the applied pressure. Both salt solution flux and pure water flux have the similar trend. 11% PES-PAC has the greatest flux followed by 9% PES-PAC, 7% PES-PAC, 1% PES-PAC and 0% PES-PAC. Higher percentage of PAC indicates that less polymer was used in membrane fabrication. It can be explained by Aryanti, Khoiruddin and Gede Wenten (2013), it has proved that by adding additive in membrane will increase marcovoid of the membrane that reduced the mass transfer resistance, increase the porosity and thus increase the water permeability of the membrane. Ma et al (2011) has also proved that increase of additive in membrane increased the number and size of finger-like pores. According to Abdul Aziz and Mojiri (2014), finger-like structure provides good membrane porosity and higher flux rate.

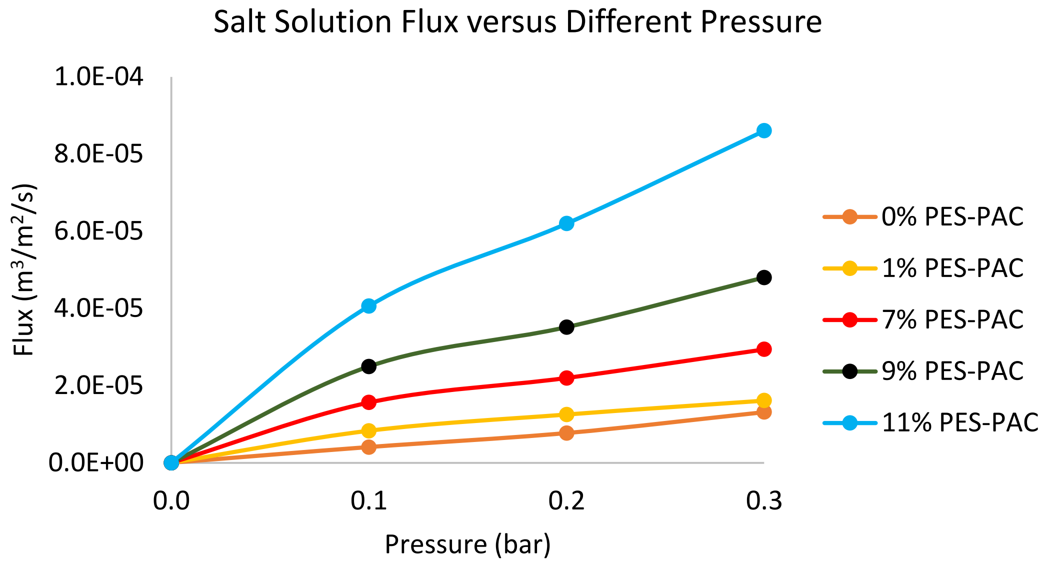


Figure 4.2: Comparison of 0.1M NaCl solution flux produced by different membrane at different pressure

## 4.3 Salt Rejection

A membrane is good if it provides both high flux and high rejection ability. Table 4.3 showed the percentage of salt rejection by different PES-PAC membranes at different pressure and the calculation was shown in Appendix E. From Table 4.3, 11% PES-PAC has the highest salt rejection which is in range of 56.67 – 79.62 %. 9% PES-PAC has the second highest salt rejection which is in range of 41.06 – 48.87 %, followed by 7% PES-PAC and 0% PES-PAC which is in range of 33.24 – 39.88 % and 31.02 – 31.12 % respectively. Lastly, 1% PES-PAC has the lowest salt rejection which is 26.94 – 30.12 %.

Table 4.3: Salt rejection produced by different membrane at different pressure

| Pressure (bar) | Salt rejection produced by membrane (%) | | | | |
|---|---|---|---|---|---|
| | 0% PES-PAC | 1% PES-PAC | 7% PES-PAC | 9% PES-PAC | 11% PES-PAC |
| 0.1 | 31.12 | 26.94 | 33.24 | 41.06 | 56.67 |
| 0.2 | 31.40 | 29.54 | 36.80 | 42.52 | 69.33 |
| 0.3 | 31.02 | 30.12 | 39.88 | 48.87 | 79.62 |

According to Figure 4.3, salt rejection increase slightly for each membrane when increase of applied pressure. 0% PES-PAC and 1% PES-PAC have almost the same salt rejection. This condition can be explained that 1% PES-PAC does not have enough effect in order to trigger out the better performance in term of salt rejection. Meanwhile, 11% PES-PAC has the highest salt rejection, followed by 9% PES-PAC and 7% PES-PAC. This is because PAC is an excellent absorbent due to its activated carbon's amphoteric surface. When increase the amount of PAC in membrane, it increase the surface area to adsorb the salt, and thus increase the salt rejection. In other word, low concentration of PAC and polymer will decrease the salt rejection. The removed molecules are held within the carbon's internal pore structure by Van der Waals forces, electrostatic attraction or chemisorption. In addition, Tennant (2004) proved that Activated Carbon has a similar bonding arrangement, but activation not only increases porosity but also the number of edge sites. Higher number of edges in Activated Carbon allows for more active sites, which can bond to other compounds or chemical groups. Hence, higher percentage of PAC in membrane will have better salt rejection.

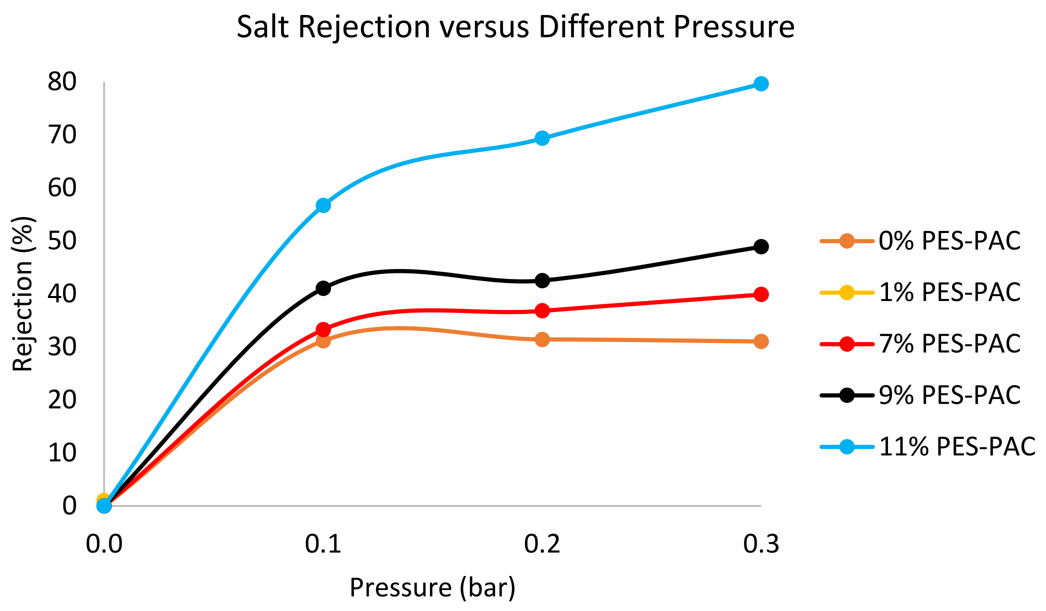


Figure 4.3: Salt rejection by different membrane at different pressure

## 4.4 SEM for Membrane Morphology

From Figure 4.4 and Figure 4.5, it is clearly observed that both of the membranes have different surface morphology. Membrane without PAC has less pores while membrane with PAC has more pores on the surface of membrane. Thus, it has proved that membranes with additives will enhance marcovoid formation of the membrane, increase the porosity and thus improve the water permeability of the membrane.

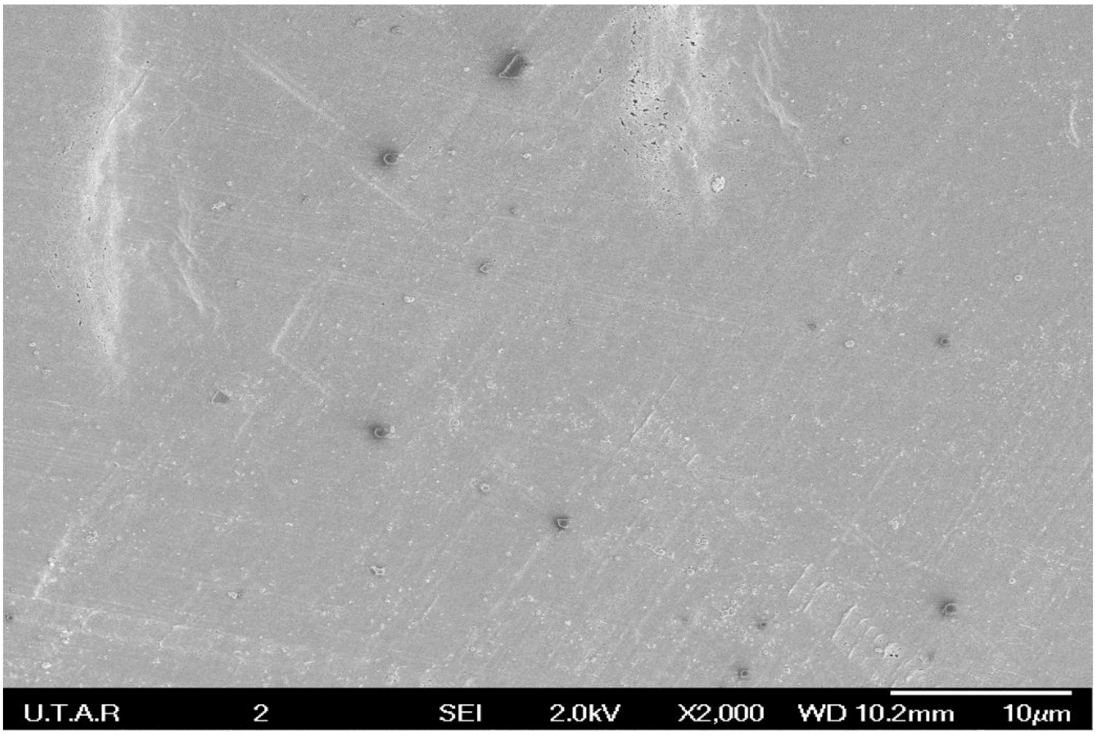


Figure 4.4: Membrane without PAC

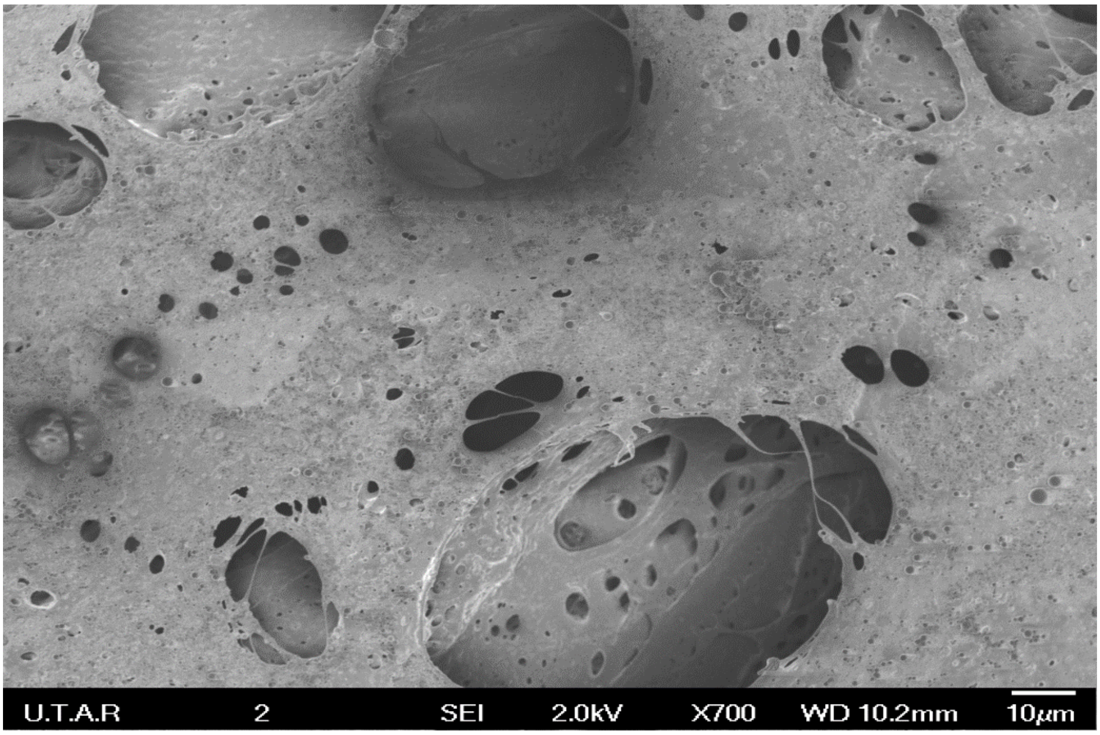


Figure 4.5: Membrane with PAC

## 4.5 Tensile Testing of Membranes

In this testing, five pieces of same type of PES-PAC membrane were griped together with serrated grips to run the testing. This is because the thickness of the one piece of membrane is too thin so the machine cannot detect it. Thus, the machine cannot output the E-Modulus, Ultimate Tensile Strength, extension of the membrane and force applied. Table 4.4 showed that increase of PAC from 0% to 9%, thickness decreased from 0.4460 – 0.3167 mm, E-Modulus decreased from 54.10 – 17.16 MPa, Ultimate Tensile Strength decreased from 4.619 – 2.594 MPa, extension of membrane decreased from 2.375 – 1.000 mm and lastly applied force decreased from 6.1875 – 2.5000 N. According Aryanti, Khoiruddin and Gede Wenten (2013), presence of additive in membrane solution influences thermodynamic and kinetic properties of membrane solution. It reduces the strength of polymer solvent interaction. However, there is a sudden change of membrane with 11% of PAC, thickness, E-Modulus, Ultimate Tensile Strength, extension of membrane and applied force increased. It could be due to the formulation of PES/NMP/PAC just right to the membrane structure.

Table 4.4: Results of tensile testing of different membranes

| Membrane | Thickness (mm) | E-Modulus (MPa) | Ultimate Tensile Strength (MPa) | Extension (mm) | Force (N) |
|---|---|---|---|---|---|
| 0% PES-PAC | 0.4460 | 54.10 | 4.619 | 2.375 | 6.1875 |
| 1% PES-PAC | 0.2870 | 28.16 | 4.199 | 1.425 | 3.6250 |
| 7% PES-PAC | 0.3030 | 27.98 | 3.850 | 1.100 | 3.5000 |
| 9% PES-PAC | 0.3167 | 17.16 | 2.594 | 1.000 | 2.5000 |
| 11% PES-PAC | 0.3587 | 41.84 | 2.974 | 1.550 | 3.2000 |

# CHAPTER 5

# CONCLUSION AND RECCOMENDATIONS

## 5.1 Conclusion

Five types of flat sheet asymmetric membrane with different PAC concentration (0%, 1%, 7% 9% and 11%) were successfully fabricated. Each different percentage of PES-PAC membrane was tested with pure water flux, salt solution flux, and salt rejection to determine the membrane performance in term of permeation rate. The effect of additives concentration and operating pressure on membrane performance were investigated. Higher percentage of PAC contained in membrane will get a better flux and better rejection. Increase of applied pressure during dead-end filtration will increase the flux. Besides that, SEM images also shows that addition of PAC as additive in membrane has improved porosity on the surface of the membrane and thus increase the permeability of membranes. However, addition of PAC in casting solution will decrease the tensile strength. In a nutshell, the overall performances of membrane improved with the increase of PAC concentrations except tensile strength. In this study, 11% PES-PAC has the highest flux and salt rejection.

## 5.2 Recommendations

Research on the membrane performance is a very interesting topic because we never know what will happen to the membrane by adding different concentration of PAC into the dope unless we figure it ourselves.

After go through this study, I recommend that for future improvements, this study can include the following sections:

i. Increase the amounts of PAC added in membrane fabricated to determine whether it will further increase the membrane performance or not
ii. Determine the membrane fouling rate of the PES-PAC membrane by using cross flow filtration
iii. Compare the membrane performance with other additive
iv. Further study on tensile strength of the membranes

# REFERENCES

Abdul Aziz, H. and Mojiri, A. (2014). Wastewater Engineering: Advanced Wastewater Treatment Systems.

Ahsan Munir, (2006). Dead End Membrane Filtration.

Andriamirado, L., Asensi, D., Baig, S., Ballard, T., Bele, P., Bernard, M., Bourdelot, J., Brunet, J., Cachot, L., Camus, M., Cousin, A., Descamps, P., Durand-Bourlier, L., Gaudy, G., Gruel, N., Haubry, A., Hesse, C., Hund, A., Julve, J., Lebosse, X., Lebrun, T., Lesoille, M., Marchand, D., Moles, J., Mouchet, P., Nicol, R., Perrin, D., Petitpain, F., Prevot, C., Roux, J., Rovel, J., Savall, V., Vion, P., Vital, J., Westrelin, J. and Wiier, S. (2007). Water Treatment Handbook. 7th ed. France: Degrémont.

Aryanti, P., Khoiruddin, and Gede Wenten, I. (2013). Influence of Additives on Polysulfone-Based Ultrafiltration Membrane Performance during Peat Water Filtration. Journal of Water Sustainability, 3(2), pp.85-96.

Baker, R. (2004). Membrane technology and applications. Chichester: J. Wiley.

Basri, H., Ismail, A. and Aziz, M. (2011). Polyethersulfone (PES)–silver composite UF membrane: Effect of silver loading and PVP molecular weight on membrane morphology and antibacterial activity. Desalination, 273(1), pp.72-80.

Carr, G. and Neary, J. (2008). Water quality for ecosystem and human health. Burlington, Ont.: UN GEMS/Water Programme Office.

Delgado, S., Villarroel, R., Gonzalez, E. and Morales, M. (2011). Aerobic Membrane Bioreactor for Wastewater Treatment – Performance Under Substrate-Limited Conditions. Biomass - Detection, Production and Usage.

Easa, A. and Abou-Rayan, A. (2010). Domestic Wastewater Effect On The Pollution Of The Groundwater In Rural Areas In Egypt. Fourteenth International Water Technology Conference, IWTC, pp.909-923.

Environmental Protection Agency, EPA, (2004). Primer for Municipal Wastewater Treatment Systems.

Environmental Protection Agency, EPA, (2012). N-Methylpyrrolidone: Paint Stripping Use.

Environmental Protection Agency, EPA, (2015). Drinking Water Treatability Database.

Gao, D., Fu, Y., Tao, Y., Wu, W., An, R. and Li, X. (2009). Current research and development of controlling membrane fouling of MBR. African Journal of Biotechnology, 8(13), pp.2993-2998.

Government of Western Australia Department of Water, (2010). Wastewater treatment and disposal - domestic systems. Western Australia.

Hendricks, R. and Pool, E. (2012). The effectiveness of sewage treatment processes to remove faecal pathogens and antibiotic residues. Journal of Environmental Science and Health, Part A, 47(2), pp.289-297.

Hogan, C. (2014). Water pollution. In: 1st ed.

Jamal Khan, S., Visvanathan, C. and Jegatheesan, V. (2012). Effect of powdered activated carbon (PAC) and cationic polymer on biofouling mitigation in hybrid MBRs. Bioresource Technology, 113, pp.165-168.

Koch Membrane Systems, Inc., (2012). An Overview of Membrane Technology and Theory. [image] Available at: http://www.kochmembrane.com/PDFs/Application-Bulletins/KMS-Membrane-Theory.aspx [Accessed 29 Mar. 2015].

Lau, W., Guiver, M. and Matsuura, T. (1991). Phase separation in polysulfone/solvent/water and polyethersulfone/solvent/water systems. Journal of Membrane Science, 59(2), pp.219-227.

Le-Clech, P., Jefferson, B. and Judd, S. (2003). Impact of aeration, solids concentration and membrane characteristics on the hydraulic performance of a membrane bioreactor. Journal of Membrane Science, 218(1-2), pp.117-129.

Li, J., Xu, Z., Yang, H., Yu, L. and Liu, M. (2009). Effect of TiO2 nanoparticles on the surface morphology and performance of microporous PES membrane. Applied Surface Science, 255(9), pp.4725-4732.

Li, Y., He, Y., Liu, Y., Yang, S. and Zhang, G. (2005). Comparison of the filtration characteristics between biological powdered activated carbon sludge and activated sludge in submerged membrane bioreactors. Desalination, 174(3), pp.305-314.

Ma, Y., Shi, F., Ma, J., Wu, M., Zhang, J. and Gao, C. (2011). Effect of PEG additive on the morphology and performance of polysulfone ultrafiltration membranes. Desalination, 272(1-3), pp.51-58.

Mara, D. (2004). Domestic wastewater treatment in developing countries. London: Earthscan Publications.

Marchese, J., Ponce, M., Ochoa, N., Prádanos, P., Palacio, L. and Hernández, A. (2003). Fouling behaviour of polyethersulfone UF membranes made with different PVP. Journal of Membrane Science, 211(1), pp.1-11.

Meng, F., Chae, S., Drews, A., Kraume, M., Shin, H. and Yang, F. (2009). Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane material. Water Research, 43(6), pp.1489-1512.

Ng, C., Sun, D., Bashir, M., Wai, S., Wong, L., Nisar, H., Wu, B. and Fane, A. (2013). Optimization of membrane bioreactors by the addition of powdered activated carbon. Bioresource Technology, 138, pp.38-47.

Osmonics.com, (n.d.). GE Water & Process Technologies. [online] Available at: http://www.osmonics.com [Accessed 25 Mar. 2015].

Pescod, M. (1992). Wastewater treatment and use in agriculture. Rome: Food and Agriculture Organization of the United Nations.

Razmjou, A., Mansouri, J. and Chen, V. (2011). The effects of mechanical and chemical modification of TiO2 nanoparticles on the surface chemistry, structure and fouling performance of PES ultrafiltration membranes. Journal of Membrane Science, 378(1-2), pp.73-84.

Reingruber, H., Zankel, A., Mayrhofer, C. and Poelt, P. (2012). A new in situ method for the characterization of membranes in a wet state in the environmental scanning electron microscope. Journal of Membrane Science, 399-400, pp.86-94.

Remy, M., Potier, V., Temmink, H. and Rulkens, W. (2010). Why low powdered activated carbon addition reduces membrane fouling in MBRs. Water Research, 44(3), pp.861-867.

Satyawali, Y. and Balakrishnan, M. (2009). Effect of PAC addition on sludge properties in an MBR treating high strength wastewater. Water Research, 43(6), pp.1577-1588.

Schirg, P. and Widmer, F. (1992). Characterisation of nanofiltration membranes for the separation of aqueous dye-salt solutions. Desalination, 89(1), pp.89-107.

Singh, R. (2015). Membrane technology and engineering for water purification. 2nd ed.

Tchobanoglous, G., Burton, F. and Stensel, H. (2003). Wastewater engineering. Boston: McGraw-Hill.

Techniques, (2013). Scanning Electron Microscopy (SEM). [online] Available at: http://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html [Accessed 5 Apr. 2015].

Tennant, M. (2004). Activation and use of powdered activated carbon for removing 2-Methylisoborneol in water utilities.

Tennant, M. and Mazyck, D. (2007). The role of surface acidity and pore size distribution in the adsorption of 2-methylisoborneol via powdered activated carbon. Carbon, 45(4), pp.858-864.

Torretta, V., Urbini, G., Raboni, M., Copelli, S., Viotti, P., Luciano, A. and Mancini, G. (2013). Effect of Powdered Activated Carbon to Reduce Fouling in Membrane Bioreactors: A Sustainable Solution. Case Study. Sustainability, 5(4), pp.1501-1509.

Wang, Z., Wu, Z., Mai, S., Yang, C., Wang, X., An, Y. and Zhou, Z. (2008). Research and applications of membrane bioreactors in China: Progress and prospect. Separation and Purification Technology, 62(2), pp.249-263.

Yang, W., Cicek, N. and Ilg, J. (2006). State-of-the-art of membrane bioreactors: Worldwide research and commercial applications in North America. Journal of Membrane Science, 270(1-2), pp.201-211.

Zhao, Y., Zhu, L., Yi, Z., Zhu, B. and Xu, Y. (2014). Zwitterionic hydrogel thin films as antifouling surface layers of polyethersulfone ultrafiltration membranes anchored via reactive copolymer additive. Journal of Membrane Science, 470, pp.148-158.

Zhou, C., Hou, Z., Lu, X., Liu, Z., Bian, X., Shi, L. and Li, L. (2010). Effect of Polyethersulfone Molecular Weight on Structure and Performance of Ultrafiltration Membranes. Industrial & Engineering Chemistry Research, 49(20), pp.9988-9997.

## **Appendix A**: Calculation for amount of PES, PAC and NMP needed in membrane fabrication.

The ratio of polymer (PES) to solvent (NMP) is 16:84 and the percentage of PAC was varied during membrane fabrication as shown in Table 3.1. The calculation was shown below.

### Membrane 0% PES-PAC

$0\ \%\ \text{PAC} = 0\ \% \times 16\text{g} = 0.00\ \text{g of PAC}$

$16\ \text{g (PES)} - 0.00\ \text{g (PAC)} = 16.00\ \text{g (PES)}$

Therefore, PAC = 0.00 g, PES = 16.00 g, NMP = 84.00 g

### Membrane 1% PES-PAC

$1\ \%\ \text{PAC} = 1\ \% \times 16\text{g} = 0.16\ \text{g of PAC}$

$16\ \text{g (PES)} - 0.16\ \text{g (PAC)} = 15.84\ \text{g (PES)}$

Therefore, PAC = 0.16 g, PES = 15.84 g, NMP = 84.00 g

### Membrane 7% PES-PAC

$7\ \%\ \text{PAC} = 7\ \% \times 16\text{g} = 1.12\ \text{g of PAC}$

$16\ \text{g (PES)} - 1.12\ \text{g (PAC)} = 14.88\ \text{g (PES)}$

Therefore, PAC = 1.12 g, PES = 14.88 g, NMP = 84.00 g

### Membrane 9% PES-PAC

$9\ \%\ \text{PAC} = 9\ \% \times 16\text{g} = 1.44\ \text{g of PAC}$

$16\ \text{g (PES)} - 1.44\ \text{g (PAC)} = 14.56\ \text{g (PES)}$

Therefore, PAC = 1.44 g, PES = 14.56 g, NMP = 84.00 g

### Membrane 11% PES-PAC

$11\ \%\ \text{PAC} = 11\ \% \times 16\text{g} = 1.76\ \text{g of PAC}$

$16\ \text{g (PES)} - 1.76\ \text{g (PAC)} = 14.24\ \text{g (PES)}$

Therefore, PAC = 1.76 g, PES = 14.24 g, NMP = 84.00 g

**Appendix B**: Calculation for preparation of 0.1 M NaCl stock solution

To prepare 1 L of 0.1 M NaCl stock solution,

$$
\begin{aligned}
G_s &= MW \times M \times V \\
&= 58.45 \text{ g/mol} \times 0.1 \text{ M} \times 1 \text{ L} \\
&= 5.845 \text{ g of NaCl}
\end{aligned}
$$

**Appendix C**: Calculation for stock solution dilution

The required concentration of salt solutions were 0.08 M, 0.06 M, 0.04 M, 0.02 M, 0.01 M, 0.008 M, 0.006 M, 0.004 M and 0.002 M.

$M_1V_1 = M_2V_2$
$V_1 = M_2V_2 \div M_1 \times 1000$ mL/L

0.08 M salt solution

$V_1 = 0.08 \times 0.05$ L $\div 0.1$ M $\times 1000$ mL/L
$= 40$ mL

0.06 M salt solution

$V_1 = 0.06 \times 0.05$ L $\div 0.1$ M $\times 1000$ mL/L
$= 30$ mL

0.04 M salt solution

$V_1 = 0.04 \times 0.05$ L $\div 0.1$ M $\times 1000$ mL/L
$= 20$ mL

0.02 M salt solution

$V_1 = 0.02 \times 0.05$ L $\div 0.1$ M $\times 1000$ mL/L
$= 10$ mL

0.01 M salt solution

$V_1 = 0.01 \times 0.05$ L $\div 0.1$ M $\times 1000$ mL/L
$= 5$ mL

0.008 M salt solution

$V_1 = 0.008 \times 0.05$ L $\div 0.1$ M $\times 1000$ mL/L
$= 4$ mL

0.006 M salt solution

$V_1 = 0.006 \times 0.05$ L $\div 0.1$ M $\times 1000$ mL/L
$= 3$ mL

<u>0.004 M salt solution</u>

$V_1$ = 0.004 × 0.05 L ÷ 0.1 M × 1000 mL/L

= 2 mL

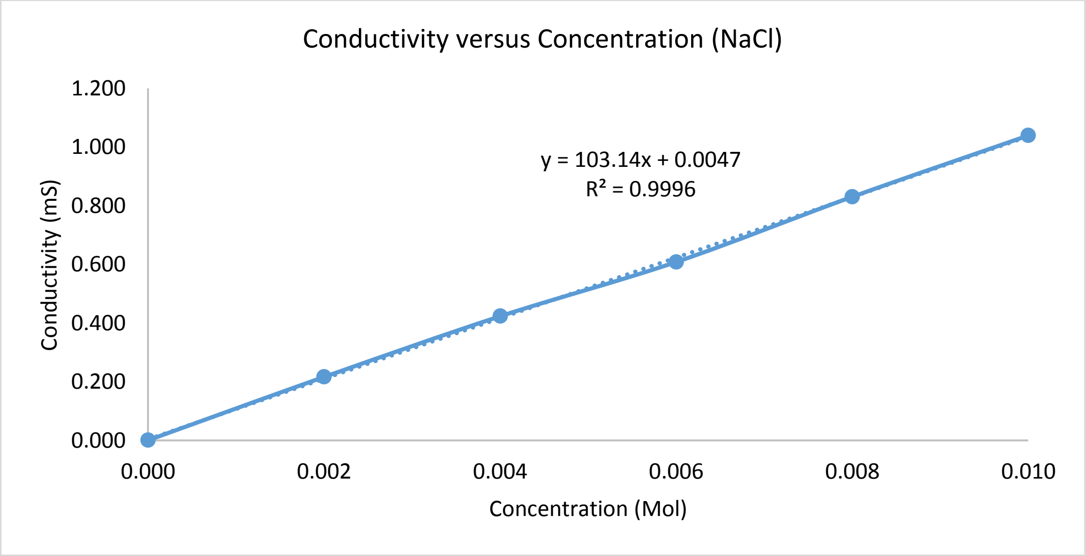
<u>0.002 M salt solution</u>

$V_1$ = 0.002 × 0.05 L ÷ 0.1 M × 1000 mL/L

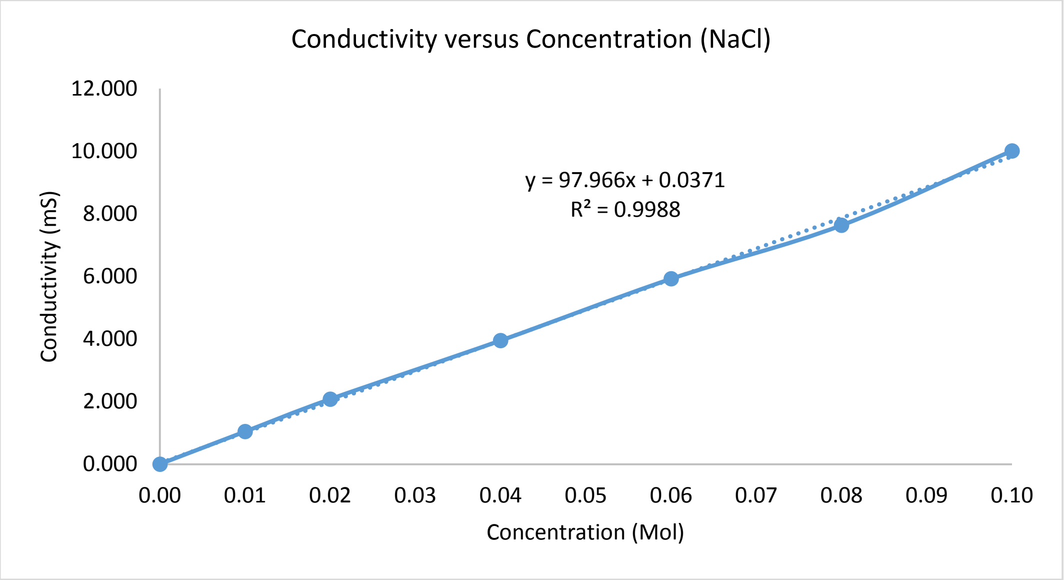
= 1 mL

**Appendix D**: Calibration curve for salt solutions for conductivity versus concentration

| Concentration (M) | Conductivity (mS) |
|---|---|
| 0.000 | 0.001 |
| 0.002 | 0.217 |
| 0.004 | 0.424 |
| 0.006 | 0.609 |
| 0.008 | 0.831 |
| 0.010 | 1.040 |



| Concentration (M) | Conductivity (mS) |
|---|---|
| 0.00 | 0.001 |
| 0.01 | 1.040 |
| 0.02 | 2.078 |
| 0.04 | 3.950 |
| 0.06 | 5.920 |
| 0.08 | 7.630 |
| 0.10 | 10.010 |


Conductivity versus Concentration (NaCl)
y = 97.966x + 0.0371
R² = 0.9988
Conductivity (mS)
12.000
10.000
8.000
6.000
4.000
2.000
0.000
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
Concentration (Mol)

**Appendix E**: Calculation for percentage of salt rejection by different PES-PAC membranes at different pressure and the calculation

0% PES-PAC

| | | Kond | Kond | Kond | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pressure | Time | Suapan | Permeate | Retentate | Flux | (Jv/k) | exp(G) | Cf | Cp | Cr | Cb | Cw | Robs | Rreal |
| bar | sec | mS/cm | mS/cm | mS/cm | (m/sec)[x10-6] | | | mol/litre | mol/litre | mol/litre | mol/litre | mol/litre | (%) | (%) |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.1 | 1415.0 | 1.092 | 0.810 | 1.077 | 4.085 | 0.0913 | 1.0956 | 0.01048 | 0.00737 | 0.01034 | 0.0104 | 0.0107 | 29.2012 | 31.1238 |
| 0.2 | 748.0 | 1.092 | 0.826 | 1.077 | 7.728 | 0.1727 | 1.1885 | 0.01048 | 0.00752 | 0.01034 | 0.0104 | 0.0110 | 27.8028 | 31.3982 |
| 0.3 | 439.0 | 1.092 | 0.857 | 1.077 | 13.167 | 0.2943 | 1.3421 | 0.01048 | 0.00780 | 0.01034 | 0.0104 | 0.0113 | 25.0932 | 31.0156 |

1% PES-PAC

| | | Kond | Kond | Kond | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pressure | Time | Suapan | Permeate | Retentate | Flux | (Jv/k) | exp(G) | Cf | Cp | Cr | Cb | Cw | Robs | Rreal |
| bar | sec | mS/cm | mS/cm | mS/cm | (m/sec)[x10-6] | | | mol/litre | mol/litre | mol/litre | mol/litre | mol/litre | (%) | (%) |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.1 | 693.0 | 1.092 | 0.876 | 1.077 | 8.341 | 0.1864 | 1.2049 | 0.01048 | 0.00797 | 0.01034 | 0.0104 | 0.0109 | 23.4325 | 26.9405 |
| 0.2 | 460.0 | 1.092 | 0.869 | 1.077 | 12.566 | 0.2808 | 1.3242 | 0.01048 | 0.00791 | 0.01034 | 0.0104 | 0.0112 | 24.0443 | 29.5374 |
| 0.3 | 357.0 | 1.092 | 0.880 | 1.077 | 16.191 | 0.3618 | 1.4360 | 0.01048 | 0.00801 | 0.01034 | 0.0104 | 0.0115 | 23.0828 | 30.1158 |

## 7% PES-PAC

| Pressure bar | Time sec | Kond Suapan mS/cm | Kond Permeate mS/cm | Kond Retentate mS/cm | Flux (m/sec)[x10-6] | (Jv/k) | exp(G) | Cf mol/litre | Cp mol/litre | Cr mol/litre | Cb mol/litre | Cw mol/litre | Robs (%) | Rreal (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.1 | 369.0 | 1.134 | 0.868 | 1.089 | 15.665 | 0.3501 | 1.4192 | 0.01089 | 0.00790 | 0.01045 | 0.0107 | 0.0118 | 25.9747 | 33.2432 |
| 0.2 | 262.0 | 1.134 | 0.865 | 1.089 | 22.062 | 0.4931 | 1.6373 | 0.01089 | 0.00787 | 0.01045 | 0.0107 | 0.0125 | 26.2305 | 36.7963 |
| 0.3 | 196.0 | 1.134 | 0.873 | 1.089 | 29.492 | 0.6591 | 1.9330 | 0.01089 | 0.00794 | 0.01045 | 0.0107 | 0.0132 | 25.5482 | 39.8792 |

## 9% PES-PAC

| Pressure bar | Time sec | Kond Suapan mS/cm | Kond Permeate mS/cm | Kond Retentate mS/cm | Flux (m/sec)[x10-6] | (Jv/k) | exp(G) | Cf mol/litre | Cp mol/litre | Cr mol/litre | Cb mol/litre | Cw mol/litre | Robs (%) | Rreal (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.1 | 231.0 | 1.092 | 0.822 | 1.087 | 25.023 | 0.5592 | 1.7493 | 0.01048 | 0.00748 | 0.01044 | 0.0105 | 0.0127 | 28.4821 | 41.0609 |
| 0.2 | 164.0 | 1.092 | 0.860 | 1.087 | 35.246 | 0.7877 | 2.1983 | 0.01048 | 0.00783 | 0.01044 | 0.0105 | 0.0136 | 25.1759 | 42.5174 |
| 0.3 | 120.0 | 1.092 | 0.867 | 1.087 | 48.170 | 1.0765 | 2.9344 | 0.01048 | 0.00789 | 0.01044 | 0.0105 | 0.0154 | 24.5669 | 48.8666 |

11% PES-PAC

| Pressure bar | Time sec | Kond Suapan mS/cm | Kond Permeate mS/cm | Kond Retentate mS/cm | Flux (m/sec)[x10-6) | (Jv/k) | exp(G) | Cf mol/litre | Cp mol/litre | Cr mol/litre | Cb mol/litre | Cw mol/litre | Robs (%) | Rreal (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.1 | 94.0 | 1.134 | 0.881 | 1.089 | 61.493 | 1.3743 | 3.9521 | 0.01089 | 0.00802 | 0.01045 | 0.0107 | 0.0185 | 24.8660 | 56.6721 |
| 0.2 | 70.0 | 1.134 | 0.864 | 1.089 | 82.576 | 1.8454 | 6.3308 | 0.01089 | 0.00786 | 0.01045 | 0.0107 | 0.0256 | 26.3158 | 69.3347 |
| 0.3 | 55.0 | 1.134 | 0.854 | 1.089 | 105.097 | 2.3487 | 10.4723 | 0.01089 | 0.00777 | 0.01045 | 0.0107 | 0.0381 | 27.1686 | 79.6190 |