

Reversibility of PVDF Membrane Performance and Structure Caused by Cold Water Temperature and Elevated Conditioning Water Temperature

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**A thesis
presented to Lakehead University in partial fulfilment of the requirements for Masters of
Science in Environmental Engineering**

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ABSTRACT

Thousands of dollars are wasted each year due to the impact that cold temperature has on membrane filters. There are many areas around the world that are subjected to cold climate, and the study of how cold temperature has an impact on membrane filters and whether or not that impact could be reversed is of great interest.

The impact that cold temperature, warm water treatment, and treatment time would have on the performance and structure of a polyvinylidene fluoride flat sheet membrane was studied. Three modules were used and the flux was maintained 30LMH while the TMP was monitored for three month duration in the cold temperature. One module stayed in the cold temperature constantly, while every two weeks, the other two modules were treated with 23°C or 35°C water for six hours. In addition, pieces of the polyvinylidene fluoride membrane were placed in the cold temperature for the three months and treated every two weeks in the same manner for six and 24 hours, and the structural changes (pore size) that occurred were tested.

The use of periodical warm water (35°C) membrane treatment could completely or almost completely recover the membrane performance and pore size structure loss caused by cold water temperature, while the use of room temperature (23±1°C) treatment recovered majority of the membrane permeability and structure loss caused by cold water temperature. Membranes periodically treated in warmer water temperature showed a better membrane performance (higher permeability) than that periodically treated at room temperature from a long-term operation of three months. The results suggest the change in polyvinylidene fluoride membrane structure caused by cold water temperature is almost completely reversible after periodical warm water treatment, and thus the use of warm water treatment and/or chemical cleanings will benefit the recovery of membrane performance and structure change caused by cold water temperature in cold regions.

ACKNOWLEDGMENTS

Foremost I wish to thank my supervisor, Dr. Liao, and my co-supervisor, Dr. Gao, for their superior knowledge on water treatment and membrane technology. If there was ever an issue, it was easy to be able to talk to them and to try to figure out ways to solve the problem. Their willingness to help me succeed in my goals will always be remembered.

I want to thank the staff and professors of the Chemical Engineering, Environmental Engineering, and Chemistry Department, who have helped me succeed in completing this thesis. A big thank you to Dr. Wu for the many wonderful talks we had while SEM was being done, it made the time fly by so quickly. I wish to thank the committee members for taking their time and reading over the thesis and making valuable comments and suggestions.

I wish to thank my group of fellow graduate students studying under Dr. Liao; their willingness to share their knowledge and to help whenever something was amiss was always appreciated. Many laughs have been shared both in joy and frustration when figuring out solutions to problems faced when conducting experiments. I want to thank Chris Merritt for assisting me in preparing samples for analysis; he made my life a little easier.

Finally, I want to thank my family and friends who have supported me throughout this journey both in my undergrad in chemical engineering and my graduate studies in environmental engineering. I wouldn't have been able to succeed without them; their encouragement, and tough love have gotten me to where I am today, and I am most grateful to them. You have made me the person I am today, so if you don't like how I turned out, blame yourself. ☺

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LIST OF NOMENCLATURE

HRT	Hydraulic retention time
Δz	Pore length
A	Effective area of the membrane
D	Diffusion coefficient
EPS	Extracellular polymeric substance
H	Height fo the membrane
HF	Hollow Fibre
IR	Irreversible fouling
J	Permeation Flux
LMH	Litres·m ⁻² ·hr ⁻¹
M	Molecular weight
MF	Microfilter
MO	Microorganisms
Na ₂ S ₂ O ₅	Sodium metabisulphite
ND	Not detectable
NF	Nanofilter
P	Specific permeability of the membrane
P ₀	Initial permeability of module (virgin) at 20°C
P _i	Permeability of the module at 20°C after treatment
PSD	Pore size distribution
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
Q	Flow rate of the permeate
r	Pore radius
RO	Reverse Osmosis
R _t	Resistance of the membrane
SEM	Scanning electron microscope
SMP	Soluble microbial product
SRT	Solids retention time
SVI	Sludge Volume Index

T	Temperature
t	Elapsed time for permeate collection
TMP	Transmembrane pressure
UF	Ultrafilter
V	Volume of permeate collected
V_m	Boiling point molar volume of solute
W	Width of the membrane
μ	Viscosity of solution being filtered
ρ_{pore}	Number of pores per unit area
τ	Tortuosity factor
φ	Association factor of solvent

CHAPTER 1. INTRODUCTION

Fresh and safe water has become scarce and one of the major threats to human activity; the scarcity is increasing due to the ever increasing population, and with it the higher standards of living, and the demands from industries (wastewater treatment, pharmaceutical, pulp and paper, textile, etc. (Goosen et al. 2005; Le and Nunes, 2016)) and agriculture (Fritzmann et al. 2006). The regulations for both drinking water and wastewater treatment/disposal have become more stringent over the years (Van der Bruggen et al. 2003), and membrane technology is able to meet this ever-increasing quality regulation (Jiang et al. 2017).

Conventional drinking water treatment processes which typically are a step by step processes of the following: coagulation, flocculation, sedimentation, filtration (ie. sand filter, carbon filter), and finally disinfection (ie. chlorine) before entering the distribution system (Joudah 2014; Angreni 2009; Betancourt and Rose, 2004) are being phased out by the use of the membrane technology.

Membrane technology has been widely used for drinking water production and wastewater water treatment all over the world, including cold regions, due to its obvious advantages, such as a decrease in chemical usage, more environmentally friendly, reduced space requirement, high product water quality, easier operation, and in some areas of the world/communities, such as cold regions, it is a more practical choice (Pearce 2007; Guo et al. 2012; Mohammad et al. 2012). However, there are various factors that can impact the performance of the membrane, which include: feed water characteristics (type of contaminants, concentration of contaminants), membrane characteristics (roughness, pore size,

hydrophobicity), operational conditions (pH, flow rate, temperature), and fouling (Ramli et al. 2002; Manawi et al. 2014).

Fouling is one of the major and well-known concerns when it comes to the utilization of membrane technology in industry (Mi and Elimelech, 2010), and therefore, many studies have been conducted in regards to characterizing the different types of foulants that can occur on membranes, and how to alleviate this issue. However, another major concern that is understudied and is not as well-known is the impact that the temperature of the feed can have on the membranes' performance and structure. Temperature is a known factor to impact feed characteristics such as: viscosity, the diffusivity of a contaminant, surface tension, etc. (AWWA, 2006; Dang et al. 2014); however, little is known as to how cold temperature has an impact on membrane structure (Cui et al., 2017). Many areas around the world such as Canada, United States of America, Russia, China, etc. are subjected to harsher cold climates and are less studied than that of areas in the range of room and warm temperatures (Ozgun et al. 2013). Similarly, some studies also observed the negative effect of psychrophilic temperature on the performance of membrane bioreactors (Wang et al. 2009; Van den Brink et al. 2011; Ma et al. 2013; Sun et al. 2014; Zhang et al. 2014; Gurung et al. 2017) and the effect of cleaning water temperature on membrane permeability recovery (Liu et al., 2000; Caothien et al., 2018).

The impact of temperature on viscosity has been the focus on why flux decreases with a decreased temperature; however, based on models that are able to compensate for the viscosity change with temperature, there still presents unaccountable factors that are contributing to flux decline, such as, the impact of temperature on the physical properties of the membrane which include, lower porosity, and higher tortuosity (Farahbakhsh and Smith, 2006; Uhr, 2001). Due to this unaccountability, thousands of dollars are wasted each year due to the lack of understanding

of how cold water temperature impacts the physical properties of the membrane and how to recover the membrane structure loss caused by cold water temperature (Avina, 2006), as many industries assume that flux decline is due to fouling, and therefore, perform unnecessary chemical cleaning on the membrane, which has been shown to deteriorate the membrane structure and decrease their lifespan (Abdullah and Bérubé, 2013). In addition, the factor that impacts the resistance of the membrane the most is the pore size, which means that any small change in pore size can result in a large increase in resistance, therefore, causing an increase in pressure that is required to maintain the desired flux (Robinson et al. 2016). In practical situations it would not be feasible to elevate the temperature of cold feed water as this would increase operating cost, especially, for large scale drinking water membrane filtration plants; therefore, it is important to have a better understanding of the impact of cold water temperature on the performance and structure of the membranes and eventually develop strategies to recover membrane structural changes (Ozgun et al. 2013).

1.1 Objective

The impact of cold water temperature on membrane filters has not been studied in great detail, and to the best of our knowledge, no attention has been paid as to whether or not the impact of cold water temperature on the membrane structure can be recovered or reversed completely by operating and cleaning strategies. The objectives of this study were to determine the impact of cold water temperature of 0.3°C (a feed water temperature often seen during the cold season for many treatment plants across Canada, USA, Russia, China (Ozgun et al. 2013)), on membrane performance and structure and to investigate if periodical warm water conditioning/chemical cleaning would be able to partially or completely reinstall the potential membrane structure changes caused by extreme cold water temperature.

CHAPTER 2 LITERATURE REVIEW

2.1 Membrane filtration

2.1.1 Material and Design

It was in the late 1960s when membrane technology was first developed, and throughout the decades the material and the cost of the fabrication decreased, and therefore, is being seen in more and more industrial applications today (Mi and Elimelech, 2010) (Shi et al. 2014).

Membrane filters can be made of varying materials, such as polymer, and ceramic. Membranes composed of ceramic material offer thermal, chemical and mechanical stability/superiority over the polymer based membranes, however, due to the cost of them, polymeric materials are typically used (Van der Bruggen et al. 2003).

In industry, the traditional polymers used for the membranes are: PVDF, polyethylene, polypropylene, which are hydrophobic, and polycarbonate, polyamide, and polysulfone which are hydrophilic (Van der Bruggen et al. 2003). Hydrophobic polymer materials such as PVDF, are known to be: thermally stable, therefore, allowing hot feed to be passed through them without damage to the membranes; chemical resistant, which means that less deterioration would occur when the membrane requires chemical cleaning, and therefore less replacement. However, due to its hydrophobic nature, PVDF material has a higher chance for fouling, therefore, hydrophobic materials are occasionally blended or coated with hydrophilic functional groups which would then decrease the occurrence of fouling, and therefore, operational time could increase, with a decrease in downtime for maintenance cleaning (Abdullah and Bérubé, 2013).

Membranes can also be made out of inorganic polymers which include material such as: aluminum oxide, silicon nitride, and metal alloys. These polymers present a more thermally stable membrane, which is also more resistant to harsh environments than the membrane may

be subjected to than that of organic material. However, the production of inorganic membranes is more complex, and there are limited resources to make the inorganic membranes; as well they are more expensive to create than organic polymer membranes (Tan et al. 2001; Xu et al. 2010).

The material in which the membrane is made out has a great influence on the performance of the membranes ability to treat the feed (ie. hydrophobicity, thermal stability, pH tolerance) (Ramli et al. 2002; Ozgun et al. 2013). The material used is also very important in terms of when it comes to cleaning the membrane due to fouling, as the chemicals used can attack the membrane and corrode it if it is not chemically resistant (Ramli et al. 2002).

Membranes also have varying structures, and configurations (Xu, 2009). The structure can either be asymmetric or symmetric for membranes (Xu, 2009). The configurations that are normally seen in industry are flat sheet, capillary, and hollow fiber (Xu, 2009).

2.1.2 Operation

The most commonly used membrane filters are pressure driven, and the four types are: microfilters (MF), ultrafilters, nanofilters (NF), and reverse osmosis (RO). As is seen in Figure 2-1 as the pore size of pressure driven membrane filter decreases (MF>UF>NF>RO), the amount of contaminants that are able to be rejected increases, however, with a decrease in pore size a higher TMP is required to operate the membrane. The mechanisms through which membrane filters operate at are: sieving (size exclusion of particles), charge (cation, anion), and diffusion (Van der Bruggen et al. 2003).

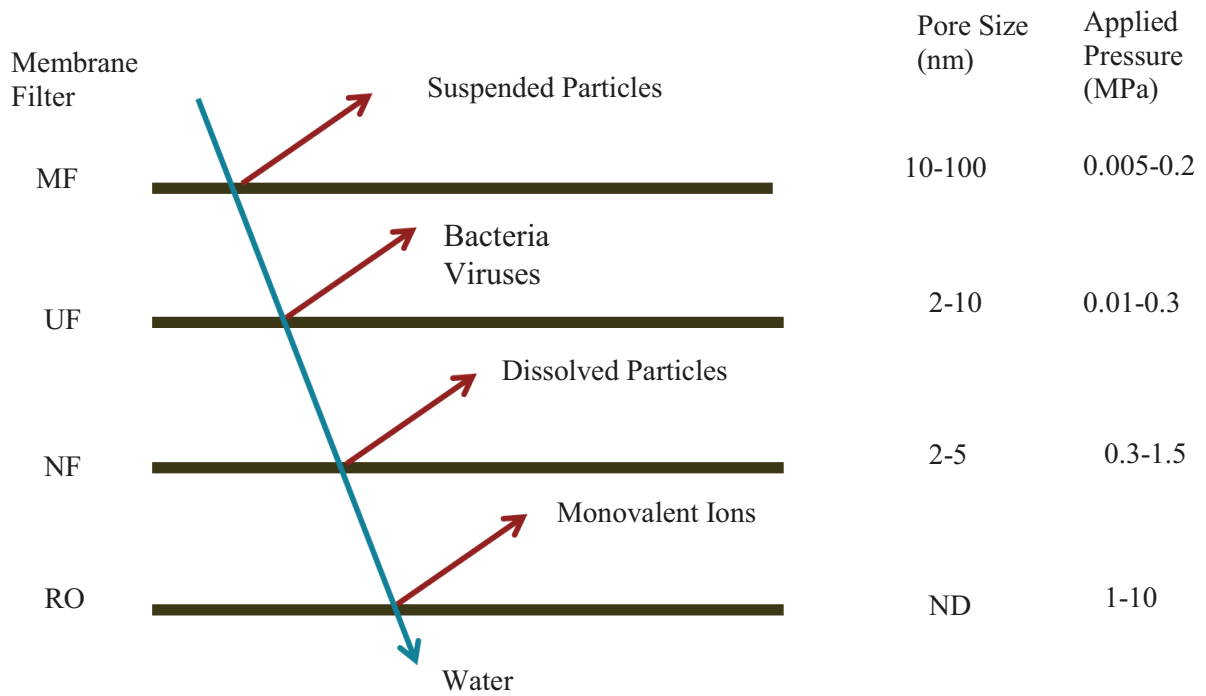


Figure 2-1: Comparison between pressure driven membrane filters (Ramli et al. 2002) (Van der Bruggen et al. 2003) (ND= not detectable)

Figure 2-2 shows the set-up of a flat sheet membrane module, where the feed passes through the membrane in an outside-inside mode, where the plate is used to support the membrane.

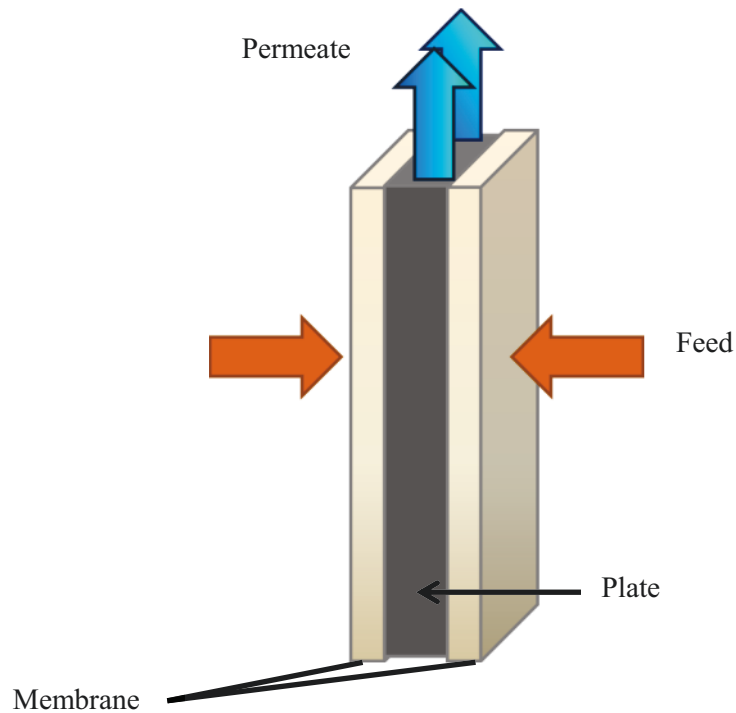


Figure 2-2: Schematic of flat sheet module

2.2 Performance and Structure

2.2.1 Background

Performance of the membrane can be thought of as two aspects, the amount of permeate being passed through the membrane, and the quality of the permeate; if either one or both decrease, it is considered a negative impact on the performance.

Darcy's Law (Robinson et al. 2016) which is represented by Equation (1), shows that the permeate flux is equal to the TMP applied to the membrane divided by the viscosity of the fluid and the total resistance of the membrane.

$$J = \frac{TMP}{\mu R_t} \quad (1)$$

where:

J=Permeation Flux ($\text{m}^3/\text{m}^2 \cdot \text{s}$)

TMP= Transmembrane Pressure (Pa)

μ =Viscosity of solution being filtered (Pa·s)

R_t =Resistance of the membrane (m^{-1})

There are two different operational modes that a membrane can be operated under, they are, constant flux with fluctuating TMP or constant TMP with fluctuating flux (Iorhemen et al. 2016). In industry, the flux of the membrane is typically held constant as a certain criteria demand must be met for quantity of material. Therefore, if TMP had to increase during operational time, that would mean that either viscosity or resistance would have to increase. It is well known that as temperature of water decreases, the viscosity increases (AWWA, 2006). If the temperature is held constant, this would mean that the viscosity would then be constant, however, the TMP still may fluctuate which would be due to the change in resistance of the membrane, which can be defined through Equation (2) (Robinson et al. 2016).

$$R_t = \frac{8\tau\Delta z}{\pi r^4 \rho_{pore}} \quad (2)$$

where:

τ =tortuosity factor (dimensionless)

r = pore radius

Δz =pore length

ρ_{pore} = number of pores per unit area

For resistance of the membrane, the most important term is the radius of the pore, due to the fact that it is to the power of four (AWWA, 2006), which means that any small change in pore size can result in a large change in resistance; the smaller the pore, the more resistance the membrane will have, therefore, the greater the TMP required to operate the membrane at a constant flux. In addition, resistance can also be caused by external factors such as fouling, which can act as an additional resistance barrier to the membrane (Liu et al. 2000).

Contaminants are rejected by the membrane based on properties including: size, shape and charge of the contaminant (Van der Bruggen et al. 2003).

2.2.2 Impact of Temperature

Temperature is a very important parameter when evaluating the performance of the membrane as it can impact not only the feed solution physical properties such as viscosity, diffusivity, and impact the fouling rate, but also it can cause structural changes to the membrane itself (AWWA, 2006; Dang et al. 2014; Cui et al. 2017).

The impact of temperature on the performance and structure of the membrane for temperatures ranging from 0°C to 65°C is presented in Table 2-1 along with the summary of the studies' findings. Unless otherwise stated all the studies shown in Table 2-1 were performed at a constant flux.

It has been suggested through various studies that temperature can cause structural reorientation, pore size contraction, and pore size diameter change (Mänttari et al. 2002; Goosen et al. 2002; Sharma and Chellam. 2005; Jin et al. 2009; Xiao et al. 2012). Through SEM analysis, Cui et al. (2017) observed that the pore size distribution of the membrane shifted towards a smaller pore size when subjected to operation in a cold water environment. Based on transport models (Sharma and Chellam. 2005; Dang et al. 2014), it is observed that as temperature decreases, pore size decreases, and as temperature increases, pore size increases. With a change in pore size, TMP and resistance of the membrane would also change. It is shown through Guo et al. (2009) and Xiao et al. (2012) that as temperature decreased the TMP and resistance increased; however, they also attributed this increase due to fouling, however, suggested that pore size may have changed. Guo et al. (2009) also noted that they did not observe any significant change in TMP until a certain temperature threshold was crossed; this suggests that membrane material has some resistance to cold temperature.

Diffusion is a very important factor; it is associated with the solute, and it influences transport through the membrane (Dang et al. 2014). As can be seen in Equation (3) (diffusion of trace organic contaminants in the water), as the temperature of the solution increases, which also decreases the viscosity of the solution, the diffusion will increase.

$$D = \frac{1.173 \times 10^{-13} (\phi M)^{0.5} T}{\mu V_m^{0.6}} \quad (3)$$

where:

D=diffusion coefficient

Φ =association factor of solvent

M=molecular weight

T=temperature

μ =viscosity

V_m =boiling point molar volume of solute

In addition, solute passage is also influenced by the pore size of the membrane. Based on Jawor and Hock (2009), and Dang et al. (2014) as the temperature of the feed increased, the rejection of the contaminants decreased or the solute passage increased, which could be caused both by the temperature impact on diffusion rate, and on the increase in pore size diameter. On the other hand, when membranes were subjected to a cold environment, and then were tested at 21°C to determine their ability to reject dextran, there was a slight increase in the amount the membrane was able to reject, through which Cui et al. (2017) concluded was due to the shrinkage of the pores.

Table 2-1: Summary of impact of temperature on performance and structure of the membrane

Type/material	Influent	T Operation (°C)	Summary	Reference
NF, flat sheet (material unknown)	Glucose solution	25 to 65 to 37	<ul style="list-style-type: none"> • Impact that exceeding manufacturers' T • Hysteresis phenomenon with flux and T (even with pure water) • <u>Possible</u> structure reorientation 	(Mänttari et al. 2002)
NF, flat sheet, polyamide	Organic solute	5 to 41 **	<ul style="list-style-type: none"> • <u>Hydrodynamic transport model</u>-pore size decrease as T decrease, pore size increase as T increase but pore density decreases 	(Sharma and Chellam. 2005)
UF, HF, PVC	Tianjun city water (China)	0 to 13	<ul style="list-style-type: none"> • 13 to 5°C TMP slightly increased • 5 to 0°C TMP 2.75x higher • Fouling caused increase TMP • <u>Suggest</u> that pore size contracted (no data) 	(Guo et al. 2009)
RO, flat, polyamide	Humic acid, and salt solution	15, 25, 35	<ul style="list-style-type: none"> • <u>Empirical predictive model</u> for salt rejection lacks info (structural changes) (higher at low T, lower at high T) 	(Jin et al. 2009)
RO, flat sheet, polyamide	Salt solution	15 - 25 25 - 35	<ul style="list-style-type: none"> • TMP 15% decrease • Solute passage 40% • TMP 23% additional decrease • Solute passage 75% 	(Jawor and Hock, 2009)
UF, HF, PVC	Yangtze River (China)	3 to 31.5	<ul style="list-style-type: none"> • Resistance increase in cold T $(2.11 \text{ to } 3.26) \times 10^{12} \text{m}^{-1}$ • Roughness increase from 5.688 to 7.455nm (due to foulants, greater jump in cold months) 	(Xiao et al. 2012)
NF, flat sheet, polyamide	Various trace organic contaminants solutions	20, 30, 40	<ul style="list-style-type: none"> • <u>Hindrance transport model</u>- Pore radius- 0.39-0.44nm (20 to 40°C) • Rejection decrease with increase T (due to diffusion, pore size) 	(Dang et al. 2014)
UF, HF, PVDF	1% sodium metabisulphite (3 month operation)	0.3	<ul style="list-style-type: none"> • Conditioned every two weeks 21°C for 12hrs • <u>SEM</u> Pore analysis (Pore size distribution) -Virgin and 21°C = 20.5-22.5nm -0LMH (0.3°C)=18.2-19.8nm -35LMH (0.3°C)= 15.8-19.4nm -45LMH (0.3°C)=15.0-16.5nm • Dextran rejection slight increase for membranes at 0.3°C • Permeability decrease with 0.3°C, slight recovery at 21°C condition • Lumen diameter shrinkage at 0.3°C 	(Cui et al. 2017)

**This study was performed with varying flux and constant TMP
Temperature=T, Polyvinyl chloride= PVC, Hollow Fibre=HF

2.3 Fouling

2.3.1 Types and Mechanisms

Fouling is the undesirable accumulation/deposit of particles on the surface or inside the membrane that is unavoidable when using membrane technology (Mosqueda-Jimenez et al. 2008). There are four different categories in which fouling can be classified under, they are: colloidal/particulates, organic, inorganic, and biofouling (Guo et al. 2012; Jiang et al. 2017; Zhang et al. 2016). Organic material which is the major foulant in water treatment is caused by the decomposition of organic matter (animals, plants), and can be broken down to humic acid, polysaccharides, amino acids, proteins, etc. (Shi et al. 2014; Guo et al. 2012). Inorganic materials which include iron, manganese, nickel, barium, etc. are typically found when treating the wastewater in the mining industry (Goosen et al. 2005).

From the four different foulants that can occur, biofouling is considered the most serious as it not only can be extremely difficult to remove from the membrane, but it also grows (Goosen et al. 2005). There is a large occurrence of biofilm in industry, through a study conducted by Guo et al. (2012) it was found to affect 12 out of 13 pilot plants investigated. There are three phases of biofilm, they are: the transport of the bacteria; the second stage is the attachment of the bacteria to the wall of the membrane; and the third stage is the reproduction/growth of the bacteria on the membrane, by the bacteria consuming the available nutrients in the water (Goosen et al. 2005; Jiang et al. 2017).

Figure 2-3 depicts the various mechanisms of fouling that can occur on membranes. Adsorption occurs when the particle adsorbs onto the membrane, this mechanism is associated with impacting the surface and hydrophobicity of the membrane (Shi et al. 2014). The second mechanism is pore blocking which can be categorized as either partial or full blockage of the

membrane pore; this mechanism is mostly seen near the beginning of the membrane's operation (Shi et al. 2014; Tijing et al. 2015). The third mechanism is the cake formation which occurs when a certain amount of foulant deposits onto the membrane causing an additional layer of thickness to the membrane, which causes more resistance for the feed to pass through (Shi et al. 2014; Li et al. 2017; Guo et al. 2012). These fouling mechanisms typically will occur together, as the feed that needs to be treated typically consists of varying sizes and characteristics (Shi et al. 2014).

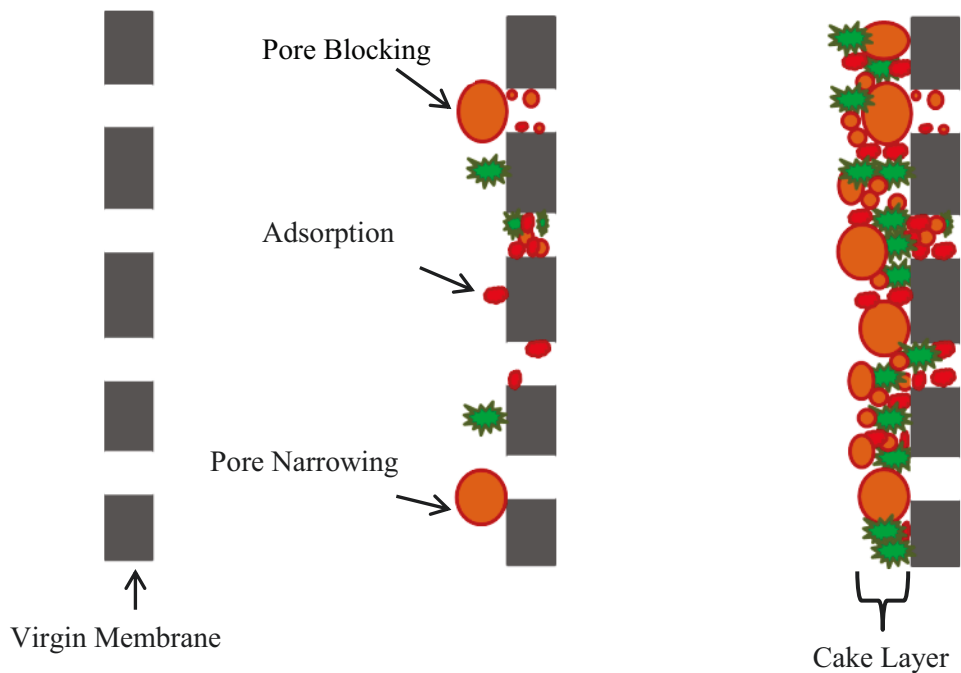


Figure 2-3: Fouling mechanisms on membranes

Fouling has a negative impact on the performance of the membrane as it alters the characteristics of the membrane material, causing it to become more hydrophobic, and therefore, making it more susceptible to fouling (Shi et al. 2014).

When fouling occurs it creates an additional cost associated with membrane use, as it means that operation must be halted to remove the foulants, which means chemicals are required which costs money to purchase and to dispose of the waste produced by the chemical cleaning (Al-Amoudi, 2010). In addition, the lifespan of the membrane is reduced after being subjected to the chemicals as it causes degradation (Al-Amoudi, 2010).

2.3.2 Cleaning strategies/methods and prevention methods

There are two distinctions between foulants, that is if they are reversible or irreversible (IR) (Shi et al. 2014). Fouling that is reversible can be removed via physical (backwashing) or chemical cleaning, while IR fouling cannot be removed by either method (Shi et al. 2014). Generally it is believed, that internal fouling of the membrane pores causes IR fouling (Jiang et al. 2017).

The two methods that are used to clean fouled membranes are through physical (backwashing, mechanical scouring) and chemical cleaning, either one or both will be used (Shi et al. 2014). Various chemical cleaning agents can be employed to remove foulants from the membranes depending on the type of foulant present (Mohammed et al. 2012). Typically what is seen is caustic solutions (sodium hypochlorite, sodium hydroxide) are used to remove both organic and microbial foulants, while acids (hydrochloric acid, nitric acid, sulfuric acid, citric acid) are used to remove inorganic foulants from the membrane (Mohammed et al. 2012; Abdullah and Bérube, 2013; Jiang et al. 2017). When chemical cleaning is performed to restore the performance of the membrane, the chemical not only removes the foulants but it also had a negative impact on the membrane itself (Abdullah and Bérube, 2013). Through various studies with various polymeric membranes, when sodium hypochlorite is implemented in the removal of the foulants, the membranes mechanical strength deteriorates while the surface of the membrane

becomes more hydrophobic, and the pore size of the membrane changes (Abdullah and Bérube, 2013).

Though fouling can never be fully eliminated there are precautions that can be taken to mitigate the rate of fouling, and therefore, lessen its impact on the membrane. These precautions include: the modification on the membrane surface (making it more hydrophilic), using hydrophilic functional groups; lowering pH of the feed solution; and pretreating the feed solution before it is allowed to come into contact with the membrane (Goosen et al. 2005; Mohammed et al. 2012). One such pretreatment which is most notable and seen is adding coagulants such as aluminum and ferric salts (Kim et al. 2006). In addition, lowering the pH of the feed solution modifies the colloids by causing them to lose their charge, therefore, they can come together to make stable suspensions which is shown to cause less fouling problems (Goosen et al. 2005).

2.3.3 Factors Impacting Fouling Rate

There are various factors that impact the fouling rate on the membrane, and they can be categorized into three main categories: membrane characteristics (pore size and distribution, roughness, hydrophobicity, charge), foulant properties (concentration, types of foulants), and the operating conditions (flux, temperature, pH) (Jiang et al. 2017; Shi et al. 2014).

2.3.3.1 Membrane characteristics and operational conditions

It has been shown through studies that hydrophobic membranes are more susceptible to fouling than hydrophilic membranes, it has been found that both elements, that the nature of the particle and the nature of the membrane both play a key role in the extent of fouling and the adherence of the particle to the membrane (Goosen et al. 2005); therefore, by modifying the membrane through the use of adding hydrophilic groups to the membrane could significantly

reduce the fouling rate, and therefore, reduce the amount of time and frequency that are required to clean the membrane (Mohammed et al. 2012; Abdullah and Bérubé, 2013).

In addition, the charge on the membrane can play a key role in the fouling rate, as it was found that humic acid, which is the result of the degradation of organic matter, caused more fouling on a positively charged membrane than that of the a negative charged membrane (Goosen et al. 2005).

The membrane surface also has a great impact on fouling, as a rough surface will have a higher chance of becoming fouled while having the particles trapped in the crevices, and can than cause flux decline more severely than with a smooth surface (Al-Amoudi, 2010; Nicolaisen, 2002). Mi and Elimelech (2010) studied two different RO membrane materials, one was of polyamide and the other was cellulose acetate; it was found that the polyamide membrane had a higher initial fouling rate than the membrane made out of cellulose acetate, and they attributed to the fact that polyamide membrane had a rougher surface than cellulose acetate membrane.

It is also suggested by Mohammed et al. (2012) that membranes should be operated below the critical flux so as to cause less damage to the membrane, and increase its lifespan; critical flux is defined as the flux at which the membrane can be operated without causing IR fouling. A higher pressure operated system can result in a more firm, dense yet thin layer of fouling, compared to when lower pressure is used which can result in a soft, fluffy but thick layer as was observed by Mi and Elimelech (2010). They found that the recovery of the forward osmosis membrane was higher than that of the RO membrane after cleaning, due to the fact that the forward osmosis membrane used a lower operating pressure. Li et al. (2017) also suggested that operating membranes at a higher flux (ie. higher pressure) would result in a higher cake layer formation.

2.3.3.2 Temperature

Though much research has been done to the understanding of fouling, there is still much to learn (Jiang et al. 2017). The impact of temperature on the types of foulants and fouling of the membrane for temperatures ranging 5 to 32°C is presented in Table 2-2 along with the summary of the studies' findings.

Extracellular polymeric substances (EPS) are composed of polysaccharides, proteins, humic substances, nucleic acids, etc.; the most dominant components however are polysaccharides and proteins (Zheng et al. 2016). There are two forms of EPS that exist; one is bound, and the other soluble EPS, also known as soluble microbial product (SMP) (Sheng et al. 2010). EPS are believed to have a great influence on the properties of microbial aggregates as they are able to affect: surface charge, flocculation, settling ability of the sludge particles, and fouling (Sheng et al. 2010; Ma et al. 2013). EPS are the construction blocks for creating biofilms (Guo et al. 2012), the composition of biofilms is made of 15% cells and 85% EPS by volume (Ercan and Demirci, 2015), and the composition and quantity of EPS vary from species to species. Vu et al. (2009) along with Czaczyk and Myszka (2007), believe the purpose of EPS is to help with the attachment (act as a glue) of microorganisms (MO) to the surface of materials such as membranes, to help create the biofilm, and to act as a resistance or provide protection against threats that the environment possess to the MO, such a threat could be temperature change.

Several authors (Wang et al. 2009; Ma et al. 2013; Sun et al. 2014) have observed that as temperature of feed decreases the EPS, SMP, and polysaccharide concentration increases. With an increase in EPS and its correspondents this would cause a significant decrease in resistance and cause TMP to increase (Yu et al. 2014; Babel et al. 2002). Zhang et al. (2014) found

conflicting results, showing that as temperature decreased, the concentration of EPS decreased; however, for their study they used synthetic wastewater, while the other studies used municipal wastewater, which may have had different MO's, therefore, this may account for the different trend observed.

Zhang et al. (2014) observed that as temperature decreased, the sludge volume index (SVI) increased which would mean that less settle ability of the foulants occurred. This loss of settle ability could be caused by deflocculation which would cause a decrease in particle size of the foulants which was observed by Van den Brink et al. (2011). In addition, Van den Brink et al. (2011) found that after cleaning the membrane, recovery was lower when the membrane was used in colder temperature, which could be caused by the shift in foulant particle size, as there is a higher chance for pore narrowing/blocking to occur, which would cause IR fouling (Iorhemen et al. 2016; Hwang et al. 2008). A high SVI would mean that the membrane would be subjected to higher amount of foulants, therefore, the rate of TMP would increase, the rate of permeability loss would increase, as well as the frequency of cleaning the membrane would increase which was observed in numerous studies (Van den Brink et al. 2011; Ma et al. 2013; Sun et al. 2014; Zhang et al. 2014; Gurung et al. 2017).

Temperature of the feed impacts fouling in both a direct and indirect way. Temperature changes the size/morphology of the particles which can then change the type of fouling that occurs on the membrane. With temperature change, the pressure that is required to operate the membrane changes which could cause different types of compaction of the fouling layer, as is observed with the RO and forward osmosis membrane (Jin et al. 2009).

Table 2-2: Summary of impact of temperature on fouling on membranes

Type/material	Influent	T Operation (°C) and time	Summary	Reference
MF, Flat sheet, Polyether-sulfone	Municipal wastewater	5 to 32 (400 days)	<ul style="list-style-type: none"> • EPS= 140mgVS/gSS (18°C) • EPS=250mgVS/gSS (5°C) • Fouling rate higher at lower T 	(Wang et al. 2009)
MF, Flat sheet, PVDF	Municipal wastewater	15-7-15-25-15 (5hrs each)	<ul style="list-style-type: none"> • Low T required higher TMP • Particle size decreased at low T • No change between 15 and 25°C • No change for intrinsic membrane resistance (no data shown) 	(Van den Brink et al. 2011)
MF, HF, PVDF	Municipal wastewater	8.7 to 19.7 (3years)	<ul style="list-style-type: none"> • EPS=22.3 mg/gMLSS (9.2°C), 5.92mg/gMLSS (19.7°C) • SMP=28.1mg/gMLSS(8.7°C), 2.2mg/gMLSS (19.7°C) • Rate of TMP increase higher at low T 	(Ma et al. 2013)
UF, HF, PVDF	Wastewater treatment (China)	13 to 27 (12month)	<ul style="list-style-type: none"> • Polysaccharide decreased 15mg/L to less than 5mg/L (Spring to Summer), increased in winter • TMP higher at low T 	(Sun et al. 2014)
MF, HF, PVDF	Synthetic wastewater	22 (70 days) 13 (80 days)	<ul style="list-style-type: none"> • SVI = 102mL/gVSS • Cleaning every 30 days • EPS=18.5mg/gVSS • SVI= 146mL/gVSS • Cleaning every 15 days • EPS=15.3mg/gVSS 	(Zhang et al. 2014)
MF, Flat sheet, MF	Municipal wastewater (Finland)	7 to 20 (120days)	<ul style="list-style-type: none"> • Chemical cleaning performed when TMP reached 20kPa • TMP increased with decrease in T • 75% decrease in permeability when T <10°C (due to fouling) 	(Gurung et al. 2017)

Temperature=T

CHAPTER 3 MATERIALS AND METHODS

3.1 Chemicals and Membrane

In this study, sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) supplied by Anachemia (now owned by VWR) was used, and made into a 1% (w/w) $\text{Na}_2\text{S}_2\text{O}_5$ solution as a filtration solution to prevent potential biofilm growth. Deionized distilled water was used throughout this experiment. For this investigation virgin flat sheet membranes made out of PVDF with a pore size of $0.1\mu\text{m}$ (Dafu Membrane Technology Co., Ltd, Jiangsu, PRChina) were used.

3.2 Module

The module consists of: a plastic plate used to provide stability; two pieces of plastic mesh material to prevent the membrane from sticking to the surface of the plate; two pieces of flat sheet PVDF membrane with a total effective area of 0.03m^2 ; two rubber gaskets; two stainless steel frames along with nuts and bolts used to secure the membrane and the gasket to the plate.

3.3 Lab scale-set up

The schematic diagram of the experimental apparatus used in this study is shown in Figure 3-1. The holding tank holds both the 1% (w/w) $\text{Na}_2\text{S}_2\text{O}_5$ solution and the membrane module. $\text{Na}_2\text{S}_2\text{O}_5$ is used in this study to prevent any biofilm growth on the membrane for the duration of the three months filtration operation (Xu et al. 2010; Cui et al. 2017). The permeation was achieved by continuously pumping and recirculating the $\text{Na}_2\text{S}_2\text{O}_5$ solution by a MasterFlex C/L pump (Cole-Parmer, Montreal, Quebec), and the TMP is monitored by an analog Omega vacuum gauge (Omega, Korea). The permeate was then collected and measured using a

graduated cylinder in a predetermined time interval to ensure that the system is at steady and stable flux. The system was operated at a constant flux of 30LMH and monitored on a daily basis, where minor adjustments are made if necessary to maintain the desired flux. The temperature of the 1% (w/w) $\text{Na}_2\text{S}_2\text{O}_5$ solution was monitored daily to ensure that the temperature is held constant at 0.3°C (maintained by a well-controlled walk-in-cold room (Climate Testing Systems Inc., Warminster, PA)), and the TMP is measured from the pressure indicator.

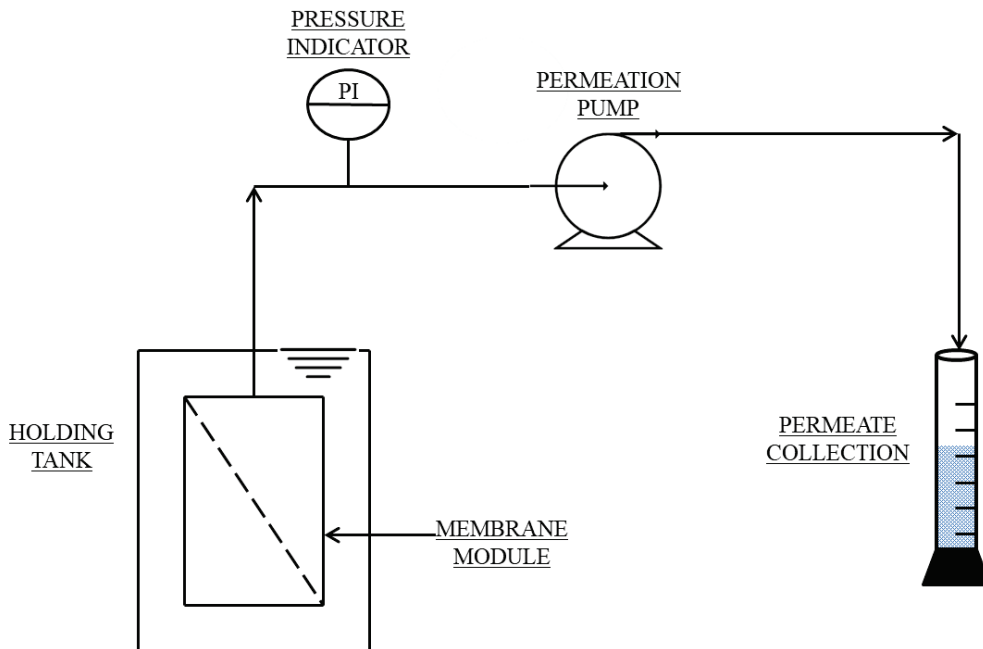


Figure 3-1: Simple schematic of the experimental apparatus

The following is the coding system applied for the membrane modules operated in a 1% (w/w) $\text{Na}_2\text{S}_2\text{O}_5$ solution for the duration of the three month filtration study.

- a) Every two weeks, after being operated at 30.0 ± 0.6 LMH in 0.3°C , the module was placed in $\sim 23^\circ\text{C}$ water for a six hour treatment (coded 0.3CT-23) and then the clean water flux

was determined. The module was placed back into the cold room (0.3°C) for continuous filtration immediately after the clean water flux measurement at room temperature.

- b) Every two weeks, after being operated at 30.0 ± 0.7 LMH in 0.3°C, the module was placed in 35°C water for a six hour treatment (coded 0.3CT-35) and then the clean water flux was determined. The module was placed back into the cold room (0.3°C) for continuous filtration immediately after the clean water flux measurement at room temperature.
- c) Module left in 0.3°C cold room, continuously operated at 30.0 ± 0.6 LMH, no treatment was conducted during three month operation (coded 0.3CT-NT).

Two pieces of membrane, named D and E, approximately 10cmx15cm each, were placed in 0.3°C 1% (w/w) $\text{Na}_2\text{S}_2\text{O}_5$ solution in the cold room with no filtration operation (0LMH). After every two weeks, membranes D and E were taken out of the 0.3°C $\text{Na}_2\text{S}_2\text{O}_5$ solution and placed into room temperature (23°C) and warm water temperature (35°C), respectively, for 6 and 24 hours pre-treatment. After 24 hours, membrane D and E were placed back into the cold room immediately.

All the membranes for the modules and membrane pieces were from the same roll of PVDF flat-sheet membrane. The initial clean water permeability of 0.3CT-23, 0.3CT-35, and 0.3CT-NT were 1015 ± 23 LMH/bar, 1007 ± 5 LMH/bar, and 1074 ± 4 LMH/bar at 20°C, respectively.

3.4 Permeability

Every two weeks, two of the modules (0.3CT-23 and 0.3CT-35) were taken out of the cold room then placed/treated in either ~23°C or 35°C water for a duration of six hours, while the third module (0.3CT-NT) having a flux of 30 LMH was kept in the cold room and operated continuously without room temperature and warm water treatment. The 35°C water was

maintained using a water bath. After six hours the clean water permeability of the modules was determined by using deionized distilled water at ~23°C. Once the permeability test was complete the two modules were immediately placed back into the cold room for another two weeks continuous filtration operation until the same treatment process is applied again; this will continue for the three month duration.

The permeability of the modules was determined using Equation (4), which is a modification of Cui et al. (2017) to be applied for a plate and frame module.

$$P = \frac{Q}{TMP \times A} = \frac{\frac{V}{t}}{TMP \times (2WH)} \quad (4)$$

where:

P=Specific permeability of the membrane (LMH/bar)

Q=flow rate of the permeate (L/h)

TMP=TMP (bar)

A= effective area of the membrane (m²)

V= volume of permeate collected (L)

t= elapsed time for permeate collection (hr)

W= width of the membrane (m)

H=height of the membrane (m)

The temperature of the deionized distilled water for clean water permeability determination varied from 21 to 25°C, therefore, to ensure consistency the permeability obtained was corrected using Equation (5) (Bogati, 2014) so that the permeability shown is at 20°C.

$$\text{permeability at } 20^{\circ}\text{C} = \text{permeability at } TC \times (1.0125)^{(20-TC)} \quad (5)$$

where

TC=the temperature of the water at which the permeability was taken at in Celsius.

When comparing the recovery of permeability of the membrane after being treated in ~23°C and 35°C deionized distilled water, normalized permeability is used, where the initial permeability (virgin membrane) at the beginning of the experiment is compared to that of the permeability of the modules after being subjected to cold temperature operation and treated, and is seen in Equation (6) (Cui et al. 2017).

$$\text{Normalized permeability} = \frac{P_i}{P_0} \quad (6)$$

where:

P_i =permeability of the module at 20°C after treatment (LMH/bar)

P_0 =initial permeability of module (virgin) at 20°C (LMH/bar)

3.5 Pore size distribution

After every two weeks, membrane pieces, D and E, were taken out of the 0.3°C Na₂S₂O₅ solution in the cold room and two 1cmx4cm segments were cut from each membrane immediately and put into liquid nitrogen for ten minutes for sample preparation for SEM images for PSD determination. Then the remaining membrane pieces D and E would then be placed into ~23°C and 35°C water, respectively, for six hours and 24 hour pre-treatment. One 1 cm x 4cm segment of membrane was cut from each membrane (D and E), after six hours and 24 hours pre-treatment, respectively, and put into liquid nitrogen for ten minutes. After completion of the 24 hours pre-treatment, remaining membranes D and E were immediately placed back into the 0.3°C 1%(w/w) Na₂S₂O₅ solution for another two weeks storage, and the same process was applied for the three month duration. The membrane segments (1cm x 4cm) after liquid nitrogen freezing were cut into two 1cm x 1cm samples. These 1cm x 1cm samples were placed onto a metal holder having carbon tape on it, and then a coating of carbon was sputtered on using sputter coater (Model 12560, Fullam, USA). These coated samples were placed under a scanning

electron microscope (SEM) (SU-70, Hitachi, Japan), and images of the surface of the membrane were taken at a magnification of 100k.

Two pieces of segments were prepared for each set of tests so as to have a replicate, and during SEM analysis, approximately eight images were taken for each piece of membrane segment (ie. 16 images in total for each test) for PSD. The images used to determine the PSD were randomly selected until 500 pores were measured for each set of tests. The software used to measure the pores of the membrane was ImageJ (Version 1.51p, National Institutes of Health, USA).

Similarly, at the end of the three month filtration operation, membrane samples were taken for SEM analysis. 0.3CT-23, 0.3CT-35 were taken out of the 0.3°C Na₂S₂O₅ and placed in ~23°C and 35°C water, respectively, for six hour treatment. The clean water permeability was then determined, and the modules were then placed back into ~23°C and 35°C water for an additional six hours conditioning to maintain the membrane structure at desired temperatures. After the six hour treatment, the same technique for preparing the SEM for membrane pieces D and E were applied for 0.3CT-23 and 0.3CT-35 module membrane samples; however, six segments were taken from each module (top, middle, and bottom). Six segments were also taken from 0.3CT-NT membrane module after permeation was halted for six hours in the 0.3° 1% (w/w) Na₂S₂O₅ solution. A piece of virgin membrane was also prepared for SEM so as to be able to compare any changes that may have occurred during the study.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Effect of 0.3°C temperature and recoverability

4.1.1 TMP, Permeability at 0.3°C, and Normalized Permeability

The variations in TMP of the three membrane modules operating in 0.3°C Na₂S₂O₅ solution is shown in Figure 4-1. The TMP steadily increased for 0.3CT-NT until it reached a plateau near the end of the experimental run (day 59) with an average TMP of 0.091±0.002bar. The average TMP before and after 23°C treatment for 0.3CT-23 were 0.067±0.003 bar, and 0.055±0.003 bar respectively. The average TMP before and after 35°C treatment for 0.3CT-35 were 0.059±0.003 bar and 0.048±0.004 bar respectively. The results suggested that membranes treated at 23°C and 35°C reduced TMP, as compared to that operating at 0.3°C with no treatment; and a higher treatment temperature (35°C) led to a further reduction in TMP.

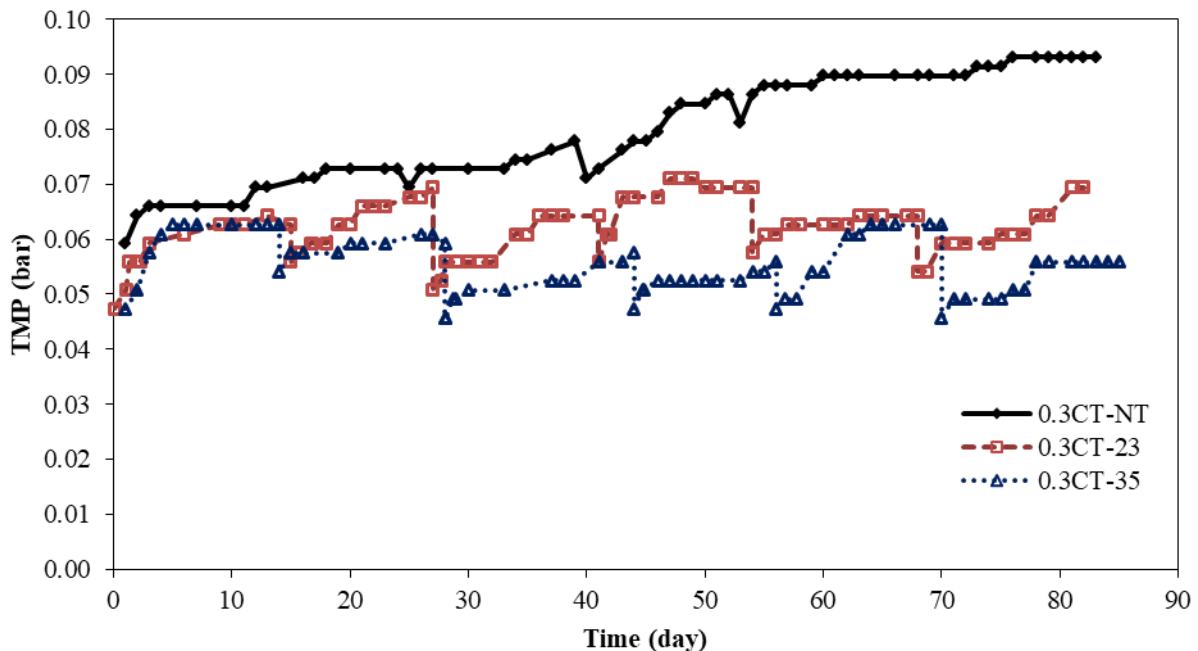


Figure 4-1: Variations of TMP of the membrane modules 0.3CT-NT, 0.3CT-23, and 0.3CT-35 during three month operation in 0.3°C 1% (w/w) Na₂S₂O₅ solution

The initial permeability of the membrane modules' at room temperature for 0.3CT-NT, 0.3CT-23, and 0.3CT-35 are 1074 ± 4 LMH/bar, 1015 ± 23 LMH/bar, and 1007 ± 5 LMH/bar, respectively. The change in permeability of the membrane modules operating in 0.3°C $\text{Na}_2\text{S}_2\text{O}_5$ solution is shown in Figure 4-2. The permeability of 0.3CT-NT slowly but steadily decreased during its duration in 0.3°C ; with an average permeability when it reaches a plateau at 59 days is 330.1 ± 11.8 LMH/bar. For the 0.3CT-23 and 0.3CT-35, after each treatment, a recovery of permeability was clearly observed; however, the permeability slowly decreased with time in the two weeks filtration but reached to a plateau value that was higher than that of the 0.3CT-NT module without treatment. The average permeability before and after 23°C treatment for 0.3CT-23 were 441.0 ± 15.3 LMH/bar, and 557.5 ± 29.8 LMH/bar, respectively. The average permeability before and after 35°C treatment for 0.3CT-35 were 501.3 ± 29.9 LMH/bar and 632.4 ± 57.3 LMH/bar, respectively. The higher treatment temperature (35°C) led to a higher recovery of permeability and maintained a higher operating permeability.

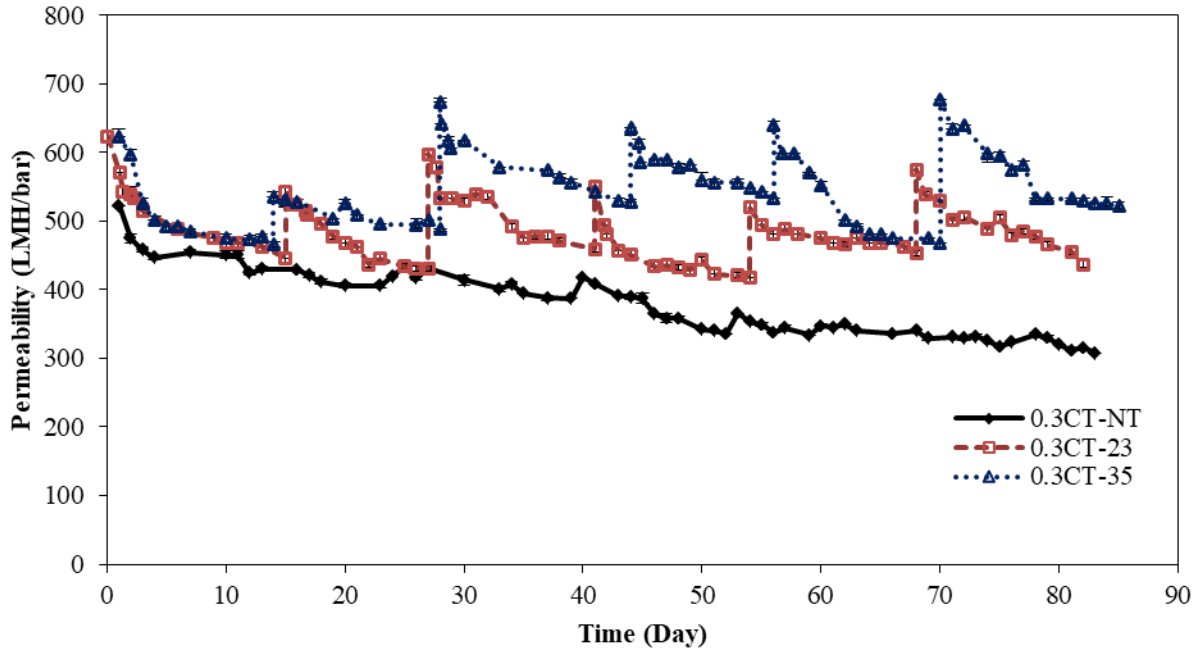


Figure 4-2: Membrane permeability of modules 0.3CT-NT, 0.3CT-23, 0.3CT-35 during three month operation at 0.3°C Na₂S₂O₅ (Results = average± standard deviation) (permeability at 0.3°C)

After being taken out of the 0.3°C Na₂S₂O₅ solution, 0.3CT-23 and 0.3CT-35 were treated with 23°C and 35°C deionized distilled water, respectively, for six hours after every two weeks operation in 0.3°C. The normalized permeability of 0.3CT-23 and 0.3CT-35 after being treated is shown in Figure 4-3. The permeability of 0.3CT-23 was never able to fully recover ($P_0=1015\pm 23$ LMH/bar), while 0.3CT-35 was completely recovered ($P_0=1007\pm 5$ LMH/bar).

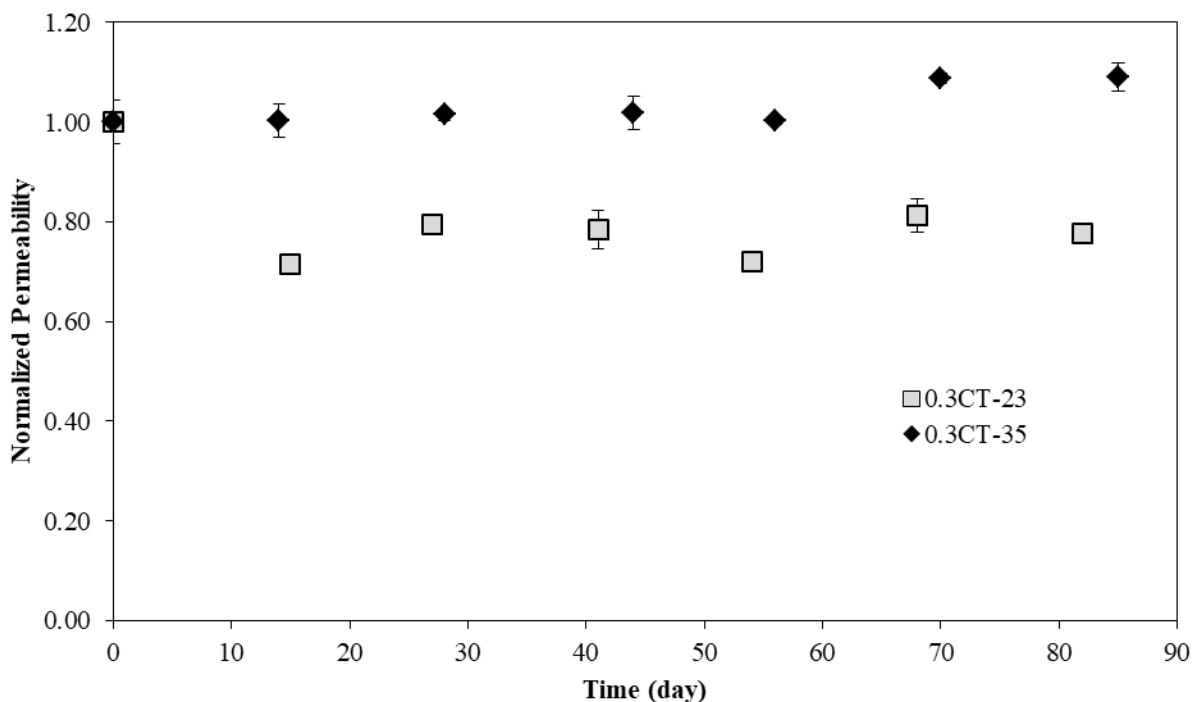


Figure 4-3: Normalized permeability (20°C) of 0.3CT-23, and 0.3CT-35 after treating for six hours at different treatment temperatures (the initial permeability of 0.3CT-23 and 0.3CT-35 were 1015±23LMH/bar and 1007±5 LMH/bar at 20°C, respectively) (Results = average± standard deviation)

4.1.2 Comparison of membrane pore size distribution of membranes conditioned at different temperatures and times

For membranes D and E, the PSD of the membrane after being pre-treated with ~23°C and 35°C water for zero (no treatment), six, and 24 hours, after every two weeks of being subjected to 0.3°C 1 (w/w)% Na₂S₂O₅ solution for a total of three months is shown in Figure 4-4 and Figure 4-5, respectively. On average the pore size has shifted towards a smaller size when the membrane was under cold temperature conditions, while after being pre-treated in warm water (23°C or 35°C), there appeared to be a higher frequency of the medium to large pores, implying there were more larger pores after pre-treatment. As compared to the results of the six hours pre-conditioning, a longer pre-treatment time (24 hours) led to a slightly higher frequency of large pores, although the difference might be small.

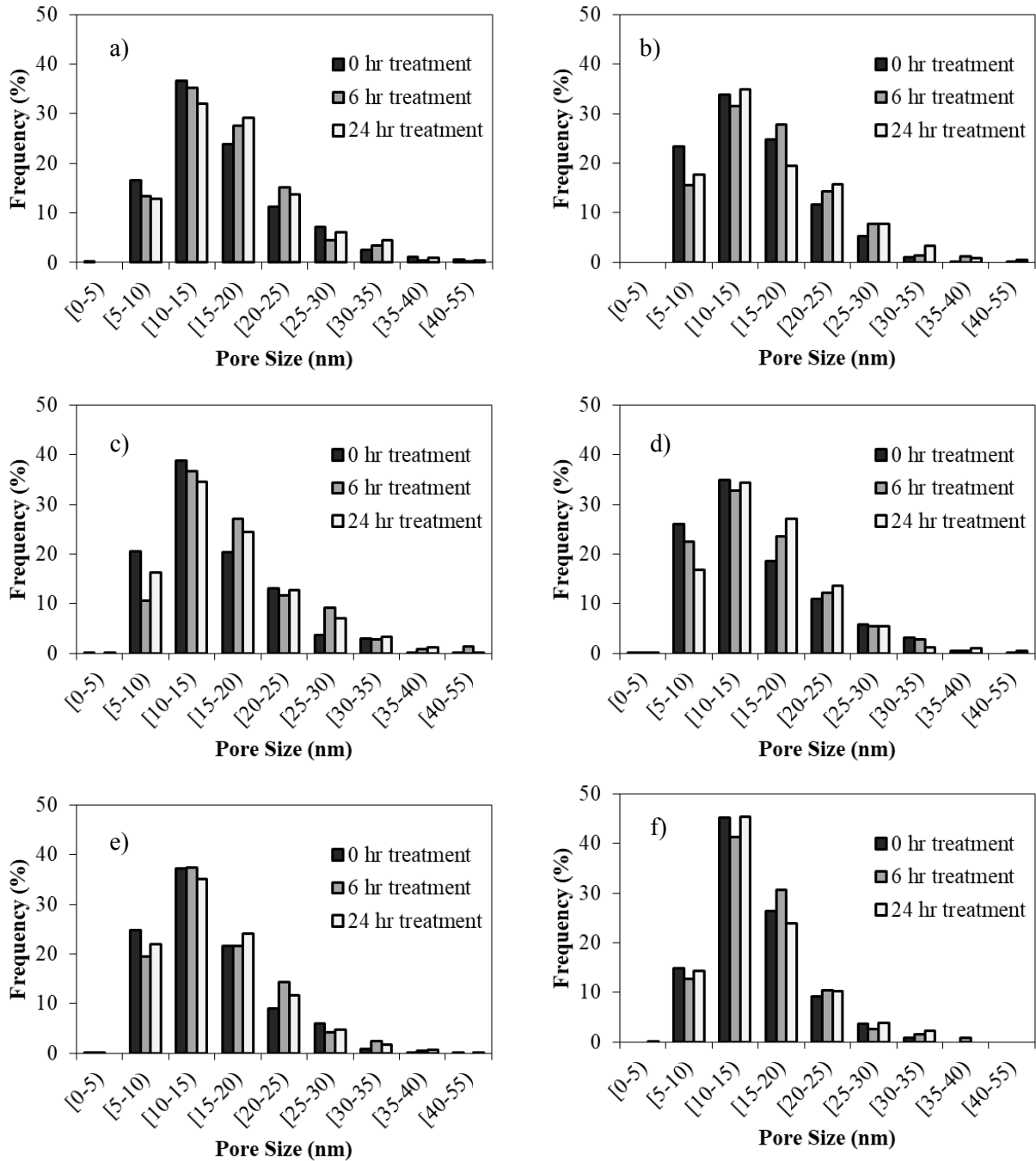


Figure 4-4: PSD of the membrane after being pre-treated at varying times (0, 6, and 24 hours) in 23°C water for different experiment times: a) 2 weeks b) 4 weeks c) 6 weeks d) 8 weeks e) 10 weeks f) 12 weeks

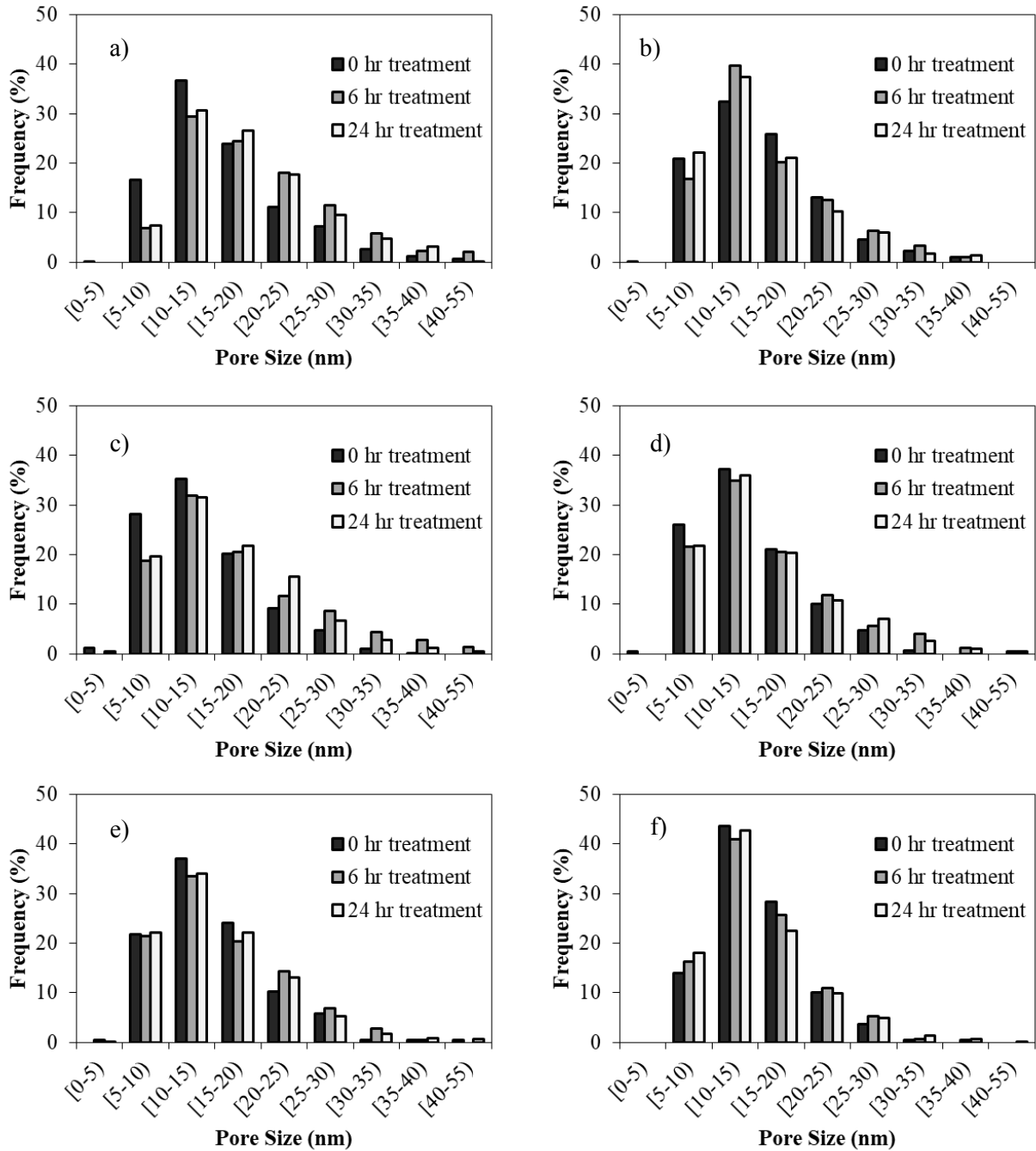


Figure 4-5: PSD of the membrane after being pre-treated at varying times (0, 6, and 24 hours) in 35°C water at different experiment times: a) 2 weeks b) 4 weeks c) 6 weeks d) 8 weeks e) 10 weeks f) 12 weeks

The effect of storage time (two, six, and ten weeks), pre-treatment water temperature (23 vs. 35°C), and pre-treatment time (6 and 24 hours) on membrane PSD is shown in Figure 4-6. When the membrane is pre-treated with 35°C water there is a higher frequency of larger pores

than that pre-treated with 23°C water. The difference between 23°C and 35°C pre-conditioning was reduced with an increase in pre-treatment time (at 24 hours). The difference between 23°C and 35°C pre-conditioning was reduced with an increase in pre-treatment time (at 24 hours), and with an increase of experimental time. The results suggested that pre-conditioning of the membrane at 23°C and 35°C could completely or almost completely reinstall the membrane structure (pore size) loss caused by extreme cold water temperature.

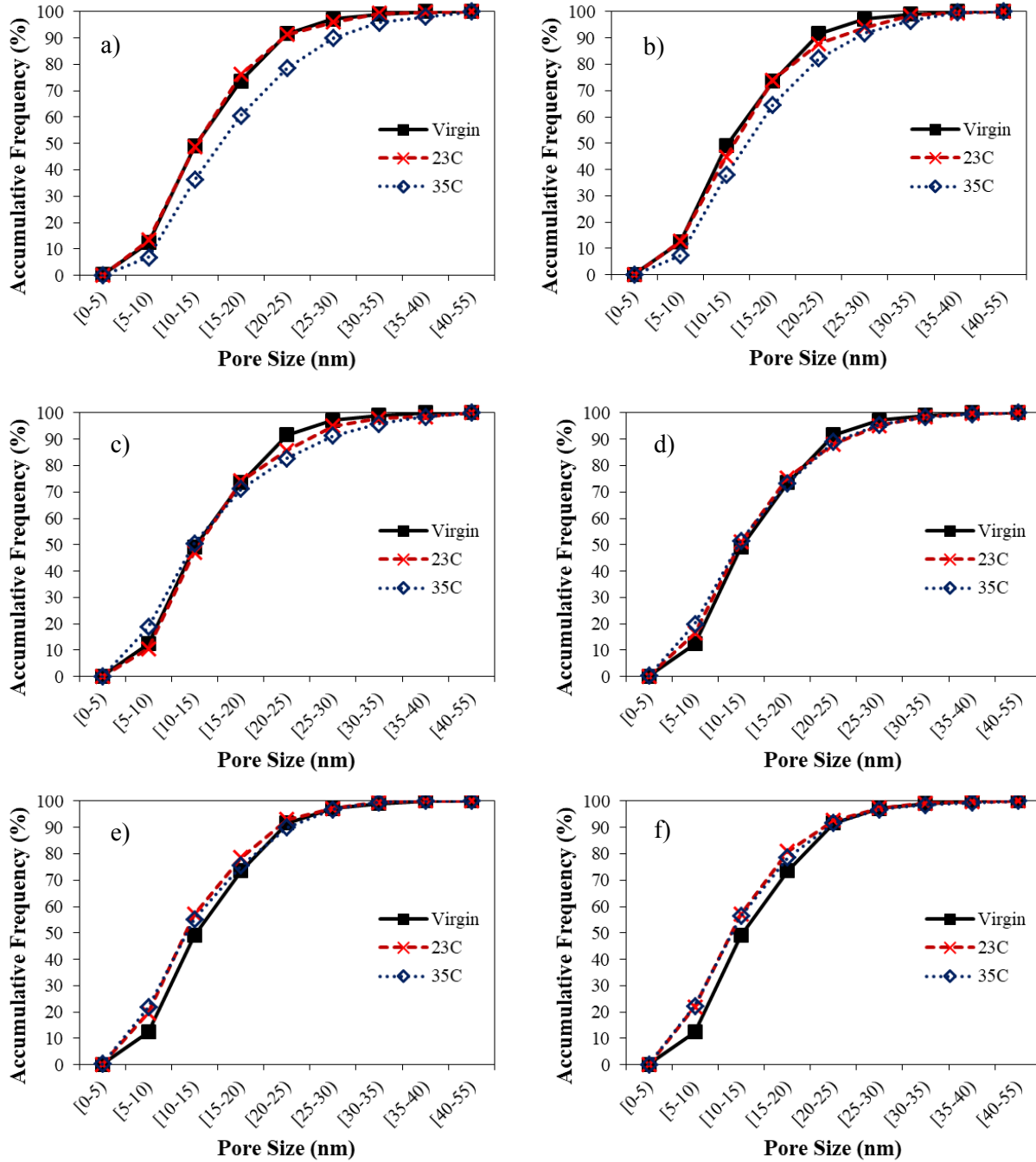


Figure 4-6: Effect of pre-treatment temperature and pre-treatment time on membrane PSD at different experimental times: [a] 2 weeks; c) 6 weeks; e) 10 weeks in 0.3°C 1% (w/w) $\text{Na}_2\text{S}_2\text{O}_5$ solution] 6 hour treatment; [b] 2 weeks; d) 6 weeks; f) 10 weeks in in 0.3°C 1% (w/w) $\text{Na}_2\text{S}_2\text{O}_5$ solution] 24 hour treatment

4.1.3 Comparison of membrane PSD of 0.3CT-23, 0.3CT-35, 0.3CT-NT at the end of filtration operation

The PSD of the virgin membrane, as well as membranes from the three membrane modules that were operated in the 0.3°C Na₂S₂O₅ solution at 30LMH for three months, are shown in Figure 4-7. 49% of the measured pores of the virgin membrane were below 15nm, while the membrane that had no treatment (0.3CT-NT) for the three month operation had a higher frequency (66.4%) of smaller pores below 15nm (or a smaller frequency (33.6%) of medium to large pores above 15nm) as compared to 0.3CT-23 (61% below 15nm, and 39% above 15nm), and 0.3CT-35 (54.2% below 15nm, and 45.8% above 15nm). Furthermore, there was a higher frequency of pores larger than 30 nm for module B (0.3CT-35) that was periodically treated at a higher temperature (35°C). The membrane PSD of module 0.3CT-35 was very similar to that of the virgin membrane. The changes in pore sizes can be better observed in Figure 4-8, which shows the plots of the accumulative frequency vs. pore size of the virgin membrane and membranes from the three modules after three month operation. The results clearly show that the use of the membrane module in cold temperature lead to a significant shrinkage of the membrane pores, while treating the membrane with elevated temperatures lead to reversibility (almost fully) to the original membrane pore size.

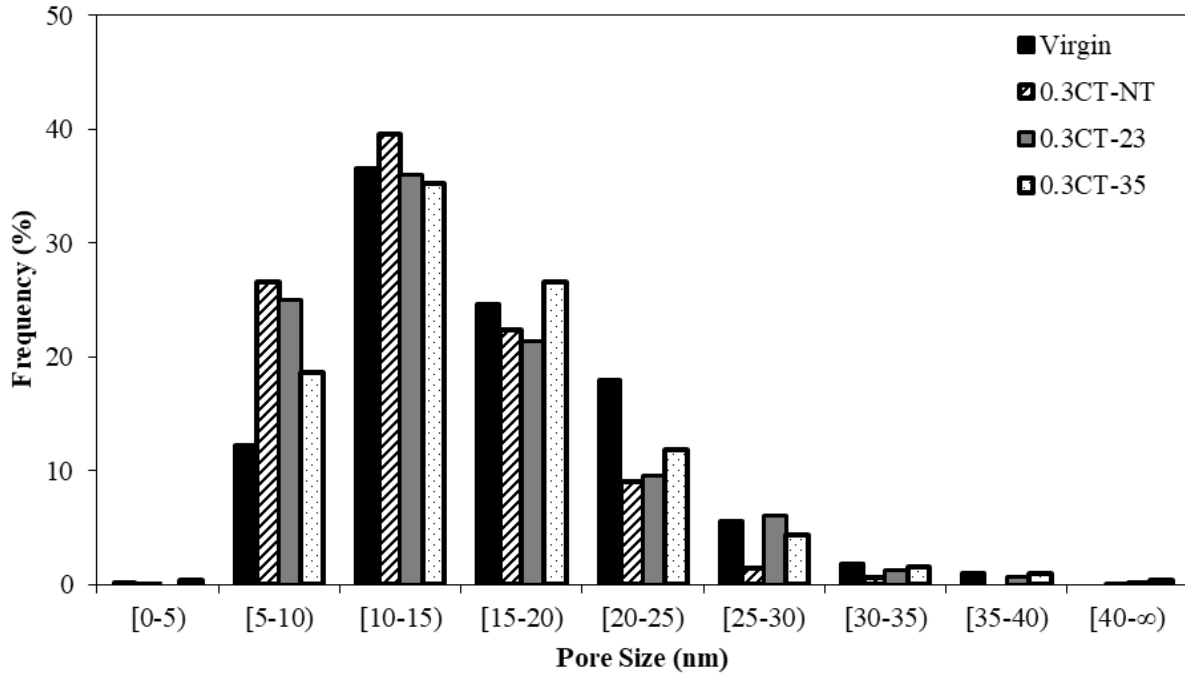


Figure 4-7: PSD of the virgin membrane and membranes from membrane modules (0.3CT-NT, 0.3CT-23, and 0.3CT-35) (treated for six hours for 0.3CT-23 and 0.3CT-35) after three month operation in 0.3°C 1(w/w)% Na₂S₂O₅ solution

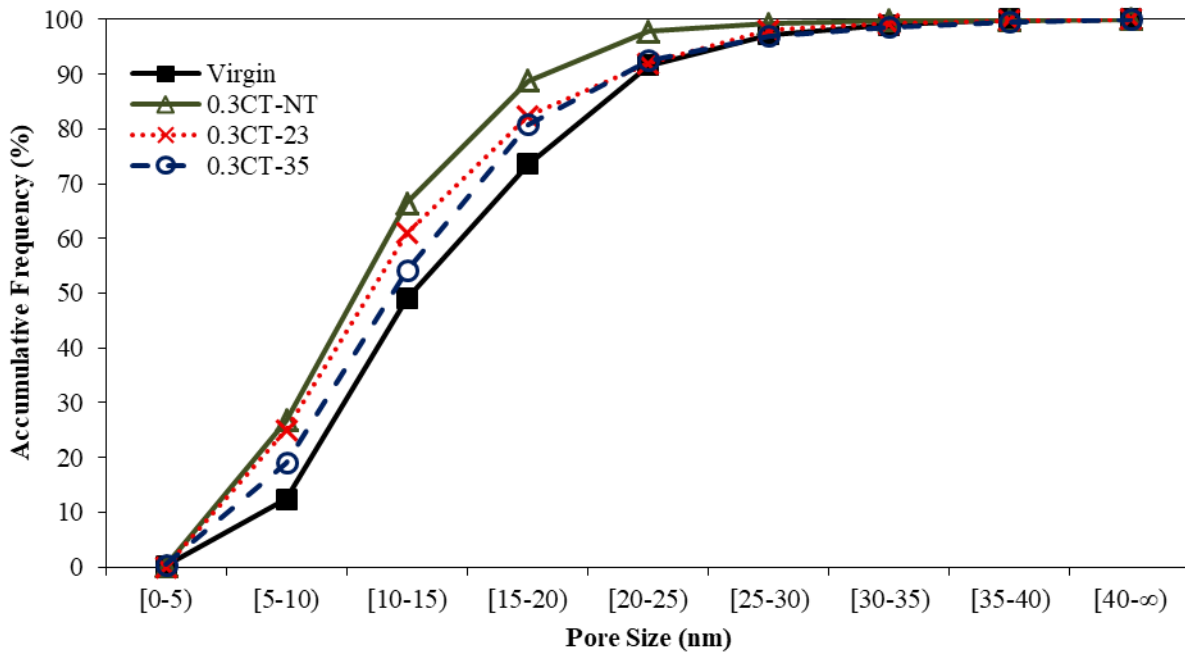


Figure 4-8: PSD (accumulative frequency) of the virgin membrane and membranes from modules (0.3CT-NT, 0.3C-23, and 0.3CT-35) (pre-treated for six hours for 0.3CT-23 and 0.3CT-35) after three month operation in 0.3°C 1(w/w)% Na₂S₂O₅ solution.

4.2 Discussion

This study shows that the membrane performance and pore size after being subjected to an extreme cold temperature of 0.3°C can be recovered, almost fully or fully, through treating the membrane every two weeks with ~23°C and 35°C water conditioning or chemical cleaning in drinking water treatment plants for six hours. The 35°C water provided a full recovery of the performance of the membrane permeability, while the ~23°C treatment provided partial recovery; it was never able to reach full restoration at room temperature which Cui et al. (2017) also observed.

The increase in TMP for the membrane modules while in the cold water temperature could be explained by the fact that the pore size decreased. With the decrease in pore size, the resistance of the membrane would increase, and to maintain the desired flux of 30LMH, the pressure that is applied to the module must increase (AWWA, 2006). The initial permeability drop observed was understandable since the viscosity of the liquid was higher in colder temperature than room temperature, however, because the cold temperature was held constant the viscosity would have also been constant, therefore, the resistance of the membrane might have increased during its time in the cold room. This increase in resistance could be attributed to the pore size shrinkage (Bert, 1969), and therefore, the pressure would have had to increase to maintain the desired flux, causing permeability loss.

Another potential reason for the permeability decline in the cold temperature, could be because the $\text{Na}_2\text{S}_2\text{O}_5$ has the potential of precipitating on the surface of the membrane, which could cause pore blocking, and therefore, lead to a decline in permeability (Shi et al. 2014). When the membrane modules 0.3CT-23 and 0.3CT-35 were taken out of the 0.3°C $\text{Na}_2\text{S}_2\text{O}_5$ solution and placed in ~23°C and 35°C water for conditioning, respectively, the $\text{Na}_2\text{S}_2\text{O}_5$

precipitates in extreme cold temperature could have dissolved, and therefore, would be removed from the membrane, since the solubility of $\text{Na}_2\text{S}_2\text{O}_5$ is 36% (w/w) in water at 16°C (Anachemia, 2012); however, as seen in Cui et al. (2017) study, a very small amount but not significant precipitation of $\text{Na}_2\text{S}_2\text{O}_5$ did occur during the membranes time in the solution at 0.3°C.

The recovery of the permeability of the membrane modules could also be explained because the pore size recovered partially or fully back to its original size after being pre-treated in 23°C and 35°C water. An increase in pore size at elevated temperatures was also found through Sharma and Chellam (2005) study on flat sheet polyamide NF with the use of a hydrodynamic transport model. Using a hindrance transport model Dang et al. (2014) found that when the temperature changed from 20 to 40°C the pore radius of the polyamide NF membrane increased from 0.39 to 0.44nm.

As the storage time at which the membrane was subjected to cold temperature increased, the impact of the pre-treatment methods (pre-treatment temperature and time) on the recovery of the pore size became less noticeable. This implies that after a certain time of exposure to cold temperature, no pre-treatment method could be able to recover the membrane structure, the membrane was permanently damaged.

As compared to the virgin membranes, the small increase in the smaller range for 0.3CT-35 (Figure 4-7 and Figure 4-8) could be related to the mechanical stress caused by continuous vacuum filtration. This effect could be compensated by backpulse during maintenance cleaning in full-scale drinking water membrane filtration plants. Therefore, the combination of periodical warm chemical cleaning and in-situ maintenance cleaning plus backpulse could achieve a full reinstatement of membrane permeability and structure loss caused by extreme cold water temperature in cold regions.

Another interesting finding was that the time in which the membrane was placed in the ~23°C or 35°C water for pre-treatment, six or 24hours, did not seem to impact the pore size significantly; therefore, it would be worth studying what the minimum time needed to recover the membrane performance and pore sizes. The selection of six hours pre-treatment is based on the fact that a six hour chemical cleaning has been used in a number of drinking water membrane filtration plants.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study investigated the effects of membrane treatment temperature and time on the recovery of membrane permeability and structure loss caused by cold water temperature of 0.3°C. The main conclusions are summarized below:

1. Extreme cold water temperature (0.3°C) led to the large deterioration of PVDF membranes' performance and structure (pore size shrinkage).
2. Periodically membrane treatment at room temperature (about 23°C) or warm temperature (35°C) significantly recovered the PVDF membranes' permeability and structure (pore size) lost by cold water temperature.
3. A higher treatment temperature (35°C) led to a better recovery of PVDF membranes' permeability and structure.
4. A longer pre-treatment time (24 hours) led to a slightly better recovery of PVDF membrane structure, as compared to that of six hours pre-treatment.
5. Structure change of PVDF membrane caused by extreme cold water temperature was fully or almost fully reversible after treatment at 35°C.

5.2 Recommendations

1. Chemical cleaning of membrane by using warm cleaning solution is recommended for drinking water and wastewater membrane filtration plants operated in cold regions.
2. Membrane material is very important parameter to take into account when determining the impact that a certain factor will have, and not all material may react in the same manner that the PVDF membrane material did when subjected to the cold temperature and the treatment method. Therefore, other membrane materials should be analyzed with the given treatment method (warm water temperature) to determine if this method is suitable for all membrane materials.
3. It would be of interest to potentially have designed a material for a membrane that is able to resist the extreme cold temperature in cold regions without having it undergo structural changes.
4. There are other factors that temperature may have an impact on, such as tortuosity of the membrane which would impact the resistance of the membrane, which could be studied to determine the impact that cold temperature has on it, as well as the treatment methods.
5. The temperature of the treatment water could also be investigated further, to determine how higher temperatures would impact the recovery of the membrane, and with that determining the minimum time in which the treatment needs to happen to restore the membranes' performance and structure.
6. Under extreme cold temperature the membrane may become brittle, therefore, mechanical treatment should be performed to re-create cleaning treatment seen in

industry (such as backpulsing) to determine if the membrane would break under extreme cold temperature.

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APPENDIX: A

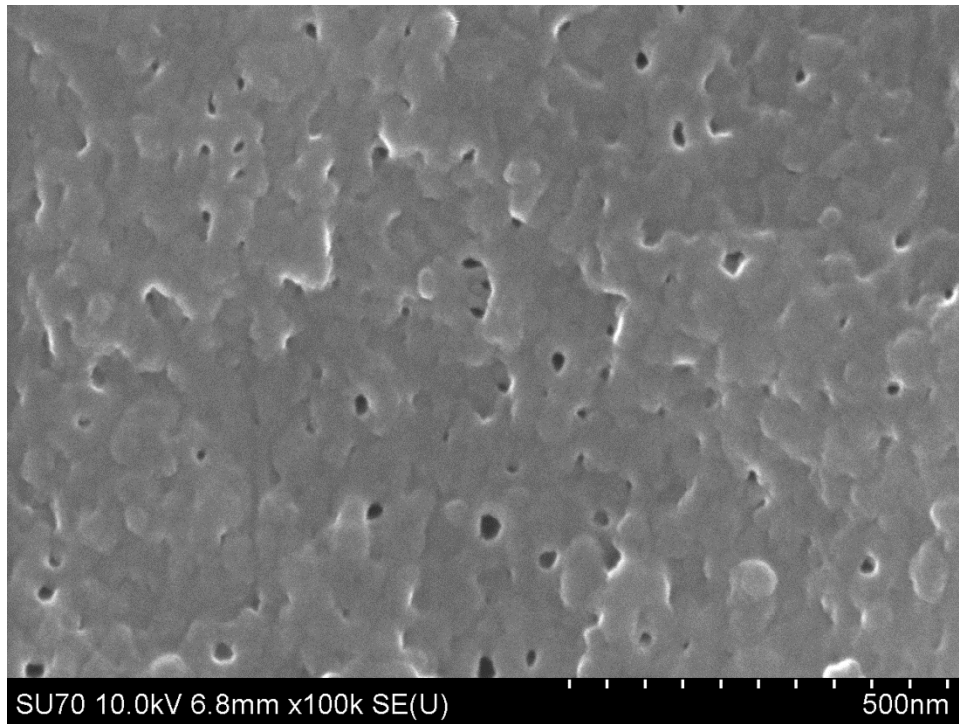


Figure A-1: SEM of virgin membrane

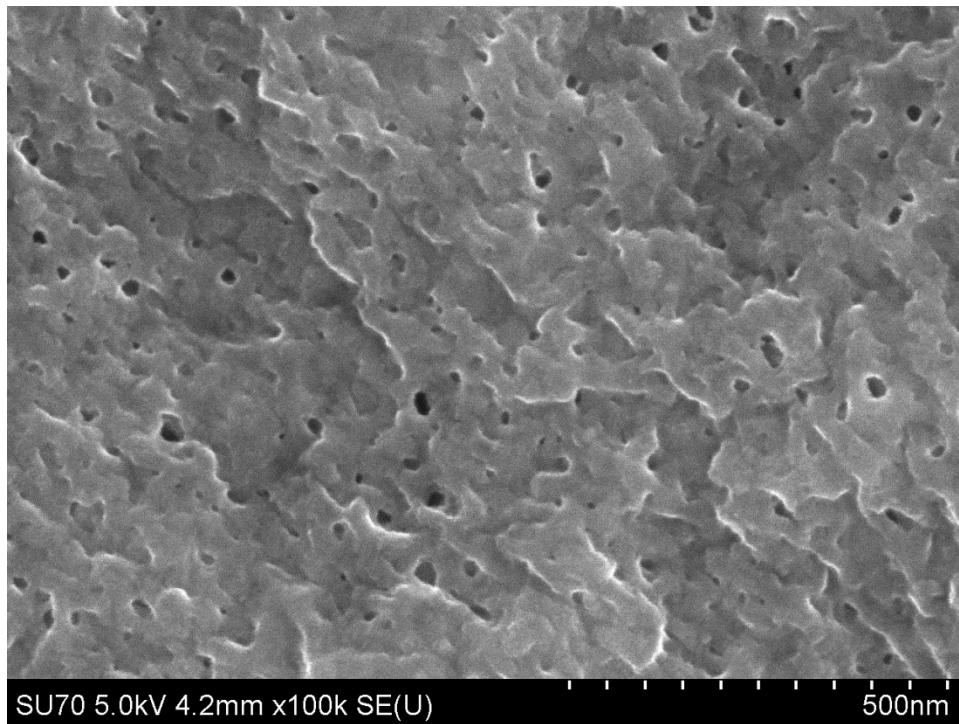


Figure A-2: SEM of module 0.3CT-NT (after three month operation in 1% (w/w) $\text{Na}_2\text{S}_2\text{O}_5$)

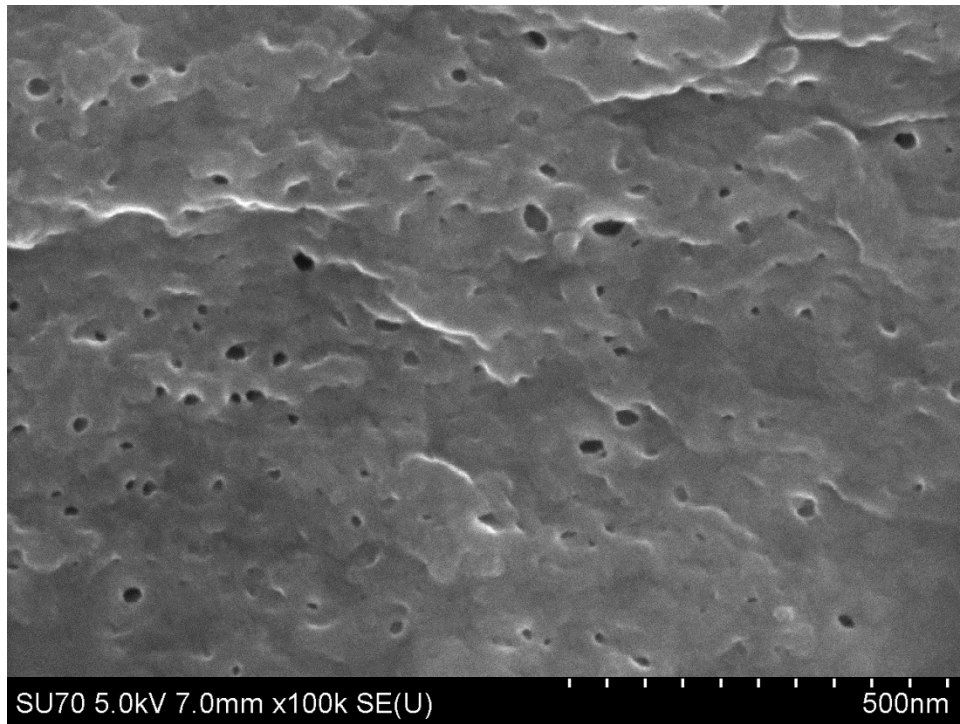


Figure A-3 SEM of module 0.3CT-23 (after being pre-treated at 23°C after three month operation in 1% (w/w) $\text{Na}_2\text{S}_2\text{O}_5$)

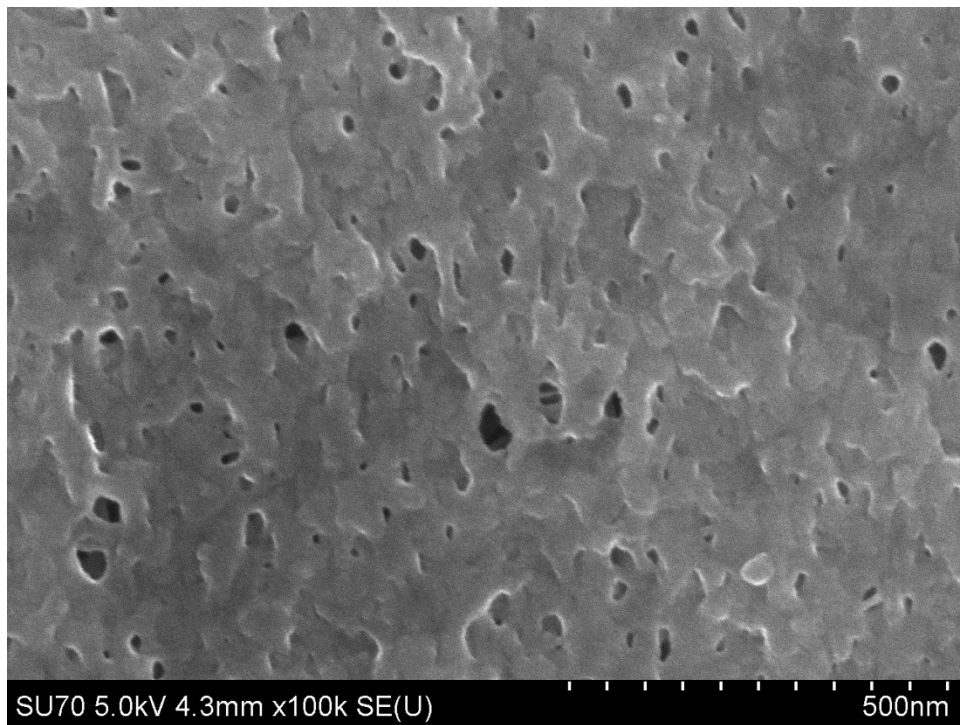


Figure A-4: SEM of module 0.3CT-35 (after being pre-treated at 35°C after three month operation in 1% (w/w) $\text{Na}_2\text{S}_2\text{O}_5$)