

Triple-Layer Hydrophilic-Hydrophobic Composite Membrane for Desalination using Direct-Contact Membrane Distillation

A Major Qualifying Project
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Abstract

The world is more technologically developed than ever, yet a tenth of it still suffers from a lack of clean water. Scientists all over the world are striving to develop innovative technologies to make water purification cheaper and accessible to everyone. In the promising field of direct contact membrane distillation, a chemist in China has developed a new type of membrane. By adding a hydrophilic layer to the permeate side of the hydrophobic membrane, hopes are that the flux will be increased. The membrane was tested for flux and rejection rate while process variables were manipulated; it was also compared to the simpler single-layer membrane made using the same materials. Unfortunately, the first version of this membrane was not able to purify water as well as a normal membrane, underperforming in flux, durability, as well as replicability of fabrication. The membrane fabrication process must be further refined to see any success in the distillation field. One recommendation could be making the support layer smoother and thinner to increase flux while making the hydrophobic layer slightly thicker to increase mechanical strength.

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Introduction

Seven and half billion people live on this vast planet; through fascinating discoveries in medicine and technology, that number will likely grow much higher. Yet with amazing advances made every day, millions of people are still suffering. Almost 800 million people, about 10.4 percent of the world, do not have access to clean water; an even larger 2.5 billion people, or a third of this planet, do not have access to adequate sanitation.¹ These problems cause millions of deaths a year and cause much suffering. With recent trends in increased water consumption worldwide, the suffering is only projected to grow further. With technology being more advanced than it has ever been, this shouldn't be a problem.

Unfortunately, the process of purifying water to a level where it's acceptable for human use and consumption is a much harder task than it seems. One easy way to clean water is to boil it, but it is more complicated than that on a global scale. Eighty-five percent of people live on the driest half of the planet.² The closest source of freshwater in a small village in the dry continent of Africa may be miles away and one person can barely carry enough water for themselves, let alone a village. If too many people are tasked with carrying water, that's leaves less people to find and make food for the village; these people must choose between drinking and being able to eat. In urban areas of the world, even if built next to sources of water, the problem is different, yet equally complicated. In places such as China and India, where the population in urban areas can be staggering, the infrastructure and cost of pumping, treating, and discharge water can be extensive. The more water, the more complicated facilities are needed, and the more expensive the task becomes. Even in large cities, the people sometimes simply lack the money and power needed to generate that much clean water.

Even with the world being as technologically advanced as it is, there still isn't an easy way to purify large amounts of water without being astronomically expensive. There are countless ways to clean water, but all have their own set of problems. The normal ways, such as distillation, take time and a large amount of energy. The use of chemicals such as iodine or chlorine are usually expensive or cause the water to be toxic in a different way. Filtration, while

¹ United Nation. "Facts and Figures." 2013. United Nations Educational, Scientific, and Cultural Organization, 2013. Web. 11 Nov. 2016.

² *ibid.*

good at removing minerals and salts, is not as successful at removing chemicals and bacteria. While many of these options are already used around the world, they are usually only used in developed countries that can afford the expensive alternative. Recently, scientists around the world have been looking for ways to make water purification easier and less expensive.

One technology that has recently stood out among the rest is membrane distillation (MD). A branch of classic distillation, instead of just vaporizing water and condensing the vapors, a membrane is created which only water vapor can pass through. This process requires less energy and smaller equipment; it can turn out to be much cheaper than its alternatives. However, with membrane technology only recently becoming cost-efficient, the technology is relatively new and much more research is needed to perfect the process. At Shanghai Jiao Tong University, graduate student Jun Li has improved on a new type of membrane that could work extremely well for desalination processes. The goal of this Major Qualifying Project (MQP) was to run tests with a direct contact membrane distillation (DCMD) setup to optimize this new membrane and find out if it was competitive with current technologies. First, it had to be determined if the new membrane could attain a higher flux as well as last longer than a normal membrane. If successful, recommendations would be made to make the membrane better. If unsuccessful, recommendations would be made to increase flux and mechanical strength.

Background

Before the membrane could be tested, it was important to understand the ins and outs of membrane distillation. Compared to other purifying technologies, MD is a very new science, being introduced at the end of the '60s, conceived as an idea for a process that can use less energy and take up less space than its competitors.³ The process involves a membrane with a feed and permeate on either side; the only thing that can pass through is the vapors caused by the pressure difference across the membrane. Figure 1 below shows a rudimentary visual of this process.

³ Camacho, Lucy Mar, Ludovic Dumeé, Jianhua Zhang, Jun-de Li, Mikel Duke, Juan Gomez, and Stephen Gray. "Advances in Membrane Distillation for Water Desalination and Purification Applications." Review. *Water* 2013: 94-196. MDPI. Web. 15 Nov. 2016.

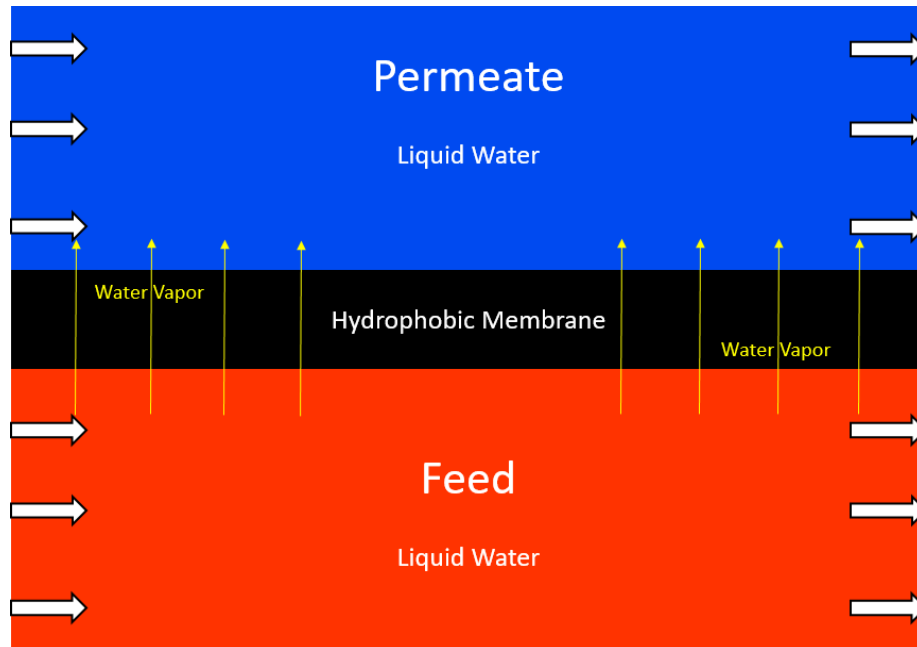


Figure 1: The basics of direct contact membrane distillation for desalination.

The expensive cost of membranes made MD economically unfavorably when compared to the leading process at the time, reverse osmosis (RO).⁴ It wasn't until the 80's, when more research that allowed for better and cheaper membranes was completed, that MD became universally recognized as a probable solution to the water filtration problem. In 1986, several characteristics were defined that a MD process must have:

- the membrane must be porous, so that vapor may pass through it,
- the membrane must not be wetted by the process liquids; in the case of desalination, it should be hydrophobic,
- capillary condensation should not be allowed to take place in the pores of the membrane,
- the membrane cannot alter vapor equilibrium of the fluids in the process,
- one side of the membrane must touch the process fluids,
- and for each component of the process liquid, the driving force is a partial pressure gradient in the vapor phase.⁵

⁴ *ibid.*

⁵ Smolders, K., and A.c.m. Franken. "Terminology for Membrane Distillation." *Desalination* 72.3 (1989): 249-62. Web. 15 Nov. 2016.

From further research into the subject, MD was found to be a great alternative to conventional forms of distillation; due to the large pore volume in the membrane, the large amount of vapor space required in normal distillation is greatly reduced.⁶ This allows for a smaller column, leading to lower equipment costs and less heat lost to the environment. Another benefit to MD is its lower requirement of operating temperatures since it is not necessary to heat the process stream higher than its boiling point as needed in classic distillation.⁷ Feed temperatures generally range from 60 to 90 degrees Celsius, but have been used at as low as 30 degrees.⁸ These lower temperatures and the more adiabatic column allow for much less money to be spent on heating utilities. In fact, the energy requirement is so much lower, alternative sources of heating, such as geothermal or solar energy, can be used in place of normal heating methods to create an even cheaper distillation process.⁹ A cheap process that can use alternative energies makes it even more attainable for people in developing and underdeveloped countries that desperately need this technology. These differences make MD not only more affordable than RO, but safer as well. Since MD is thermally driven, it generally runs at low to atmospheric pressures, which is much lower than processes that are pressure driven and require high pressures to operate such as RO.¹⁰ These low pressures also require less mechanical strength from the membrane, allowing for different materials to be used. The process of MD is based on the principles of vapor-liquid equilibrium; this allows for 100% theoretical separation, and a lowered chance of membrane fouling due to the larger pore size that are designed to support the vapor-liquid interface.¹¹

In practice, there are four main types of MD: direct-contact, air-gap, vacuum, and sweeping gas. DCMD is the simplest, most used type of MD; in this configuration, the membrane is in direct contact with both the feed and the permeate. This allows for high flux and is best suited for processes such as desalination.¹² Air-gap (in which only one process stream is touching the membrane), conversely, is the most energy efficient but suffers from low flux.¹³

⁶ Lawson, Kevin W., and Douglas R. Lloyd. "Membrane Distillation." Review. *Journal of Membrane Science* 124 (1997): 125.

⁷ *ibid.*

⁸ *ibid.*

⁹ *ibid.*

¹⁰ *ibid.*

¹¹ *ibid.*

¹² Camacho, Lucy Mar, Ludovic Dumeé, Jianhua Zhang, Jun-de Li, Mikel Duke, Juan Gomez, and Stephen Gray. "Advances in Membrane Distillation for Water Desalination and Purification Applications."

¹³ *ibid.*

Vacuum and sweeping gas are ideal for removing volatiles from aqueous solutions.¹⁴ In this project, only the DCMD style was used for testing the membrane.

DCMD is the simplest MD process. Due to the pressure difference on either side of the membrane, the evaporation that occurs on the surface of the membrane pushes the vapor to the permeate side where it condenses.¹⁵ Since the membrane is hydrophobic in nature, the feed itself cannot pass through the membrane, only the vapor molecules can exist within the pores of the membrane. While it is an extremely efficient process, the only drawback is the heat lost due to conduction.¹⁶

There are many properties that make a membrane good for distillation. In this process, two of the more important properties will be evaluated. One of the properties is the amount of flux, or amount of vapor that can pass through the membrane. Flux is proportional to the vapor pressure difference across the membrane. So, theoretically, this can be related to the temperature difference across the membrane, since vapor pressure is proportional to temperature. The higher flux in a desalination process, the more pure-water product gets made. The second big property is rejection rate. A perfect membrane has a theoretical rejection rate of 100% because of the laws of vapor-liquid equilibrium. However, no membrane is mechanically perfect. Membranes will develop small leaks in their creation, and they will foul over time, creating, and enlarging more leaks. If the membrane continues to purify water within the product specifications, it will still be considered a good membrane. Flux and rejection rate are both related to the composition and creation of the membrane. To correctly analyze the distillation process, it is important to know what the process membrane is made of and how it is created.

In this project, the membrane will consist of three layers: a hydrophobic bottom layer, a hydrophilic top layer, and a mechanically strong middle layer. Figure 2 below shows a visual of how this membrane is used.

¹⁴ *ibid.*

¹⁵ Alkhudhiri, Abdullah, Naif Darwish, and Nidal Hilal. "Membrane Distillation: A Comprehensive Review." *Review. Desalination* 287 (2012): 2-18. Elsevier. Web. 20 Nov. 2016.

¹⁶ *ibid.*

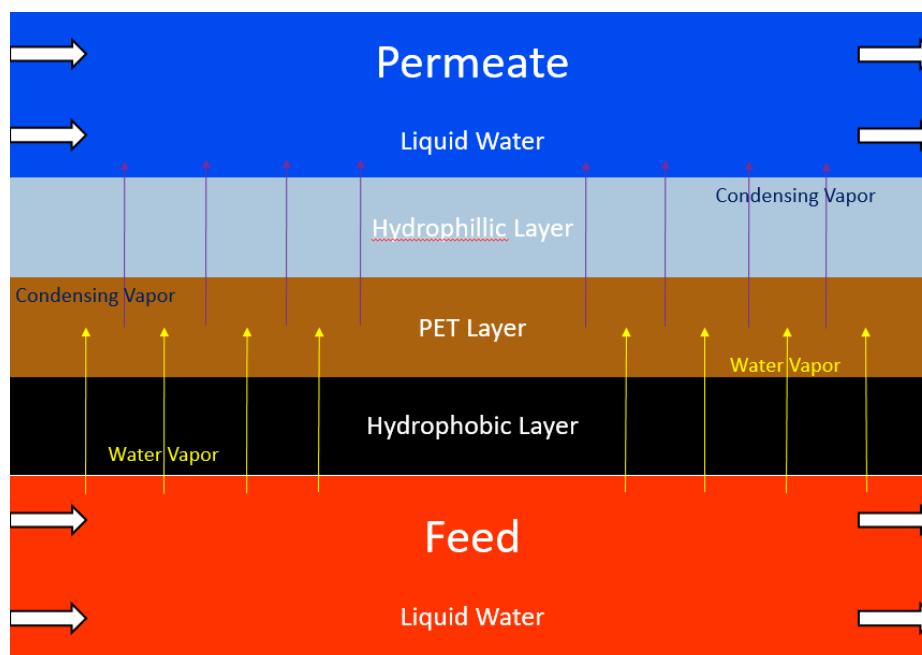


Figure 2: A visual of the triple-layer membrane created at SJTU.

The hydrophobic layer was created first. To make a membrane that is hydrophobic while having a low resistance to mass transfer and a low thermal conductivity, special materials must be used. Two of the most common materials that share these properties are PTFE, or polytetrafluoroethylene, and PVDF, or polyvinylidene fluoride.¹⁷ PTFE is more commonly known as Teflon, the chemical on frying pans that has proven itself to be extremely hydrophobic in its ability to prevent foods from sticking as well as being highly resistant to extreme temperatures. These two properties make it very favorable to MD. PVDF, which is less commonly known, shares similar characteristics; it has a low thermal conductivity, a low permeability to most liquids, a high mechanical strength, and a resistance against harsh thermal conditions.¹⁸ For this membrane, PVDF was used with PTFE as an additive to increase hydrophobicity. These materials allow for the layer to maintain good contact with and have a high permeability for the water vapor in the DCMD process.

This layer was created by electrospinning a dope solution onto the middle layer made of PET (Polyethylene terephthalate, more commonly known as polyester) micro-nonwoven mats; a material commonly used in the electrospinning process. This middle layer's goal is to add

¹⁷ *ibid.*

¹⁸ Porex Filtration Group. "Polyvinylidene Fluoride (PVDF)." Porex. Porex Corporation, n.d. Web.

mechanical strength to the thin membrane. This two-layer membrane was heat-pressed at 160°C, which is near the melting point of PVDF. On the reverse side of this layer, the hydrophilic layer is electrospun. This bottom layer was created using mainly two chemicals, Chitosan, created from the naturally occurring polymer chitin, and polyethylene oxide, or PEO. This layer is hydrophilic in nature; this draws water vapor from the middle layer by absorption which also reduces the heat commonly lost due to conduction in the DCMD style of MD. This layer is then cross-linked with a glutaraldehyde solution before being pressed at a temperature of 60 °C, close to the melting point of PEO. Heat-pressing the membrane at temperatures close to the melting points of the materials helps fuse the fibers together.

Since the one of the most significant parameters of a membrane's success is its pore size, the process of electrospinning is extremely important. Pores too big will allow salt to pass through, and pores too small will greatly inhibit mass transfer of water vapors. Electrospinning allows for the creation of specified pore sizes with a high degree of accuracy. The process starts with a charged polymer, or dope solution. The electrospinning parameters and properties of the dope solution are the two main factors in creating specific pore size and shape in the membrane.¹⁹ The formation of the Nano-fibers is caused by the repulsive electrostatic forces, or more specifically, Coulomb interactions, being emitted by the process.²⁰ The dope solution is ejected from a small diameter needle above a spinning collector drum. The Coulomb interactions cause the formation of a Taylor cone at the tip of the needle; this results in a very thin jet of solution leaving the needle. As further thinning occurs, the solvent in the dope solution evaporates, leaving only the polymer fibers to fall onto the collection drum below.²¹ In the creation of this specific membrane, several different solution concentrations were used. This is because at too low of a concentration, the dope solution will not form fibers, but instead will be reduced to particles and 'electrospraying' will occur. The opposite of this, when solution concentration is too high, will result in fiber length being too long.²²

¹⁹ Ahmed, Farah Ejaz, Boor Singh Lalia, and Raed Hashaikeh. "A Review on Electrospinning for Membrane Fabrication: Challenges and Applications." Review. Desalination 356 (2015): 15-30. Elsevier. Web. 4 Oct.

²⁰ *ibid.*

²¹ *ibid.*

²² *ibid.*

Literature Review

In a classic membrane distillation setup, there is a single-layer hydrophobic (when processing water) membrane. Throughout the years since the invention of the process, experts have tried countless different ways to create membranes. Literature can be found for double layer membranes, triple-layer membranes, as well as several ways to create them. This array of research helped develop the membrane used in this project.

One idea that this project uses is adding a hydrophilic sublayer to the membrane. The dual-layer version of this was patented in 1982 by Cheng and Wiersma.²³ One paper from the University of Ottawa titled "Nanofiber Based Triple-layer Hydro-philic/-phobic Membrane - a Solution for Pore Wetting in Membrane Distillation" uses Cheng and Wiersma's original theory to make their own triple-layer membrane; "while hydrophilic layer is wetted with liquid (normally water), transport of vapor takes place the hydrophobic layer. The higher mass transport in the MD by using the dual layer membrane is due to the shorter path required for the vapor to move between the liquid/vapor interfaces."²⁴ Their triple-layer membrane used two similar hydrophobic layers and one hydrophilic layer; creating a membrane with extreme strength and hydrophobicity that could perform for over 95 hours.

The University of Technology in Sydney, Australia also has tried their hand at a multi-layer composite membrane. In their paper titled "A Novel Dual-layer Bicomponent Electrospun Nanofibrous Membrane for Desalination by Direct Contact Membrane Distillation," they cover many of the processes used in this project. They discuss the importance of electrospinning and how it could lay the foundation for future membrane fabrication, as well as proving that PVDF is the revolutionary material that possesses "superior hydrophobicity."²⁵ The main goal of this paper was to optimize membrane thickness in a double-layer membrane. They discuss testing a triple-layer (two hydrophobic layers and one PET support layer) membrane, but settle on two-

²³ Cheng, D. Y. & Wiersma, S. J. Composite membrane for a membrane distillation system, United States Patent Serial No. 4, 316-772 (1982).

²⁴ Prince, J. A., D. Rana, T. Matsuura, N. Ayyanar, T. S. Shanmugasundaram, and G. Singh. "Nanofiber Based Triple-layer Hydro-philic/-phobic Membrane - a Solution for Pore Wetting in Membrane Distillation." *Scientific Reports* 4.6949 (2014): 1-6. www.nature.com. Web. 26 Mar. 2017.

²⁵ Tijng, Leonard D., Yun Chul Woo, Md Abu Hasan Johir, June-Seok Choi, and Ho Kyong Shon. "A Novel Dual-layer Bicomponent Electrospun Nanofibrous Membrane for Desalination by Direct Contact Membrane Distillation." *Chemical Engineering Journal* 256 (2014): 155-59. A Novel Dual-layer Bicomponent Electrospun Nanofibrous Membrane for Desalination by Direct Contact Membrane Distillation. 26 June 2014. Web. 26 Mar. 2017.

layers after discussing the importance of membrane thickness in the membrane distillation process.²⁶ This paper was one of the few found which forward the idea of making a layer out of PET to increase the mechanical strength of the membrane. Through rigorous testing, they concluded that “it suggests that a thinner more hydrophobic and high porosity layer would lead to better DCMD flux.”²⁷

Another paper from Ngee Ann Polytechnic in Singapore titled "Preparation and Characterization of Novel Triple-layer Hydrophilic-hydrophobic Composite Membrane for Desalination Using Air Gap Membrane Distillation” compared a triple-layer membrane to an equivalent double layer and single-layer membrane.²⁸ Both papers include a support layer as the third layer of the membrane, but this support layer always demonstrated an amount of hydrophobicity to help draw vapor from the feed stream. What makes this paper unique is the different way of making the membrane. While they agree that electrospinning is a valuable part of making a membrane, they believe that a membrane made solely of Nanofibrous material is not effective at MD.²⁹ They theorize that the nanofibers are most efficient when added on top of an already-made dual-layer membrane.³⁰

Many other papers were used to develop the ideas used in this project, most of them delve into the specifics about materials used (PVDF, PET, PTFE, etc.) or the processes used to create the membrane (electrospinning, heat pressing, etc.). Since this paper is focusing on the chemical engineering aspect of the distillation process and not the chemical composition of the membrane, these papers are not reviewed here.

²⁶ *ibid.*

²⁷ *ibid.*

²⁸ Prince, J.a., V. Anbharasi, T.s. Shanmugasundaram, and G. Singh. "Preparation and Characterization of Novel Triple-layer Hydrophilic-hydrophobic Composite Membrane for Desalination Using Air Gap Membrane Distillation." *Separation and Purification Technology* 118 (2013): 598-603. Elsevier. Web. 26 Mar. 2017.

²⁹ *ibid.*

³⁰ *ibid.*

Methodology

To test this new membrane, many tests needed to be run. The membrane had to be tested for flux and rejection rate. The most efficient way to do this was to set up a small scale DCMD process and make membranes to run tests. The following sections describe the equipment used, the procedures used in testing, as well as the fabrication in detail.

Equipment



Figure 3. Full DCMD Setup

The testing of membranes was performed on a small scale using the equipment pictured above in Figure 1 in the setup of a small-scale DCMD column. The system was made up of several important parts, listed below. Corresponding figures are labeled; figure numbers with a prefix of ‘A’ can be found in the appendix:

Column/DCMD Vessel (Fig. A1/A2)

The vessel in which distillation occurs; it is located at the top center of Figure 1. This piece of equipment consists of a top and bottom section that can be fastened tightly together with four wing nuts located at the corners. Two circular gaskets fit between the top and bottom pieces allow for a good seal to prevent leakage. The top section contains the permeate side of the vessel; the inlet tube comes from the right flowmeter and the outlet tube flows into the condenser coils. The bottom section contains the feed side of the vessel; the inlet flowing in from the left flow meter and the outlet flowing back into the heater.

Heater (Fig. A3/A4):

The vessel in which the feed, or process liquid, is heated before it enters the column; it is located on the left side of the apparatus. Two heaters were used during the testing of the membrane. The first, shown in figure 1 and figure A3, heats the process fluid by heating the bath of water that it is in, while the second, shown in figure A4, heats a bath of silicon based oil instead. These heaters worked efficiently from room temperature to one hundred degrees Celsius. The process fluid vessel contains two tubes; the right tube flowing into the pump, and the left tube flowing from the column.

Condenser (Fig. A5/A6):

The vessel that cools the permeate stream; located to the right side of the apparatus. This equipment is made up of two main parts. The physical condenser on the far right is where the cooling water is cooled. This device can be set and be effective at temperatures as low as ten degrees Celsius. This chilled water is recycled into and from the large insulated beaker on the right side containing the two stacks of coiled tube. The coils receive permeate from the column into the left coiled tube before sending it into the beaker on the balance from the right coiled tube.

Flow Meters (Fig. A7/A8):

Two flow meters were used to control the flow of process liquids; they are attached at the front of each side of the metallic box. Each flow meter is a rotameter with its own needle valve to control the flow rate. The rotameter on the left controls the flow rate of the feed while the one on the right controls the permeate. Both meters measure flow rates up to four liters per minute with an accuracy to one decimal point.

Thermometers (Fig. A9):

Four thermometers are located on top of the large metallic box. The two thermometers on the left measured the inlet and outlet temperature of the feed, while the two on the right correspond to the permeate (outer thermometers measured inlet temperatures, and inner thermometers measured outlet temperatures). For data collection, only the outer two

thermometers were read (feed inlet on the left, permeate inlet on the right). The leftmost thermometer was accurate to two degrees Celsius, while the right thermometer was accurate to one degree Celsius.

Conductivity Meters (Fig. A10/A11):

Two different meters were used during the testing of the membrane. The black meter and white meters, both located on the table in front of the large metallic box, could both measure the liquid in milliSiemens and microSiemens to the same degree of accuracy. The only difference between the two meters is that the black meter required a higher level of water before the probe attained an accurate reading.

Balance (Fig. A12):

One balance, located in the front of the table, was used for data collection. A beaker sits on top of the balance; this beaker contains two pipes, one flowing in from the condenser and one flowing out towards the pump.

Pumps (Fig. A13):

Two pumps, which are located inside the metallic box, are used to run the distillation process. The left pumps feed liquid from the heater into a flow meter, while the right one pumps permeate liquid from the beaker on the balance into the flow meter. These pumps are turned on by the two red switches on the front of the large metallic box.

Testing Procedure

The first step in each test required the preparation of a new feed solution. To simulate saltwater, solutions with a concentration of 35 g/L of sodium chloride in water were prepared. For the first three weeks of testing, a 2L beaker was used. For the final four weeks, a 1L beaker was used. This change and the errors it may have caused to test results is discussed in the *Causes of Error* section of this report.

Feed solution was placed in heater bath. Using the black conductivity meter, electrical conductivity of feed solution was measured and recorded. Conductivities typically ranged from 55-65 mS. Heater was then switched on and temperature was set. Heater was usually set approximately ten degrees Celsius higher than the target feed temperature.

Condenser was switched on and set to a temperature around three to five degrees Celsius cooler than the target permeate temperature, depending on the temperature of the room. The condenser contained a pump that sent the chilled water into the cooling vessel. When the large vessel was filled with cold water, another tube was snaked from the cooling vessel back into the condenser. A rubber bulb was then used for suction to create a siphon to pull liquid from the cooling vessel. A complicated mechanism made from a paper clip and a broken pen was used to put pressure on the condenser exit stream to balance the water level in the cooling vessel.

Before turning on the pumps, it was visually confirmed that the feed and permeate uptake pipes were submerged in liquid. This was to prevent large amounts of air entering the system. A thin impermeable, plastic sheet was placed in the column to prevent liquid from flowing from the feed to the permeate or vis versa. The column was sealed and the pumps were then turned on. The needle valves on both flow meters were opened and the full range of flow was inspected. If full flow was not attained, or if there were too many bubbles in the flow meter, the pump was turned off. This problem was remedied by disconnecting the tube exiting the pump and filling the tube with solution (feed solution if the left flow meter was sluggish, DI water for the right side). The pipe was then reconnected and secured and flow was reinitiated.

Feed and permeate inlet streams were then brought up to target temperatures by adjusting heater and condenser and periodically checking corresponding thermometers. During this time, the electrical conductivity of the permeate solution was measured. If conductivity measured higher than 300 μ S, the permeate side was flushed with DI water until the conductivity fell into spec.

Once both streams were at target temperatures and both solutions were at target conductivity, the flows were turned off. The column was opened and the plastic sheet was replaced with the membrane being tested. The column was resealed and the flows were turned on. The membrane was given ten minutes to stabilize before the balance was tared. At this point, data for permeate conductivity and permeate weight was recorded every ten minutes for six hours or until leakage of the membrane occurred.

During testing, it was vital to recheck inlet temperatures and adjust the heater or condenser accordingly. This also applies to flow meters, as they would occasionally fluctuate. When a leak in the membrane occurred, it was vital to shut the system down before permeate conductivity increased too much, as flushing the system would take exponentially longer.

Fabrication of Membrane

The first step in fabricating a membrane was to prepare the dope solution. In the triple-layer membrane, the hydrophobic layer was created first. In a round-bottom flask, dimethylacetamide in acetone, polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) were combined. This flask was then capped with a stirrer and placed in a machine that stirred it for 24 hours at fifty degrees Celsius. After stirring, solution was let rest for two hours to get rid of bubbles.

During this time, a depressed 20mL syringe was placed in the electrospinning machine. The backstop was brought up to the plunger of the syringe and the machine was zeroed. The backstop was then moved outward. The solution was poured into the syringe and a metal needle tip was screwed on. This filled syringe was then placed back into the machine and the backstop was brought back up to the plunger. A wide sheet of Polyethylene terephthalate (PET) was cut and wrapped around the electrospinning collector. This was fastened with small pieces of tape.

Positive and negative electrical cables were attached to the metal needle tip using small alligator clips. The electrospinning chamber was closed, and the voltage was turned on. The machine was turned on and the test began on its own. Using a built-in light, a Taylor cone was visible leaving the syringe tip. Electrospinning lasts ten hours.

After the machine was turned off, the double-layer membrane was removed from the collector by using a pen knife to slice the small pieces of tape. This membrane was then carefully placed on a flat, steel plate heater in between two sheets of aluminum foil, hydrophobic layer down. Another steel plate was then placed on top of the membrane and weighed down with several kilograms of weight. The heater was turned to 130 degrees Celsius for two hours; this allowed the electrofibers in the membrane to anneal, making them stronger.

The hydrophilic layer was then made in a similar way starting with the creation of another dope solution. This solution consisted of Chitosan, polyethylene oxide (PEO), acetic acid, and water. This solution stirred for twelve hours and was let rest for six.

The aluminum foil was removed from the PET side of the double-layer membrane and then wrapped around the electrospinning collector. The electrospinning process was repeated. After removal from the collector, the triple-layer membrane was laid above a glutaraldehyde solution for 24 hours which allowed the hydrophilic layer to cross-link. This completed membrane was then cut into sections that would fit inside the distillation vessel.

If it was only desired to fabricate the hydrophilic layer for testing purposes, the process becomes much easier. Instead of wrapping the collector in a sheet of PET, aluminum foil is used. After heat-pressing, the membrane was complete.

Experimental

Testing on the membrane involved manipulating process conditions to find which conditions yielded the best flux and rejection rate in the membrane. Four variables were chosen to be manipulated: Feed temperature, feed flowrate, permeate temperature, and permeate flowrate. In addition to the tests being done on the triple-layer membrane, they were also completed on the sole hydrophobic layer, simulating a traditional single-layer membrane. These results were compared to determine if adding the two extra layers increased the flux as theorized. The table below show which variables were manipulated and which were kept constant in each test.

Table 1. All eight different tests run with constant and manipulated variables shown.

Distillation Parameters	Membranes: SL(Single-layer) TL(Triple-layer)							
	SL	SL	SL	SL	TL	TL	TL	TL
Feed Temp (Deg C)	46-66	56	56	56	46-66	56	56	56
Permeate Temp (Deg C)	20	13-26	20	20	20	13-26	20	20
Feed Flow Rate (L/min)	0.5	0.5	0.5-1.75	0.5	0.5	0.5	0.5-1.75	0.5
Permeate Flow Rate (L/min)	0.5	0.5	0.5	0.5-2	0.5	0.5	0.5	0.5-2

Expected Results

The main driving force of the permeate flux is the vapor pressure difference across the membrane. This gradient is directly related to the temperature difference across the membrane; to achieve optimal flux, the column must be run at the largest temperature difference. However, too high of a feed temperature approaches the melting points of some of the materials used in the membrane. This can cause premature fouling or destruction of the membrane. Secondly, the higher the feed temperature and the lower the permeate temperature, the higher the utility costs. For this desalination process to work in underdeveloped places of the world that desperately need it, the costs to power it must be cheap. That means that the feed and permeate temperatures must be maximized but kept reasonable.

On the other hand, flow rate of the feed or permeate streams do not have a direct relationship with vapor pressure. These variables will still be manipulated to see which combination of the two give the highest flux and best rejection rate. A feed flow rate slightly higher than the permeate flow rate should prevent any flow in the wrong direction and help with driving the vapor through the membrane. However, with any leakage in the membrane, the higher feed flow rate will push salt through the leak and drastically reduce the quality of rejection rate in the membrane. On the other hand, if the permeate flow rate was higher, rejection rate will not drop with a leak in the membrane. This scenario should lengthen the life of the membrane, but the flux will suffer. Another area of concern was how high the flow rates can be set. With the flow rates set too high, some of the weaker materials in the membrane can wear quicker and break down. Therefore, a compromise between feed and permeate flow rates and their respective maxes must be reached to optimize the distillation process.

Results

The first variable adjusted was the temperature of the feed. Three trials with three different feed temperatures were completed on the triple-layer membrane: 46, 56, and 66°C. All three other variables were kept constant through each trial: permeate temperature was set at 20°C, permeate and feed flow rates were kept at 0.5 L/min. Additionally, initial feed and permeate were kept at approx. 56000 and under 320 $\mu\text{S}/\text{cm}$ respectively. Being the first set of tests completed, some small errors were made due to lack of experience with the system. At one point during the 56-degree trial, the temperature rose several degrees for a few data points before

being corrected. Additionally, the feed flow rate drastically dropped for a few minutes before being corrected, most likely due to air in the feed line. This test's membrane also sprung a leak at only forty minutes into the run. The 46 and 66-degree tests both ran smoothly without problems.

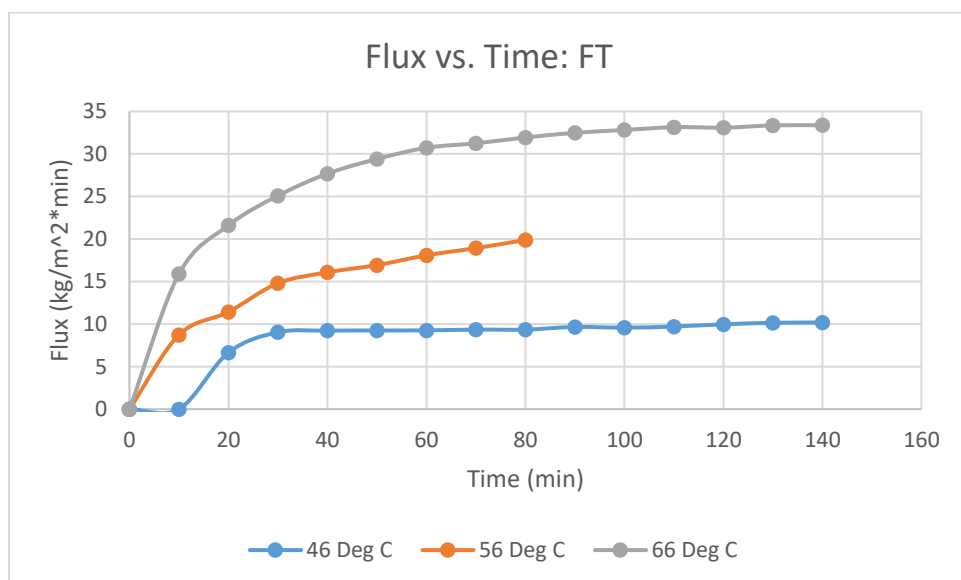


Figure 4. Permeate flux versus time regarding changing feed temperature on the triple-layer membrane

The graph above shows a visualization of the flux for all three feed temperature trials. There are several important things to note while reading these flux graphs. In the beginning of each run, the sharper slope, the better. This slope tells how fast the membrane stabilizes. In large-scale processes, the faster a membrane achieves its maximum flux, the more profitable it will be. Where the graphs flatten out it the maximum flux of the membrane at those operating conditions. Any further increase in flux after the point of stabilization usually signifies a leak being sprung in the membrane. The opposite effect, a sudden drop in flux, could signify a clog in the membrane, or the permeate flowing back into the feed stream.

For this variable, the process ran as expected. The 66-degree run performed with the highest flux and the 46-degree run achieved the lowest. The high temperature run also fared better when rejection rate was measured. A rejection rate graph for all three trials is attached below.

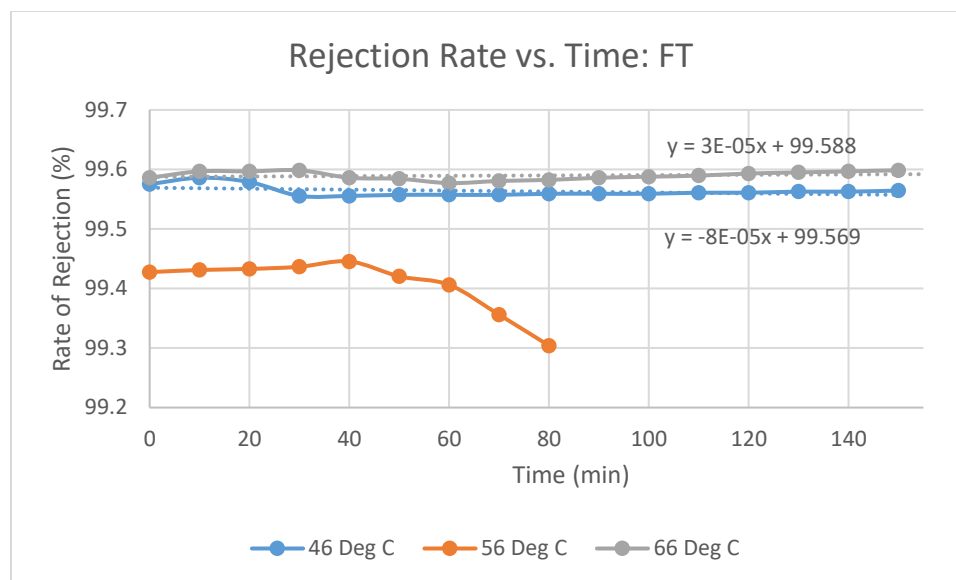


Figure 5. Rejection rate versus time regarding changing feed temperature on the triple-layer membrane

There are several important things to note when reading these graphs. Most importantly, these graphs are a measure of the percent salt rejected (i.e. 100% rejection rate would be pure water product). This causes the y-intercept of the graph to depict initial permeate concentration. Since initial permeate concentration changes every run, ignore y-intercept completely and only look at the slope of each line. Each run had an initial permeate conductivity of approximately 300 $\mu\text{S}/\text{cm}$. This value was deemed tolerable for concentration of salt in water. As a reference, pure water has a conductivity close to 0 $\mu\text{S}/\text{cm}$. In this case, a positive slope means that the membrane was producing close-to-pure water. A negative slope means that salt was entering the permeate side of the distillation system. The highest slope is the best rejection rate. In this first set of trials, the high temperature run achieved the highest rejection rate. Due to the low number of tests done, this data is not statistically relevant, but it is still an important trend to note. These graphs also make a membrane failure easier to spot. In the 56-degree run, the slope starts to decrease at around 40 minutes into the run. This shows a leak forming in the membrane.

The second variable in the distillation process that was manipulated was the flow rate of the feed stream. Due to the lack of good membranes, there are only two sets of data. The graph below shows the flux between runs with a feed stream flow rate of 0.5 L/min and 0.75 L/min.

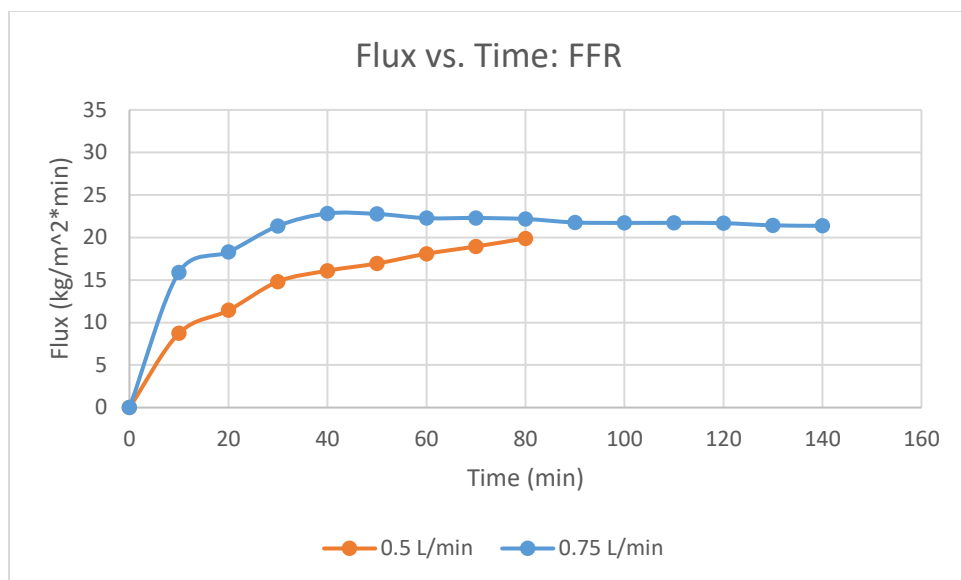


Figure 6. Permeate flux versus time regarding changing feed flow rate on the triple-layer membrane

As before, all other process variables were kept constant during the test; feed temperature was at 56°C, permeate temperature was at 20°C, and permeate flowrate was at 0.5 L/min. This graph shows that a higher flow rate increases the permeate flux. Looking at Bernoulli's equation, pressure decreases with increased velocity, so there must be another explanation for this phenomenon. Note the steady increase in flux after 40 minutes in the 0.5 L/min run. This was due to a leak in the membrane, not an increase in membrane performance, as shown below in the rejection rate graph for the same tests.

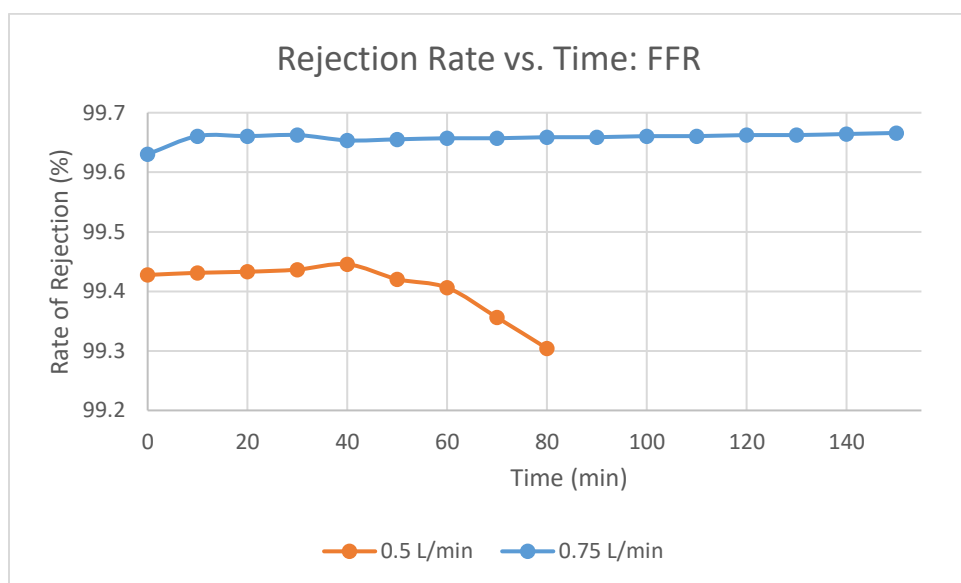


Figure 7. Rejection rate versus time regarding changing feed flow rate on the triple-layer membrane

This graph shows that the slower feed flow rate fared better in terms of rejection rate, but considering the scale, this difference is negligible.

The third manipulated process variable was permeate temperature. The graph below shows 3 tests done with varying cold temperatures on the permeate side of the distillation process.

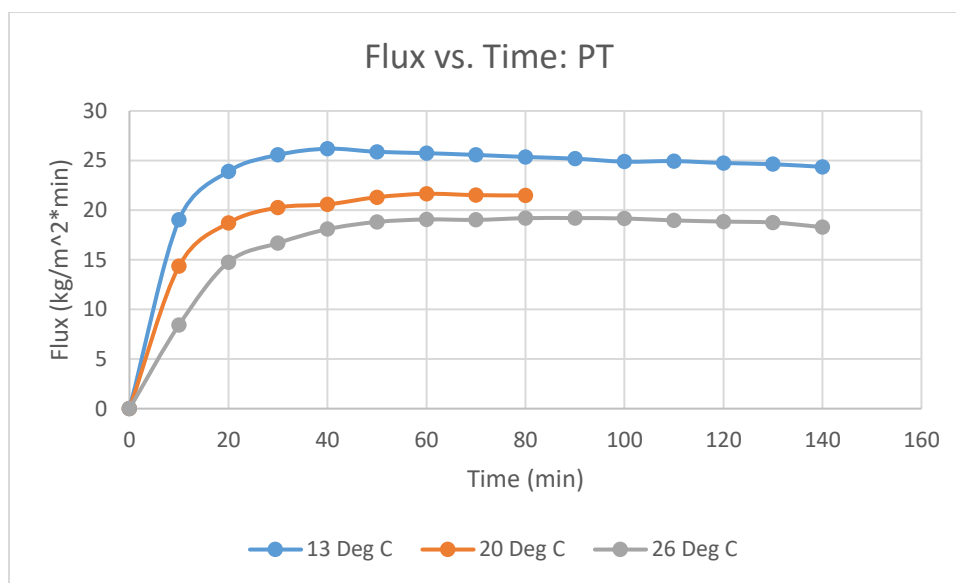


Figure 8. Permeate flux versus time regarding changing permeate temperature on the triple-layer membrane

As expected, the colder the permeate stream was, the higher the flux was. This follows the theory that the larger the temperature difference is across the membrane, the larger the vapor pressure difference and the distillation driving force will be. The slow decline in flux could indicate that a leak was slowly forming, but the permeate was leaking into the feed so the rejection rate didn't decrease. In these tests, the 20-degree run performed with the best rejection rate. Again, rejection rate isn't affected by changes in process variables. This helps solidify the theory that rejection rate is more dependent on the makeup of the membrane than the distillation process variables. The rejection rate data can be viewed in Figure A14.

The fourth and final manipulated process variable was the permeate flowrate. Unfortunately, no data was able to be collected for this set of tests. Due to the membrane fabrication process taking approximately four days, not enough good membranes were able to be

created. More information about why not all membranes were able to be used for testing can be found in the *causes of error* section of this report.

To test the performance of the triple-layer membrane, it has to be compared to a similar single-layer membrane. To simulate this, the hydrophobic layer of them membrane was fabricated on its own and used as its own membrane. For these tests, the same four process variables were manipulated.

The graph below shows the flux of the single-layer membrane as feed temperature was adjusted.

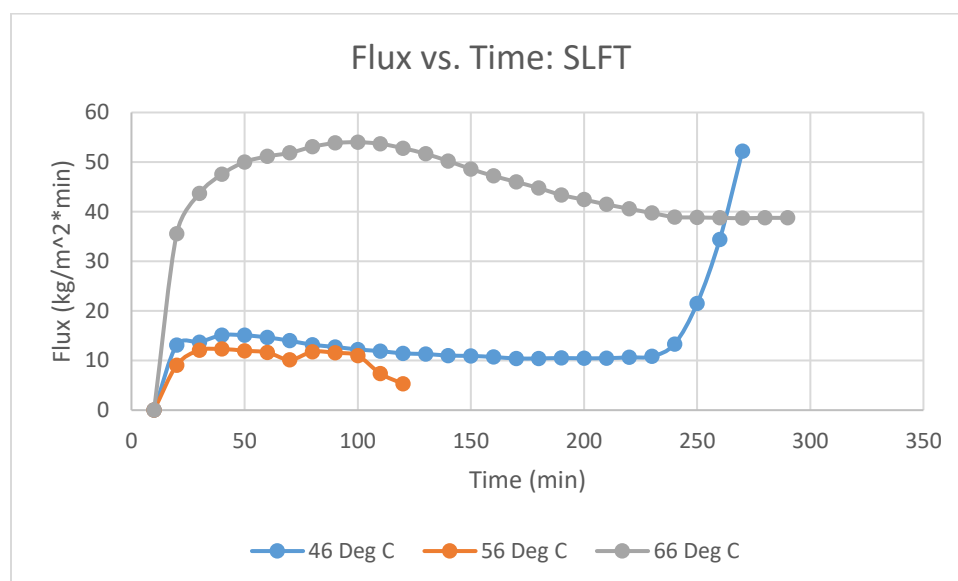


Figure 9. Permeate flux versus time regarding changing feed temperature on the single-layer membrane

There are two main results to take away from this graph. First, it's important to notice that, as expected, the highest temperature test performed the best in terms of permeate flux. The second thing to notice is how the 56-degree run, the middle temperature run, did not perform nearly as well as expected. This highlights an important problem that occurred during testing. The membrane was not successful a good portion of the time. Many times, when the test was started, the conductivity of the permeate stream would instantly skyrocket; this indicated that a leak immediately formed, or that there was already a leak that was formed in the fabrication of the membrane. This problem also rang true when using the triple-layer membrane. One benefit to the single-layer membrane was that it took only have the time, about two days, to fabricate; this meant that there was more membrane available to test with. Rejection rate was even across all three tests; a corresponding graph can be found in Figure A15.

After similar tests were done on both the triple and single-layer membranes, results were compared. The graph below shows the permeate fluxes of the best runs from both the triple and single-layer membranes. The corresponding rejection rate graph can be found in figure A16 in the appendix.

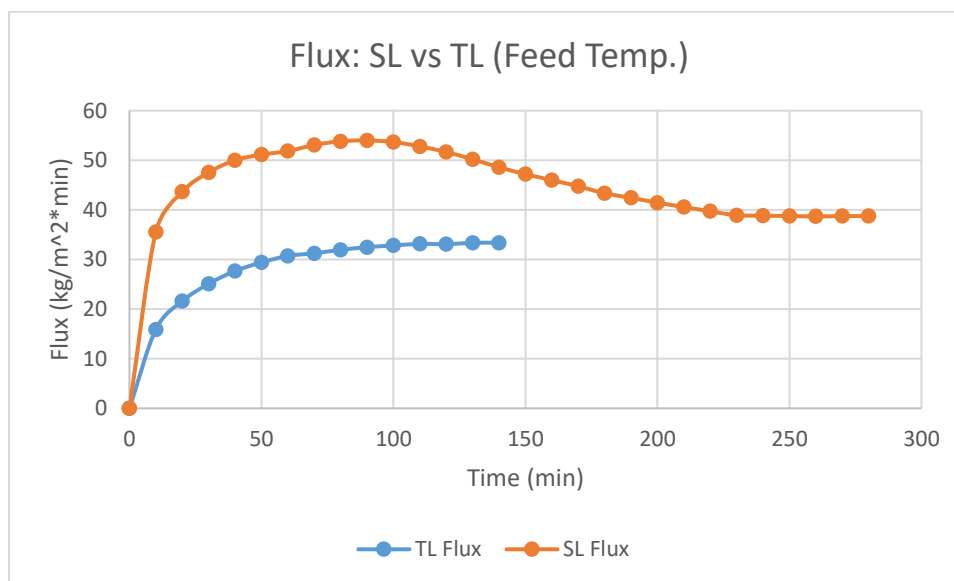


Figure 10. Permeate flux versus time with feed temperature at 66°C in both the single and triple-layer membranes

This figure is quite surprising. Originally, the theory of adding a third, hydrophilic layer to the membrane was thought to draw the water vapor through the membrane faster so that one could achieve increased flux compared to a lone hydrophobic layer membrane. However, this graph shows that the opposite result occurs. There are many factors that could cause the new membrane to perform less than expected; the main factor was most likely the thickness of the membrane. Thickness is a highly important factor pertaining the efficiency of a membrane. As the membrane gets thicker, the resistance to mass transfer increases, but as it gets thinner, the heat lost in the process increases, raising process utility requirements. In this case, adding the PET support layer and the hydrophilic layer increase the thickness too much and thus the flux of the process is affected in a highly negative way.

Manipulating the flow rate of the feed stream also gave unique test results. In this case, the strength of the single-layer membrane is clearly visible, as can be seen in figure 9 below.

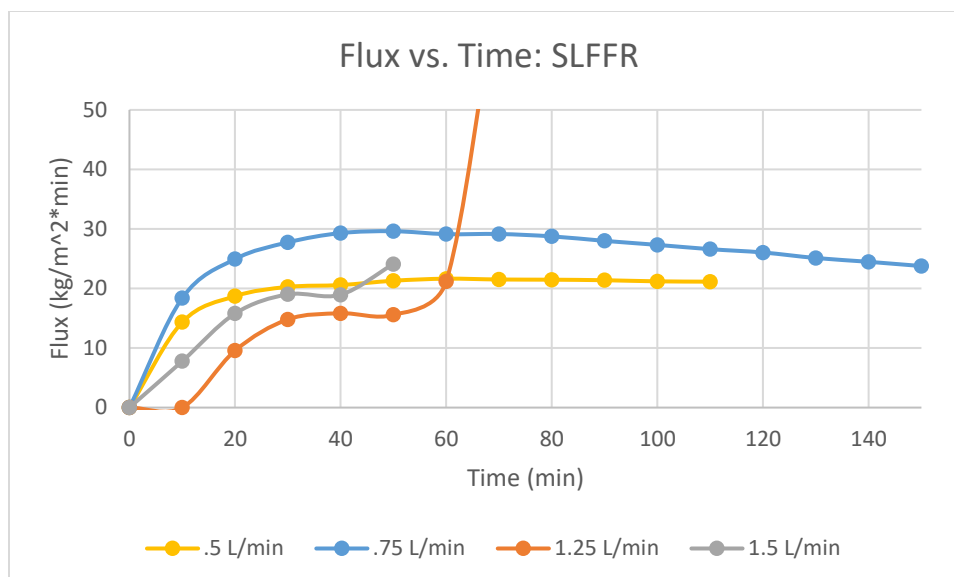


Figure 11. Permeate flux versus time for the single-layer membrane when manipulating feed flow rate.

As with the triple-layer membrane, there was a decent sized positive increase in flux when the feed flow rate was increased from 0.5 to 0.75 L/min. However, as the flow rate gets higher, there was a negative impact on the flux. Looking at the 1.25 L/min run, the membrane has a visible breakage at approximately 50 minutes. The higher flow rate, 1.5 L/min, breaks even earlier at around 40 minutes. This was most likely due to the forces being exerted on the membrane when the flowrate of one stream was much higher than the other. Since the single-layer membrane was so thin, it was structurally weak; the more forces acting on it, the more likely it was to break. Since the triple-layer membrane contains the PET support layer, it will be much more resistant to these forces. The optimal flowrate will most likely be higher than the 0.75 L/min, but more tests need to be done to determine the maximum. Again, the corresponding rejection rate graph can be found in the appendix in figure A17.

The next variable manipulated was the permeate temperature. Unfortunately, only one membrane used was successful and gave data. This graph below shows the 26°C permeate temperature runs for both the single and triple-layer membranes.

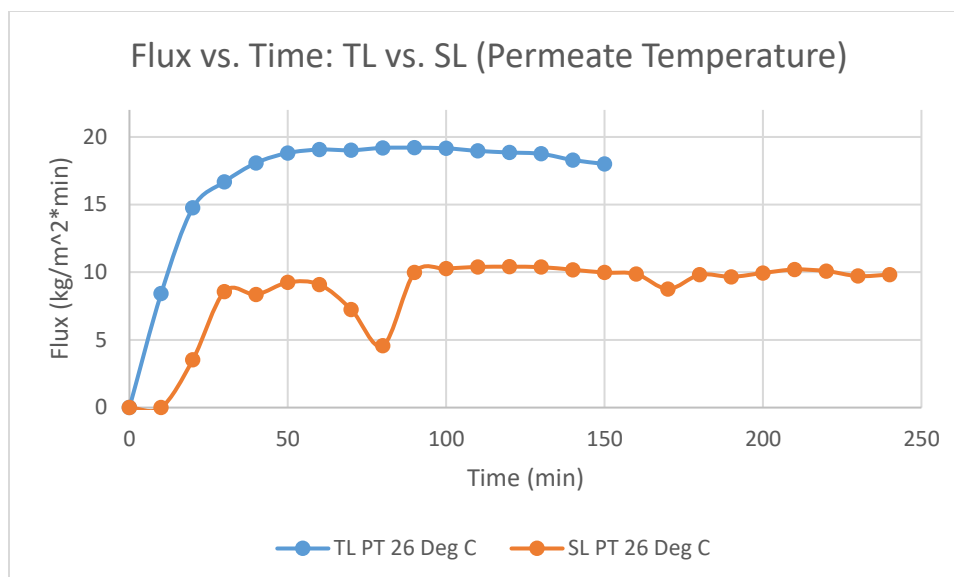


Figure 12. Permeate flux versus time with permeate temperature at 26°C in both the single and triple-layer membranes

Since there was only one successful run for the single-layer membrane, it is unknown what the flux would look like for the colder (better) permeate temperature. Also, this one successful single-layer membrane was the only working membrane in its batch. Thus, this data is most likely not relevant due to a flaw in the membrane. Additionally, the rejection rate graph did not show any significant results.

At this point in the testing process, there were not enough working membranes to get any more data. For the manipulation of the permeate flow rate with the single-layer membrane, no data was attained.

Conclusion & Recommendations

While this new innovative triple-layer membrane was a good idea, it needs more optimization before it sees success. The concept of adding a PET support layer and a hydrophilic layer was for two main reasons: to add mechanical integrity, and to increase the amount of flux

through the membrane. Unfortunately, neither aspect played out as theorized. Initial tests with the first batch of membranes suffered from leaks as early as 40 minutes into the runs. Under similar conditions, the single-layer hydrophobic membrane lasted well past 150 minutes. The second batch of membranes exceeded the 150 minutes, but the third, fourth, and fifth batches immediately lost all hydrophobicity and did not work in testing. While the membrane was capable of sustaining flux for an extended period, the process was not easily replicated, and the membrane was not nearly consistent enough. While there are many possibilities for why these problems occur, there is one theory that could make a big difference. When the hydrophobic layer was electrospun by itself, as a single-layer membrane, it was electrospun onto aluminum foil. This meant that the spinning collector had a flat surface, allowing the PVDF/PTFE to spread evenly. When the triple-layer membrane was being fabricated, this hydrophobic layer was electrospun onto a layer of PET. This layer is not smooth; it has many peaks and valleys. The already-thin membrane could be settling into these small valleys and not completely covering the peaks. This causes the structural integrity of the layer to drop even farther and could be the reason the membrane immediately leaks instead of being hydrophobic. Even the smallest leak in this type of membrane becomes amplified because of the hydrophilic layer pulling the water through. There are several ways that this process can be improved in the future. The PET layer could be smoothed down by sanding, or the hydrophobic layer could be made thicker. However, it may be that the membrane is already too thick.

The membrane also performed worse in terms of permeate flux. In the test where the single-layer achieved a maximum flux of $54 \text{ kg/m}^2 \cdot \text{min}$, the triple-layer only achieved $33 \text{ kg/m}^2 \cdot \text{min}$. This is most likely due to the increased thickness in the membrane from adding two extra layers. There are several ways to solve this issue as well. The PET and Chitosan/PEO layer could be made thinner or the PET support layer could be removed completely and a process could be developed to stick the hydro-phobic/philic layers together.

While the membrane has the potential to be very impactful, it is still in its early stages and much needs to be improved. The main goal should be to get a membrane that can consistently work in the DCMD process, and then make improvements from that point.

Causes of Error

During the testing process, many errors occurred that could have introduced errors into the data. Most of these errors were due to unfortunate circumstances encountered during the seven weeks of testing.

A few weeks into testing, another lab in the university needed the conductivity meter that was measuring the permeate stream of the process. A backup meter was found, but with a bigger electrode. This meter required a higher level of water, so a smaller beaker was used. This limited the amount of liquid that could be processed by the membrane. Theoretically, a six-hour test would probably not all fit in the beaker. Luckily, there were no tests after this point that approached that point.

Halfway through the testing process, the heater broke. A new heater was acquired within a day, but it was a different size. This presented a few problems; mainly, the size of the feed beaker had to be changed from two liters to one liter. During the DCMD process, with salt water in the feed and pure water in the permeate, as more fluid gets processed, the lower the feed level becomes. Since the sodium chloride does not pass through the membrane, it stays in the feed, increases the concentration as the supply dwindles. With a beaker half the size, the concentration rises twice as quick. Thankfully, since the feed beaker was much larger than the amount of fluid being sent to the permeate during a test, this change in concentration should be negligible.

For most of the testing, the triple-layer membranes would not work, or would spring a leak within a few minutes of turning on the MD process. This inefficiency of the membrane caused me to shorten the testing time so that more membranes could be tested in the given time. The testing time was shortened from 360 minutes to 150 minutes. For membranes that did not fail within that shortened time, it was unclear how much longer they would have lasted. Fortunately, few membranes lasted that long.

Appendix

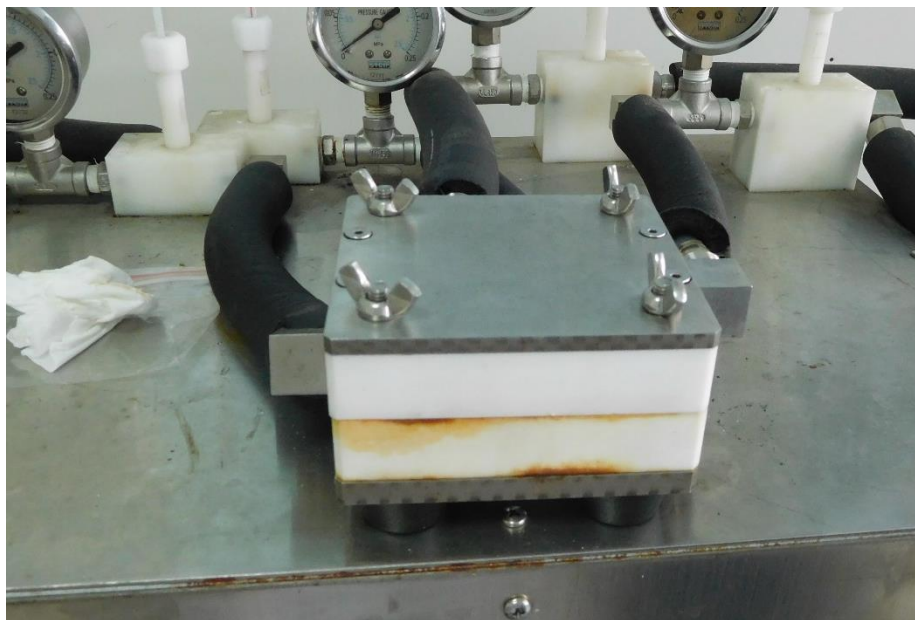


Figure A1: Distillation Column/Vessel in the sealed position.

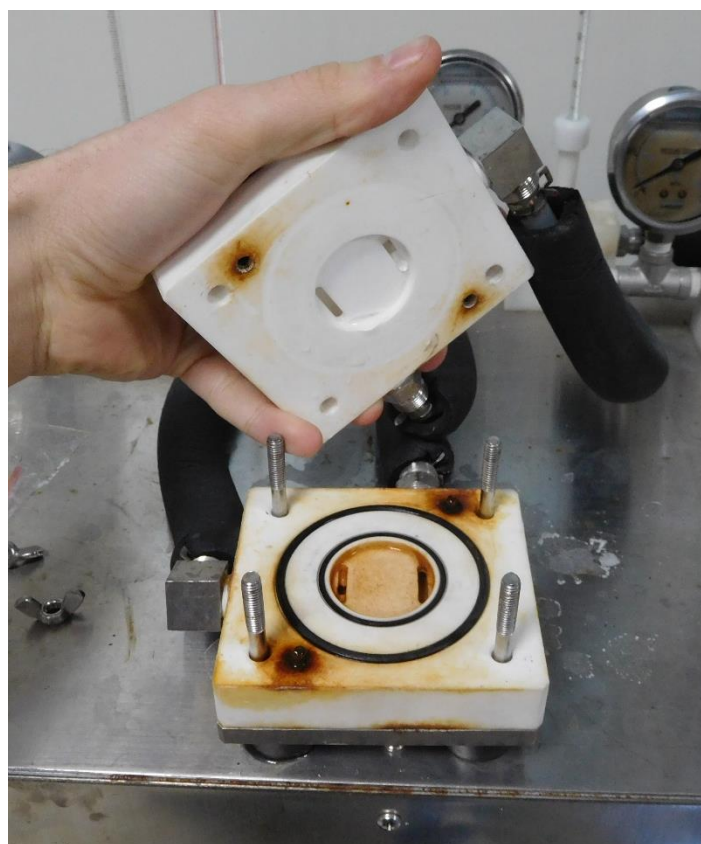


Figure A2: Distillation Column/Vessel in the open position.

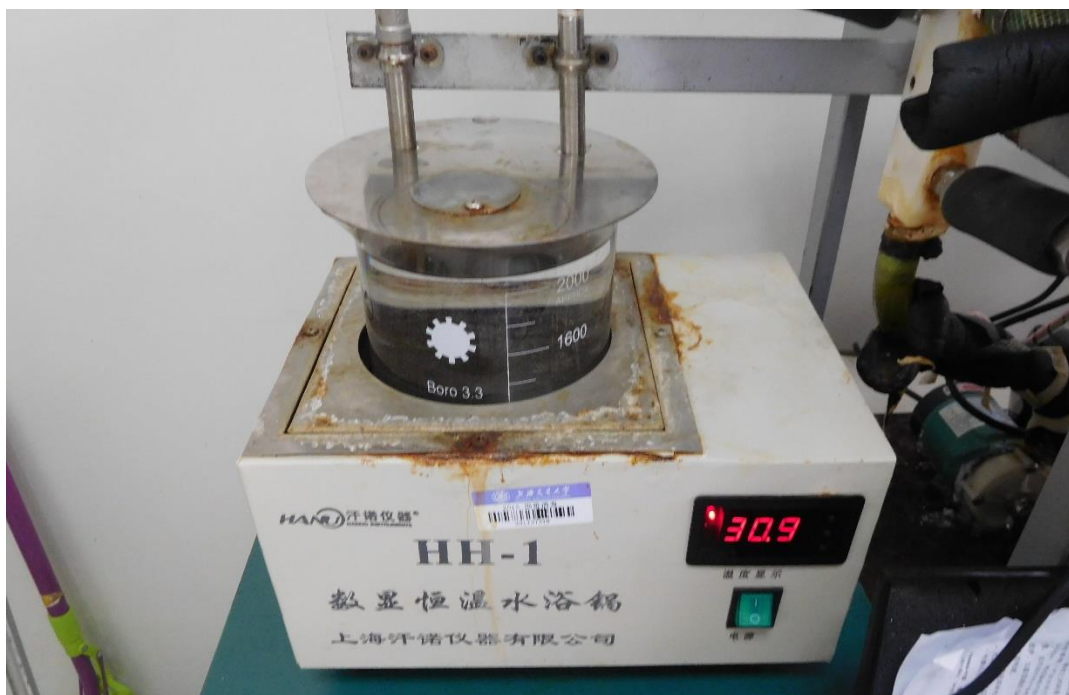


Figure A3: Heater used for the first three weeks of testing.



Figure A4: Heater used for the final four weeks of testing.



Figure A5: Machine that chills the cooling water.



Figure A6: Vessel containing the cooling water in which permeate stream flows through in the two coiled tubes.

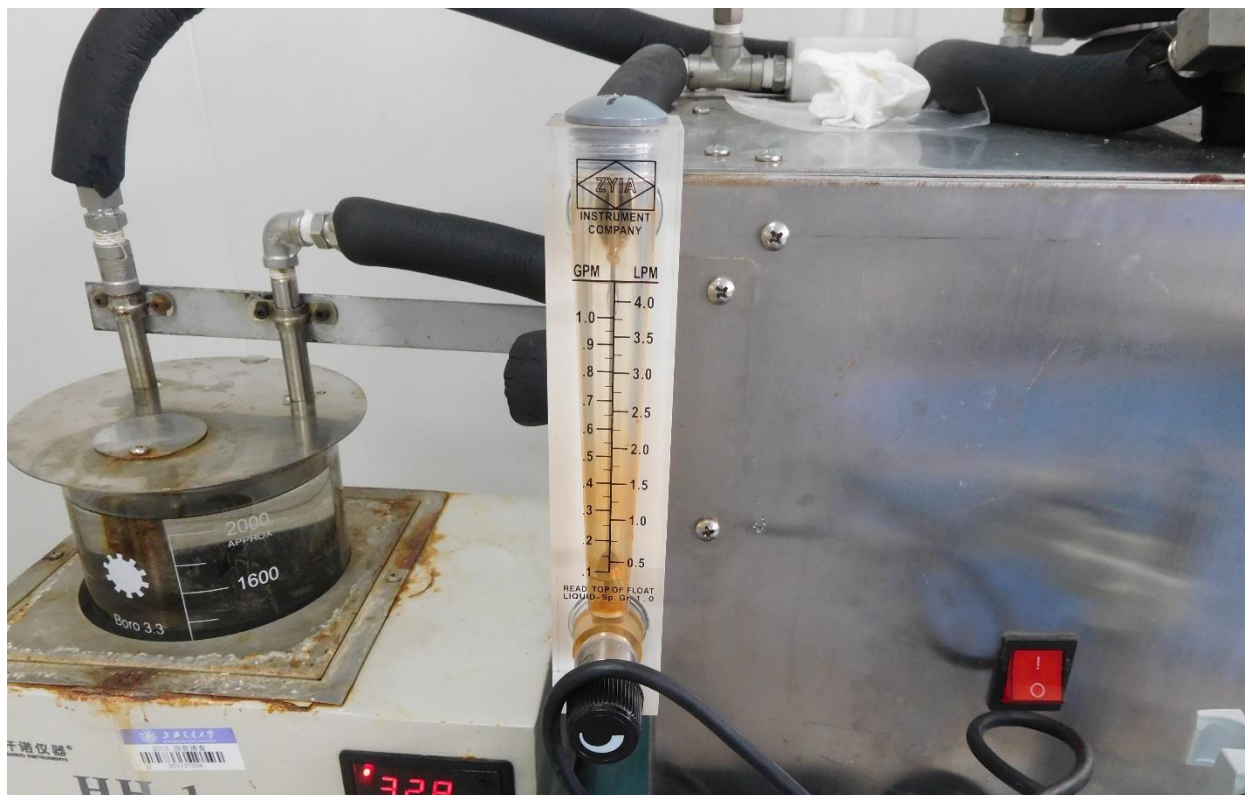


Figure A7: Left flow meter which controls flow of feed stream.



Figure A8: Right flow meter which controls flow of permeate stream.

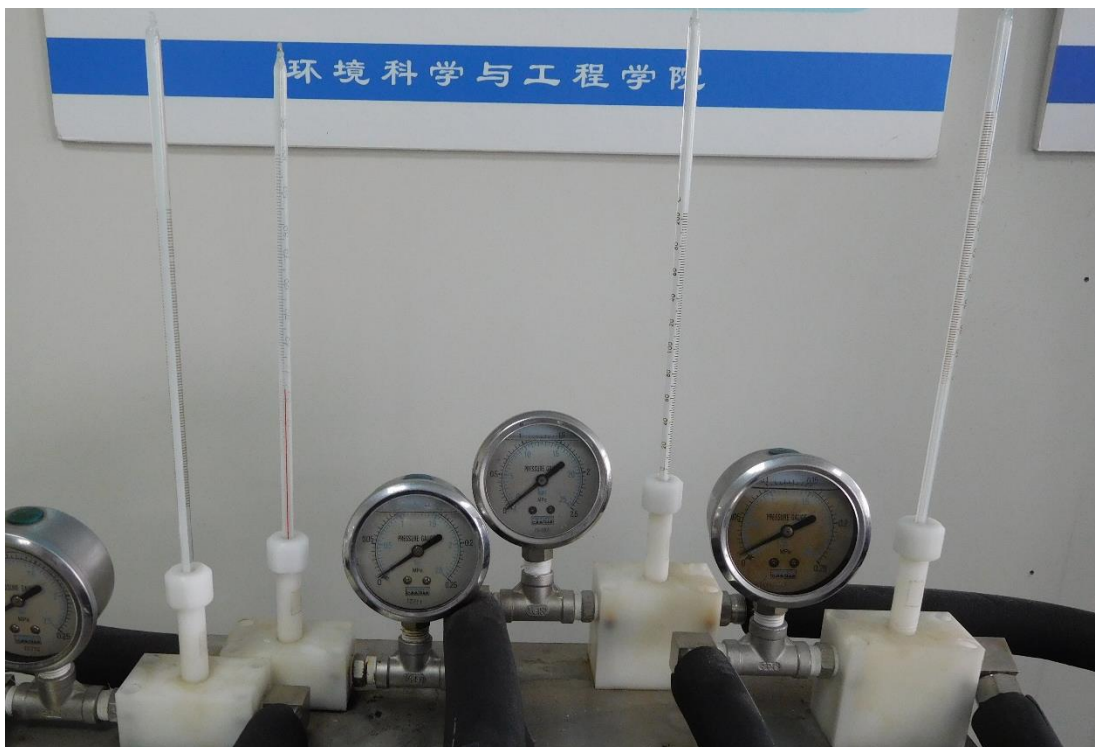


Figure A9: Thermometers measuring stream temperatures from left to right: Feed inlet, feed outlet, permeate outlet, permeate inlet.



Figure A10: Black conductivity meter used for the first two weeks to measure feed solution conductivity and the final five weeks measuring feed and permeate solution conductivity.



Figure A11: White conductivity meter, used to measure the conductivity of the permeate solution for the first two weeks of testing.

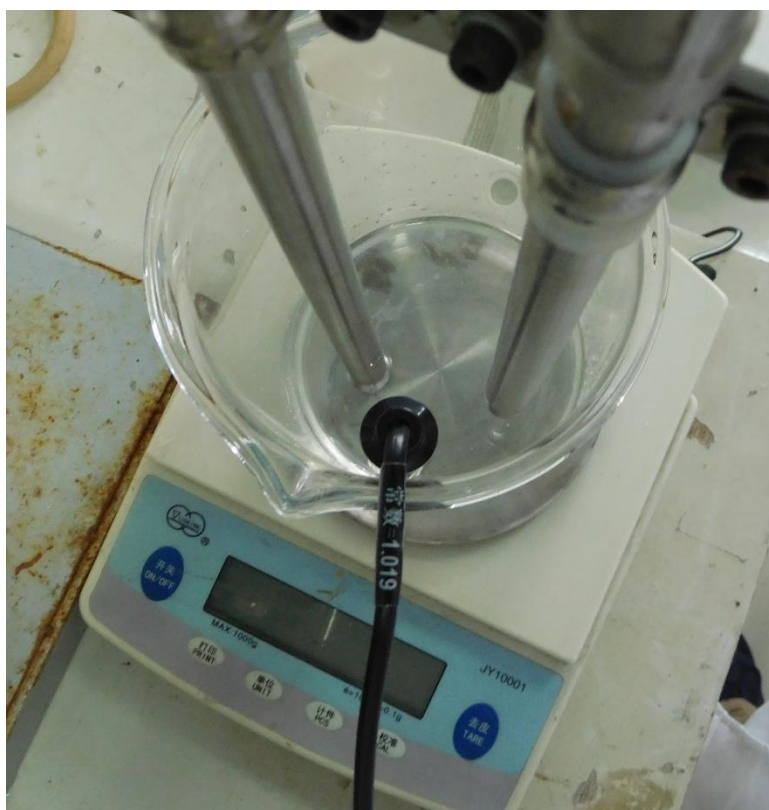


Figure A12: Balance used to weight the accumulation of distilled process liquids.



Figure A13: Two pumps used in distillation process; small pump for feed, large pump for permeate.

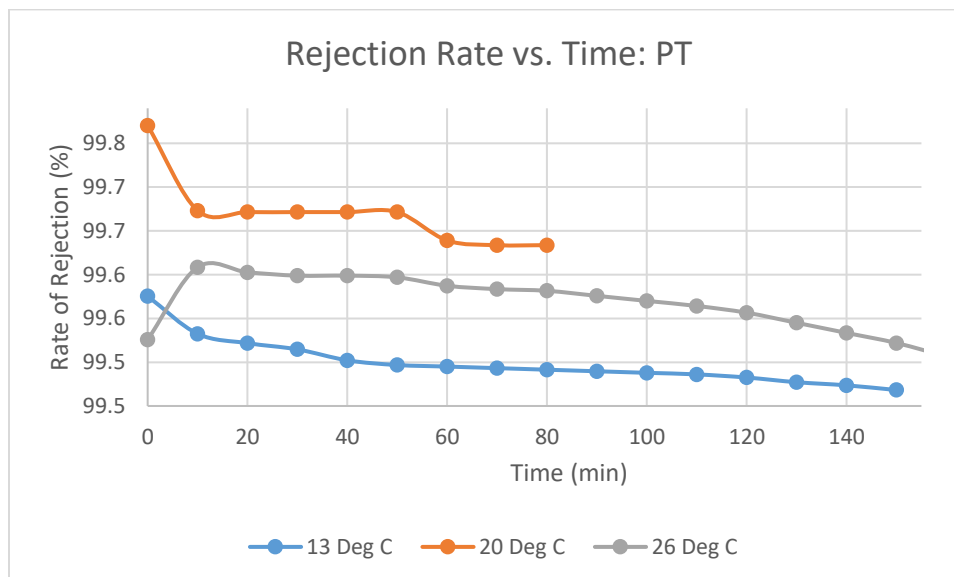


Figure A14: Rejection rate versus time regarding changing permeate temperature on the triple-layer membrane

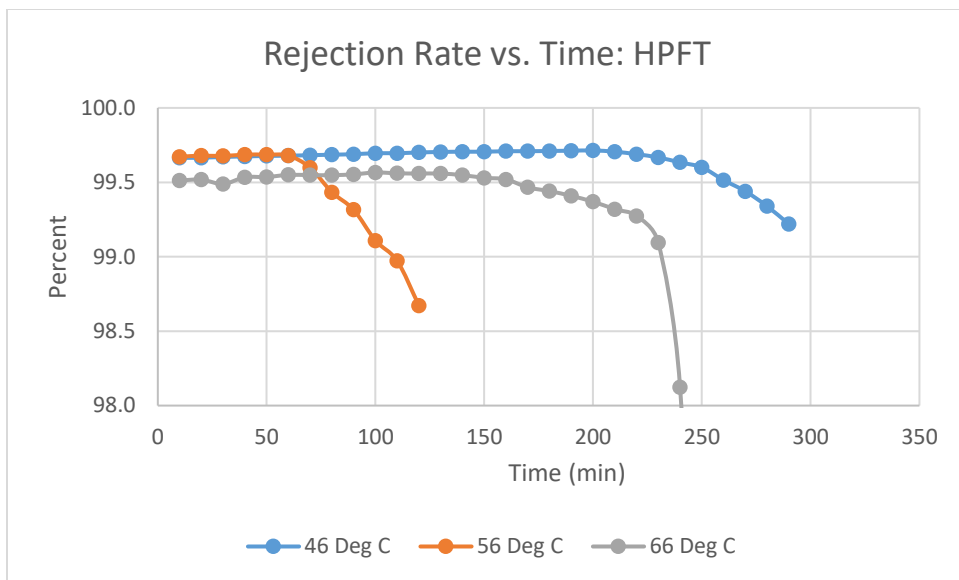


Figure A15: Rejection rate versus time regarding changing feed temperature on the single-layer membrane

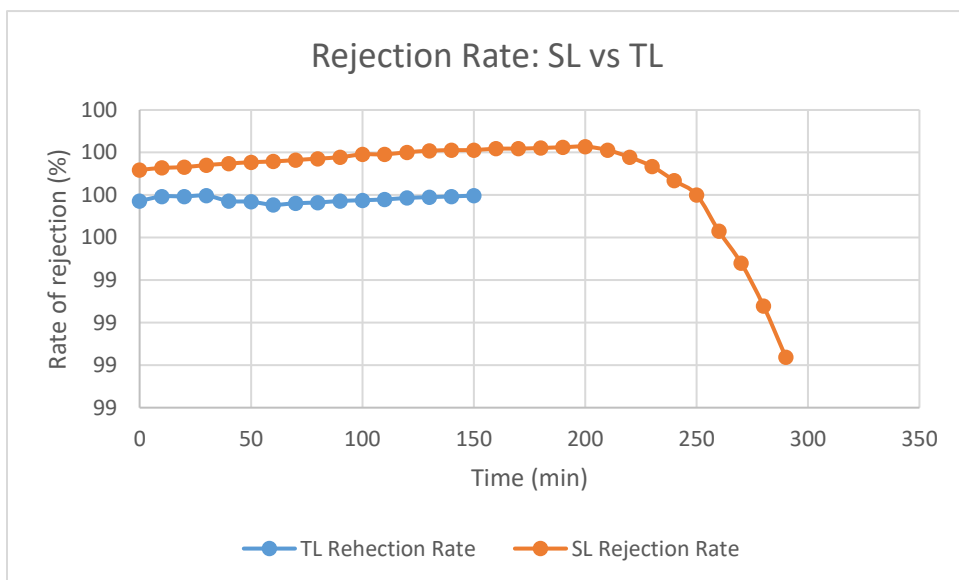


Figure A16: Rejection rate versus time with feed temperature at 66°C in both the single and triple-layer membranes.

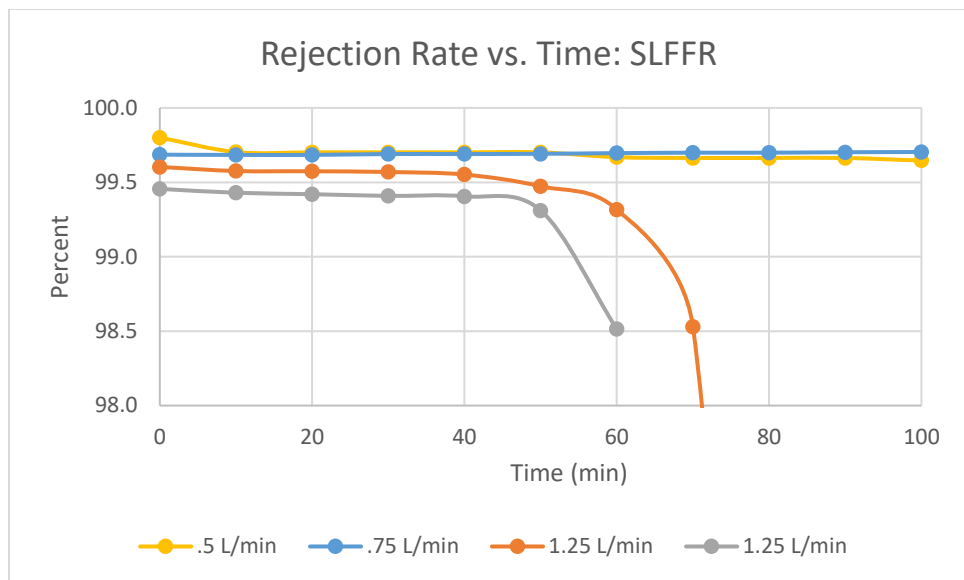


Figure A17: Rejection rate versus time in the single-layer membrane while manipulating feed flow rate.