

CREATING HYDROPHILIC WATER PATHWAY ON MEMBRANE WITH  
STRAIGHT PORES

A Thesis

by

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## ABSTRACT

Water is a strategic resource for cities and industries, and reserving this fresh water is a big challenge for them. Osmosis pressure has become the most popular way to treat water; to get drinkable water or to remove contaminated water. Several technologies have emerged from the osmosis phenomenon; reverse osmosis (RO), forward osmosis (FO), and pressure retarded osmosis (PRO) are examples to manage water for varieties of uses. Each of these technologies needs specific semipermeable membrane with distinct attributes to optimize their performance.

This work is focused on advancing the semipermeable membrane for the use in RO and FO settings. To maximize water flux, straight pores have been made by using dimethyl sulfoxide (DMSO) crystals as a solvent for polyvinylidene fluoride (PVDF) above its melting temperature. As PVDF is inherently a hydrophobic material, the entrance of water can be hindered, and the flux of water can be slowed down. To address this issue hydrophilic metal-organic frameworks, (MOF) MIL-101 was introduced to the polyamide (PA) active layer of the membrane. The addition of MOF showed higher flux through the membrane but lower salt rejection by increasing the MOF concentration.

## CONTRIBUTORS AND FUNDING SOURCES

This work was supervised by Dr. Choongho Yu of the Departments MSEN/MEEN and the committee members are Dr. Terry Creasy of the Department MSEN, and Dr. Shiren Wang of the Department of ISEN.

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## NOMENCLATURE

CA	Cellulose Acetate
FO	Forward osmosis
H	Hour
P	Pressure
Pa	Pascal
PA	Polyamide
PES	Polysulfone
PRO	Pressure retracted osmosis
PS	Polystyrene
PSF	Polysulfone
PVDF	Polyvinylidene fluoride
RO	Reverse osmosis
s	Second
S	Structural parameter
T	Time
TFN	Thin-film Nano-composite
MOF	Metal–organic framework

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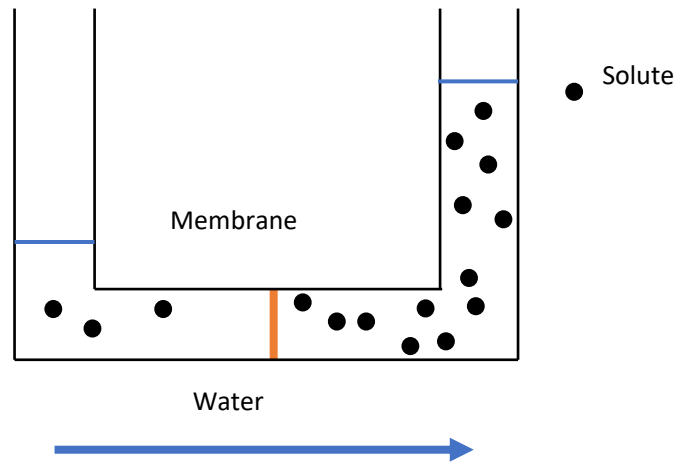
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## 1. INTRODUCTION

### 1.1. What is Osmosis

The diffusion of water across a semi-permeable membrane is called Osmosis. Subsequently, Osmotic pressure is the force that will bar water movement through the semi-permeable membrane (Figure 1.1). Water will continuously cross the membrane from a high to lower potential until the Osmotic pressure pauses the flow.[1] To simulate this phenomena, two solutions of different salinities can be placed on either side of the membrane. [2]



**Figure 1.1 Osmosis pressure; with presence of semi-permeable membrane. The flow can be noticed [3]**

For an ideal solution, the osmotic pressure can be calculated as:

$$\pi=icRT$$

Where  $i$  is the Van't Hoff factor,  $c$  is the molar concentration,  $R$  is the universal gas constant and  $T$  is the operating temperature. [2]

## **1.2. Osmotic Pressure Technology**

Different osmotic pressures make three possible types of osmotic phenomena:

### **1.2.1. Forward osmosis (FO)**

This occurs when the osmotic pressure gradient between low salinity (called feed solution) and high salinity solution (called draw solution) is positive ( $\Delta\pi > 0$ ), and the solutions have the same pressure ( $\Delta P=0$ ). [1]

Based on the equation the osmotic pressure gradient is dependent on the concentration of each solution, so water moves across the membrane from the low-concentration solution to the high concentration side. The FO process has potential in water treatment, pharmaceutical separation and protein enrichment. [1]

### **1.2.2. Pressure-retarded osmosis (PRO)**

If the pressure difference ( $\Delta P$ ) is between 0 and  $\Delta\pi$ , the driving force for osmosis is reduced based on the amount of pressure on the high concentration side. Water will permeate as it did for the FO system, but the flux is lower. The volume will increase on the draw solution until there is an equilibrium ( $\Delta\pi = \Delta P$ ) and the permeation will be halted. [1]

### **1.2.3. Reverse osmosis (RO)**

Currently the most popular of the three; it can be achieved by applying a higher pressure than the osmotic pressure on the high concentration side ( $\Delta P > \Delta\pi$ ). The force drives the water from the high concentration to the low-concentration solution and

potentially leaving slat and other minerals behind. RO systems are famous for their use in the desalination technologies. [1]

### **1.3. Another First Level Subheading**

To take full advance of Osmosis technologies, development of the membrane is key. Membranes can be divided in two categories.

#### **1.3.1. Cellulose Acetate (CA) Membrane**

CAs have high hydrophilicity to boost water flux and reduce fouling, and high resilience toward chlorine attack. On the other hand, they have low tolerance toward pH change.[2]

One of the commercial membranes are cellulose triacetate (CTA) membrane produced in flat sheet or hollow fiber configurations by Hydration Technology Innovations (HTI). (More data at [2])

#### **1.3.2. Thin Film Nano-Composite (TFN) Membrane**

The films are usually made in two steps; first the supporting porous layer and then a thin selective layer on top of it. Different polymers such as Polyvinylpyrrolidone (PVP), Polysulfone (PSF), and Polyvinylidene Fluoride (PVDF) have been tested and studied to improve the flux, and mechanical strength of the membrane. Polyamide (PA) is the most used selective layer polymerized on TFCs. In addition, there is a porous or nonporous nanoparticle added to the selective layer [2]

## 2. LITERATURE REVIEW

### 2.1. Membranes

Organic and inorganic contamination in water is a global issue; several methods have been tested and the osmosis systems seem the most promising. The membrane is the fundamental concept of RO, FO and PRO and should be designed based on the needs.

For example, FO process has several drawbacks; concentration polarization, reverse solute flux, and low permeability, are the main ones which all can be fixed by properly manufacturing the membrane. [3]

### 2.2. Thin film nanocomposite (TFN)

TFNs are membranes with nanomaterial in their active layer; there are three obstacles in this kind of membrane, support layer, active layer, and nanoparticles. [4]

Non-porous Nano particles, e.g. TiO<sub>2</sub>, SiO<sub>2</sub> and Ag, have been extensively studied. Porous Nano particles like metal-organic framework (MOF) have not been studied as much as other Nano materials in FO TFNs. [4]

### 2.3. Metal-organic framework (MOF)

MOFs are organic and inorganic compounds; they are ideal porous materials for TFN membranes. MOFs membranes are widely used as gas absorption and separation, now they are being used as water separation membranes. [5]

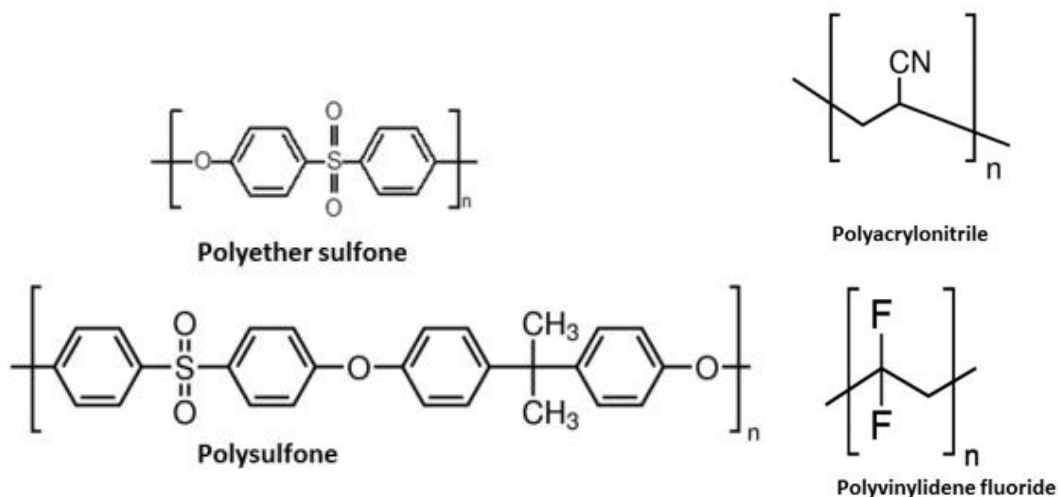
Multiple MOFs, like ZIF-8, UIO-66, and MIL-101 can be used in water as they are hydrostable. [5] Hydrophilic MOFs have pores that can be used as a channel of water

and increase the flux. MIL-101 has a large pore size of 29-34 Å inside its organic-inorganic structure. [6]

#### 2.4. Support layer

The structural parameter (S) is a resistance of the support membrane towards solute diffusion. The smaller the S parameter the better flux performance can be seen in FO process.

The support layer of the membrane is very important factor to have an efficient osmosis system. Multiple substrate have been used, such as polyacrylonitrile (PAN), Polysulfone (PSf), and Poly(ether sulfone) (PES); they have been extensively studied for RO and FO systems (Figure 2.1). [7]



**Figure 2.1** Chemical structure of polymers used for membranes [3]

Poly(vinylidene fluoride) is a thermal stable, chemically resistance polymer with high mechanical strength. The polar polymer can be easily dissolved in most common solvents like N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP). All of these features have made PVDF an attractive choice for commercial water desalination. [8]

Membranes have to be thick and dense in order to withstand the high pressure of water in osmosis systems, but this will cause a phenomenon called internal concentration polarization. [9] As the name suggests, ICP happens inside the porous support membrane and makes polarization, e.g. the salt concertation. This will hinder the osmosis pressure as the salt concentration is the core concept of the osmosis systems, especially in the FO process. To reduce ICP, water has to pass through the membrane as fast as possible to avoid the aggregation of salt inside of the membrane. [10]

Recently there has been a new way to make pores for water in membranes: vertically oriented porous substrates (VOPSs). VOPS can significantly reduce the internal concentration polarization (ICP) that is usually caused by high tortuosity, thickness and low porosity in membranes. [9] Dimethyl sulfone (DMSO<sub>2</sub>) was used as a templet and a solvent for PVDF in the case of the new membrane. DMSO<sub>2</sub> is a solid crystal with melting point of 109.0°C [11], and PVDF is a white powder with a 172°C melting temperature.[12]

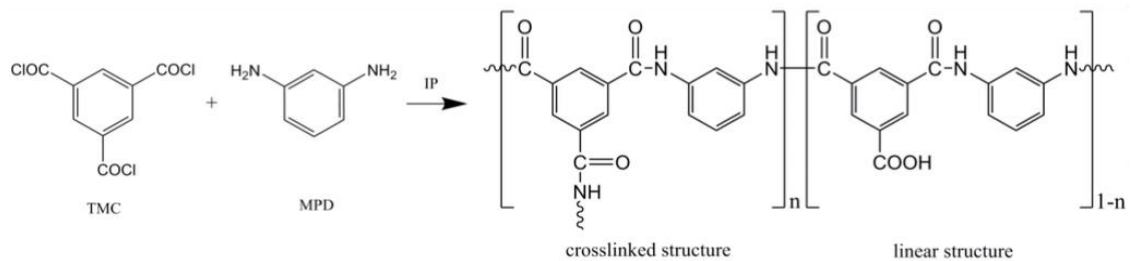
To grow the VOPSs template bidirectional freezing was implemented. By creating two directions of growth the straight holes were guaranteed, the first gradient is

between two plates with different thermal conductance and the second gradient is the added water that forces the pores grow straight. [13]

## 2.5. Active layer

Depositing ultrathin skin layer on the surface of support membrane is the last step to creating an osmosis semipermeable membrane. [14] A process called Interfacial Polycondensation was introduced in 1959 to polymerize Polyamide in a fast reaction. To create polyamide layer on top of a support membrane, two immiscible solutions of an organic solution and an aqueous solution with monomers in each, have to come in contact with each other. [15]

The most commonly used monomers are MPD and TMC, and they are usually used with deionized water and Hexane solvent. [14] The monomers and reaction are schematically shown in Figure 2.2. [16]



**Figure 2.2 TMC and MPD monomers and the interfacial polymerization [16]**



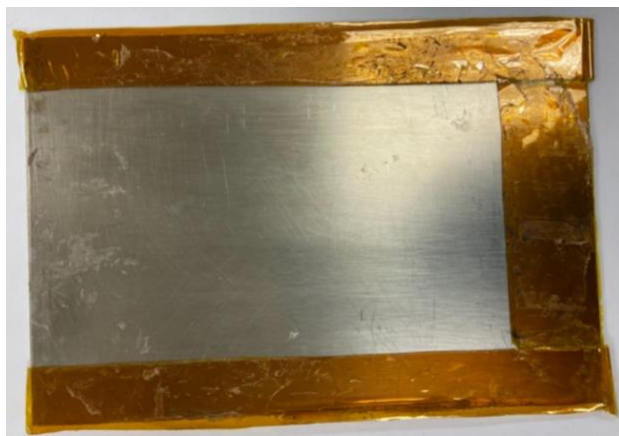
### 3. EXPERIMENT

#### 3.1. Material

PVDF powder (<150,000 Mw) was purchased from BeanTown Chemical as the support material in composite membrane. Dimethyl sulfone (DMSO2 >99.0%), m-Phenylenediamine (MPD flakes, 99%), trimesoyl chloride (TMC, 98%), camphorsulfonic acid (CSA) and sodium dodecyl sulfate (SDS, >95.0%) were obtained from VWR.

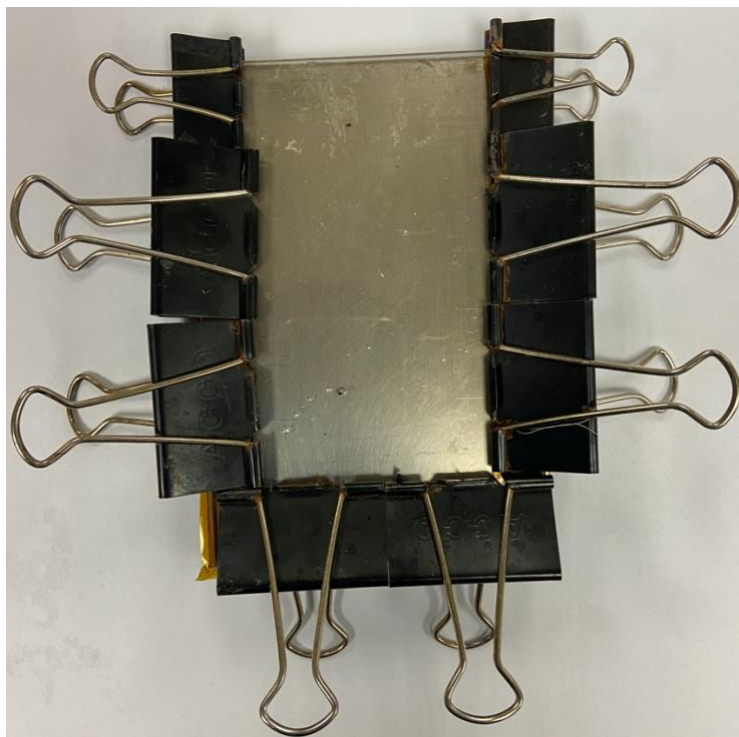
#### 3.2. Creating the mold

To cast the support membrane, we have designed a specific mold. To create a temperature gradient; 10x5x2 mm stainless steel 304 and Borosilicate glass were provided from McMaster-Carr. Kapton tape was used to control the membrane's thickness. (Figure 3.1)



**Figure 3.1. Steel plate with Kapton tape**

To complete the mold, after making a semi-rectangular shape with the Kapton tape on the stateless steel, the two plates are joint together tightly with the help of metal clamps (Figure 3.2).



**Figure 3.2 SS 304 and Glass clamped together**

### **3.3. Preparing the solution**

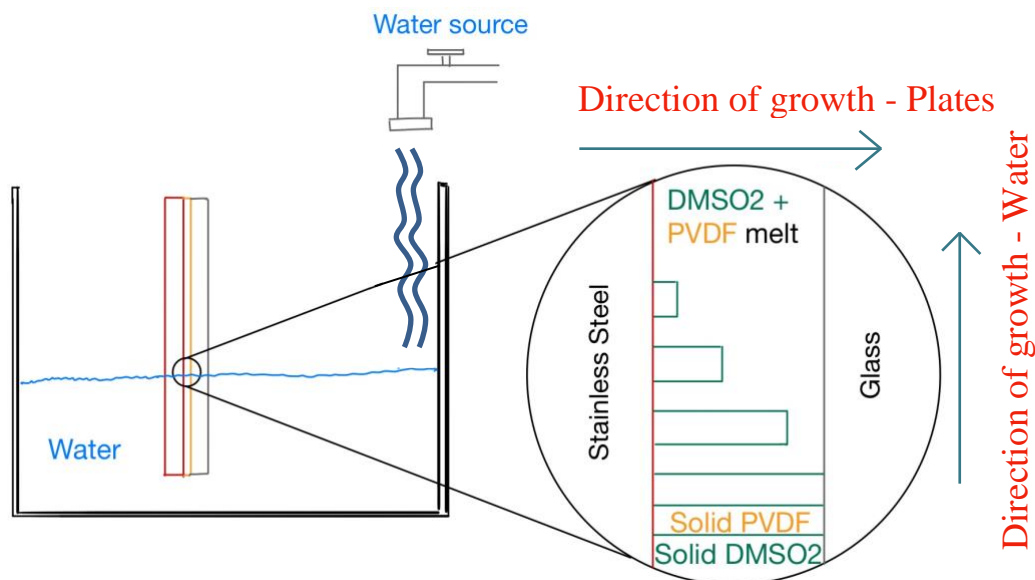
30% PVDF and 70% DMSO<sub>2</sub> were mixed together and placed inside a 170°C conduction oven. After 30 minutes the solution becomes a viscose solution with visible bubble inside. The solution was stirred for several minutes on a hot plate set to 170°C, to make the solution homogeneous.

The bubbles in the solution can cause problems in the casting process. To avoid holes on the membrane, the solution was placed in a 170°C vacuum oven for at least an hour to remove all the bubbles. At the end, we have a clear viscose solution with no bubbles.

### 3.4. Casting polymer membrane

The mold was heated in a 170°C conduction oven for 20 minutes. The stainless steel with Kapton tape was put on a hot plate to 170°C and the homogeneous PVDF/DMSO<sub>2</sub> solution was poured on the plate.

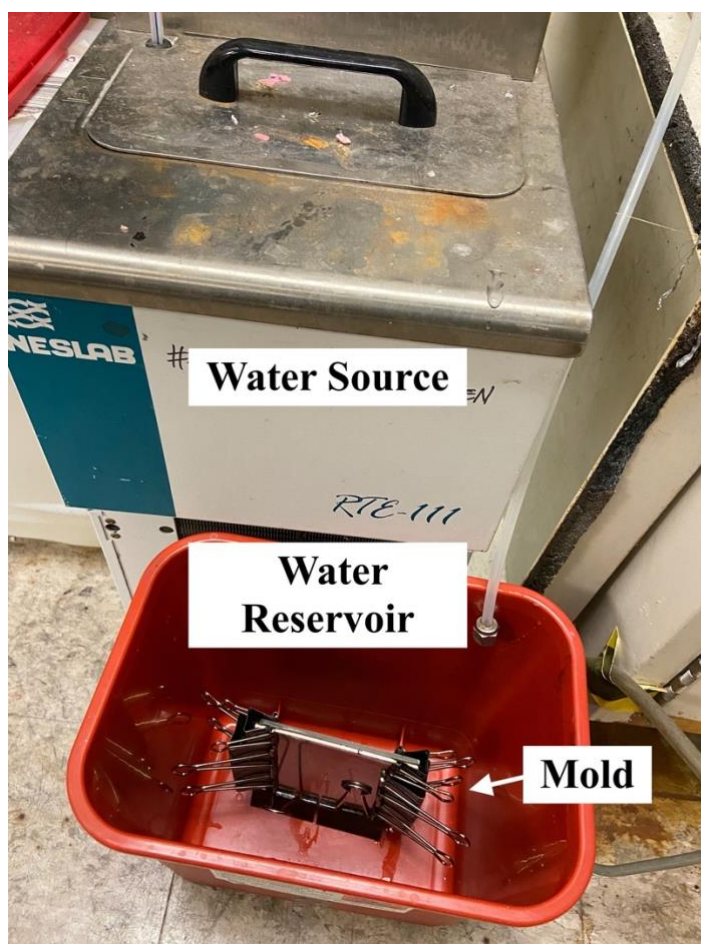
The Steel and glass plates are clamped tightly to avoid any entrance of water in the solution. The direction of the crystal growth is determined by the temperature gradient implemented by the two plates and water (Figure 3.3).



**Figure 3.3. Casting process of PVDF/DMSO<sub>2</sub> between steel and glass plates in water.**

The completed mold is placed in a container and water is added with the rate of 4 cm per min (Figure 3.4). After cooling down, the membrane is removed with the help of a razor blade.

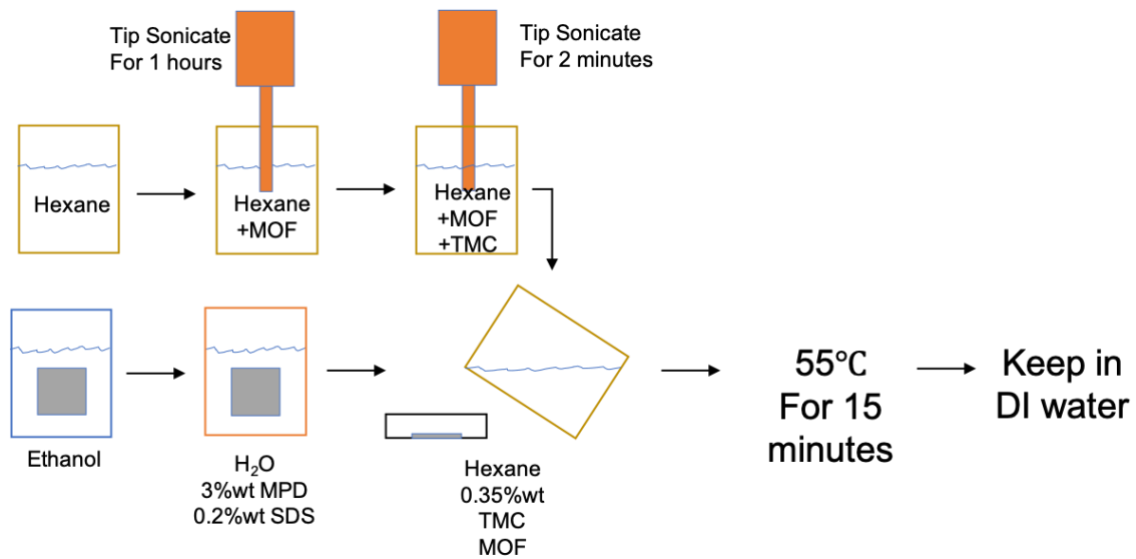
The DMSO<sub>2</sub> is washed away by immersing the membrane in Hexane. The membrane is kept in DI water until further processing.



**Figure 3.4 Adding water to a reservoir with the mold to create the temperature gradient**

### 3.5. Active layer

PA layer was produced by MPD and TMC monomers. To activate the membrane, UV Ozone cleaning machine was used for 5 minutes. To fully wet the pores, the membrane was first immersed in Ethanol for an hour and then washed with DI water. Next the PVDF membrane was immersed in a solution aqueous solution of 2% wt MPD, 2% wt CAS, 0.2% wt SDS for one hour. Afterwards, the excessive solution was removed from the surface of the membrane and 0.15% TMC - Hexane solution was poured on the membrane for 90 second. After the polymerization, the PA layer is curried at 55°C. The completed membranes are kept in DI water until use. (Figure 3.5)



**Figure 3.5 Process of producing the active layer**

### **3.6. Characterization**

Scanning electron microscope (SEM), atomic force microscope infrared-spectroscopy (AFM) and X-ray powder diffraction (XRD) tests were performed to verify the presumptions about the PVDF/PA/MIL-101 membrane.

### **3.7. Mechanical test**

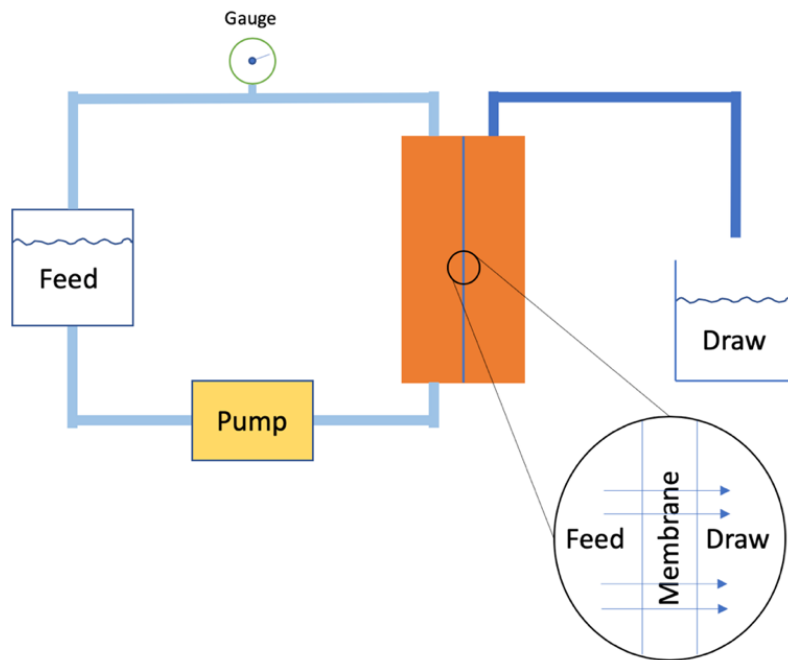
Dynamic Mechanical Analysis (DMA) was used to measure the mechanical strength of the membrane. Stress – strain plot was generated at the end.

### **3.8. Osmosis test**

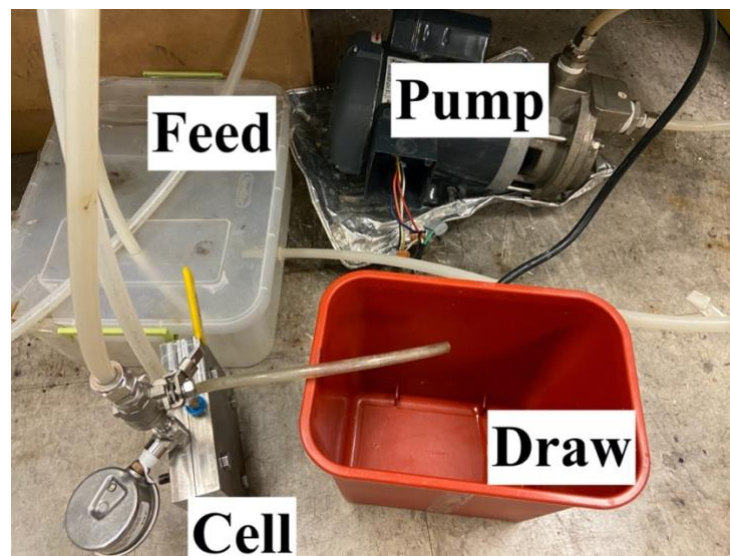
#### **3.8.1. Reverse osmosis test**

Dead-end reverse osmosis test is performed by using a feed solution containing 1000 ppm of NaCl. Water is circulating on the feed side and the pressure is controlled with a value (

Figure 3.6, Figure 3.7). The pressure is set to 3.5 bars on all of the tests in this work. The salinity tester was used on both side of the membrane.



**Figure 3.6 Reverse osmosis system**

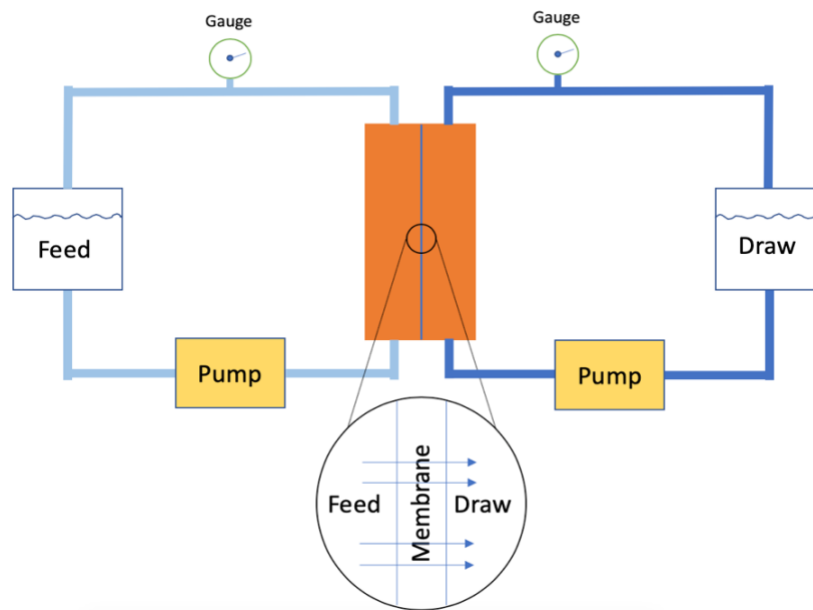


**Figure 3.7 Reverse osmosis setup**

### 3.8.2. Forward osmosis test

Equal pressure on both sides of the membrane is set in the forward osmosis test.

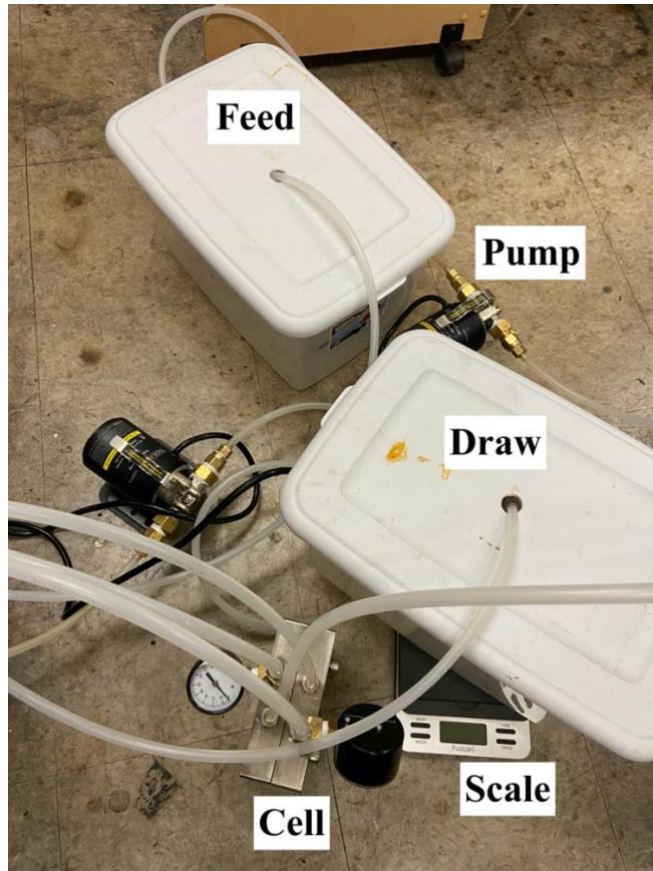
The only pressure driving the transfer of water is the osmosis pressure (Figure 3.8).



**Figure 3.8 Forward osmosis system**

The pressure on both sides are set to 1 bar, but the salinity on the feed side is set to 1000 ppm. The weight of the draw water solution is measured using a scale to determine water transfer rate. (Figure 3.9)



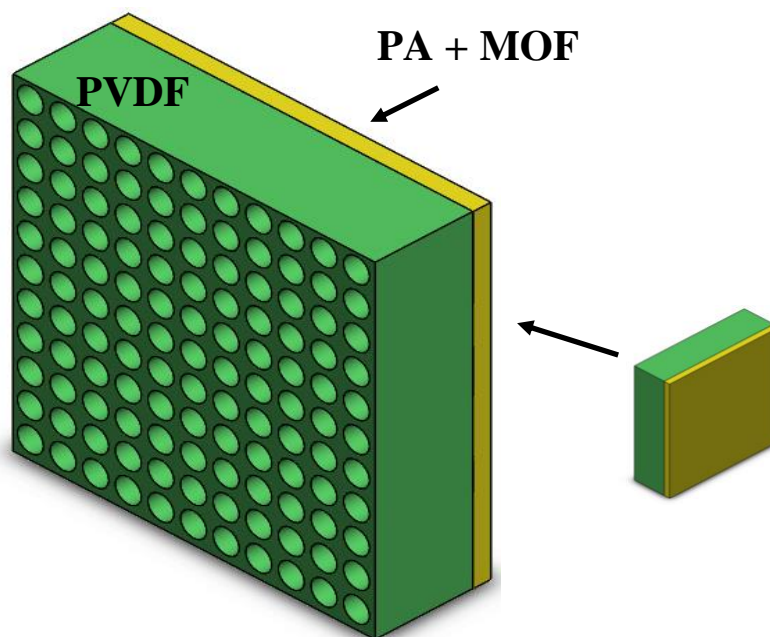


**Figure 3.9 Forward osmosis setup**

## 4. RESULTS

### 4.1. Objective

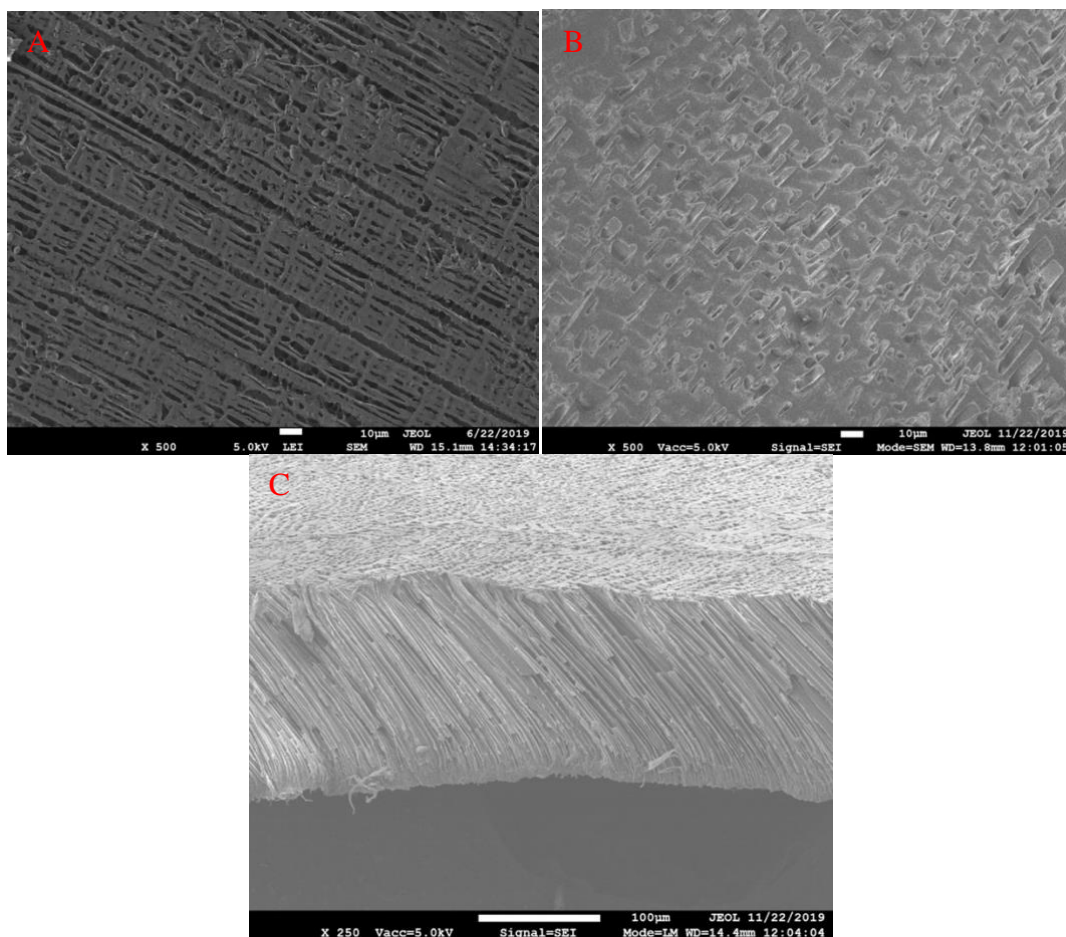
The objective of this work is to have a high-water flux and low salt rejection membrane. To maximize the water flux in RO and FO systems we have produced a support membrane from PVDF with straight holes. The hydrophobic nature of PVDF will help the membrane to reach a very high-water flux. Hydrophilic pores in the membrane can slow down the water with wetting the surface of the pore. [17] The PA selective layer has been added to the surface of the membrane. Hydrophilic MOF-MIL-101 (Cr) was added to the thick active layer to help water pass the membrane easier (Figure 4.1). MOF-101 with a large pore (29 and 34 Å) is used as a good entrance for water during the osmosis process.



**Figure 4.1.** A schematic of the desired membrane

## 4.2. Support layer

The reason that PVDF and DMSO2 were chosen is the close solubility parameter, also the lower melting point of DMSO2 compare to PVDF (Table 4.1). The PVDF support layer was successfully made (Figure 4.3); straight holes with the average of 1.8 micron can be seen in the SEM images (Figure 4.2).



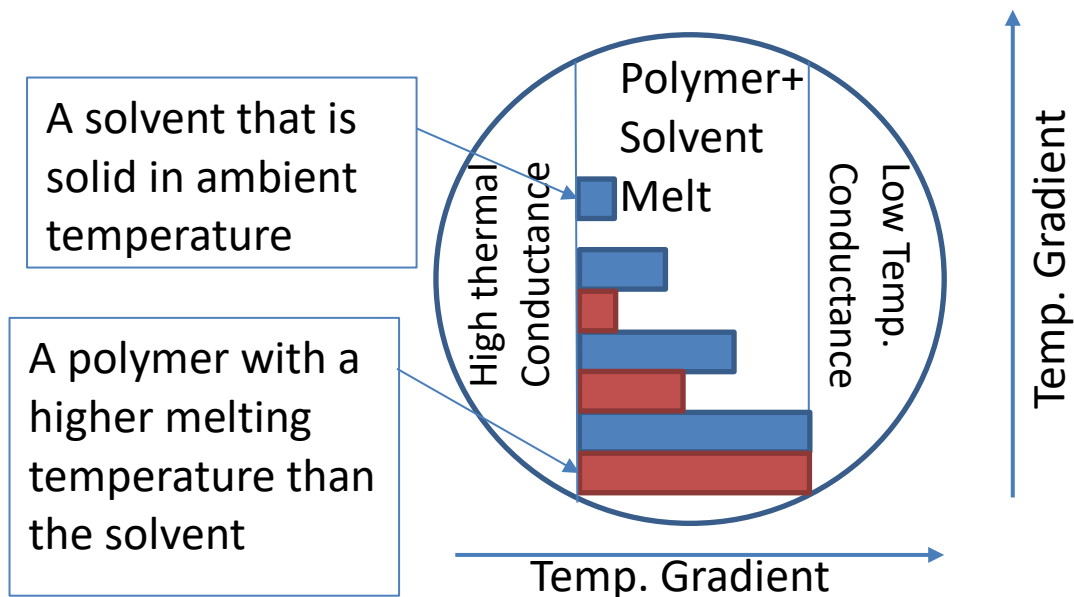
**Figure 4.2. A. Glass and B. Steel side of the membrane, C. cross section of the membrane broke with liquid nitrogen**

**Table 4.1 Solubility parameter and melting point of PVDF and DMSO2**

	<b>DMSO2 (Methylsulfonylmet hane)</b>	<b>PVDF (Polyvinylidene fluoride)</b>
Solubility parameter ( $\sigma$ ) MPa <sup>1/2</sup>	29.9	23.2
Melting Point °C	109	160-170

All the membrane has been made in a mold with thickness set to 200 microns.

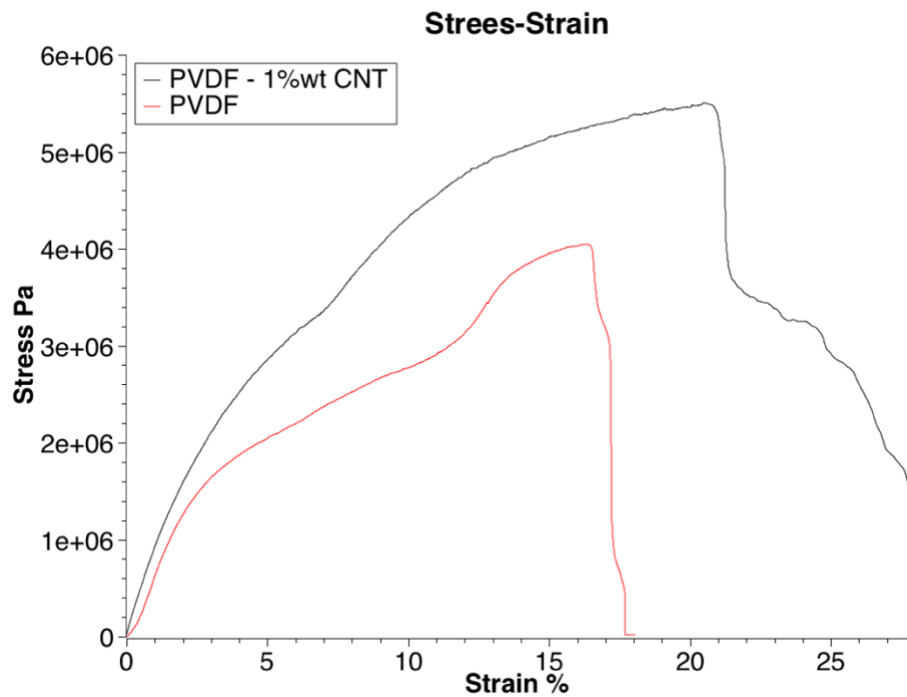
Some measurement variation ( $\pm 10$  microns) has been seen in different membranes, but it is negligible.



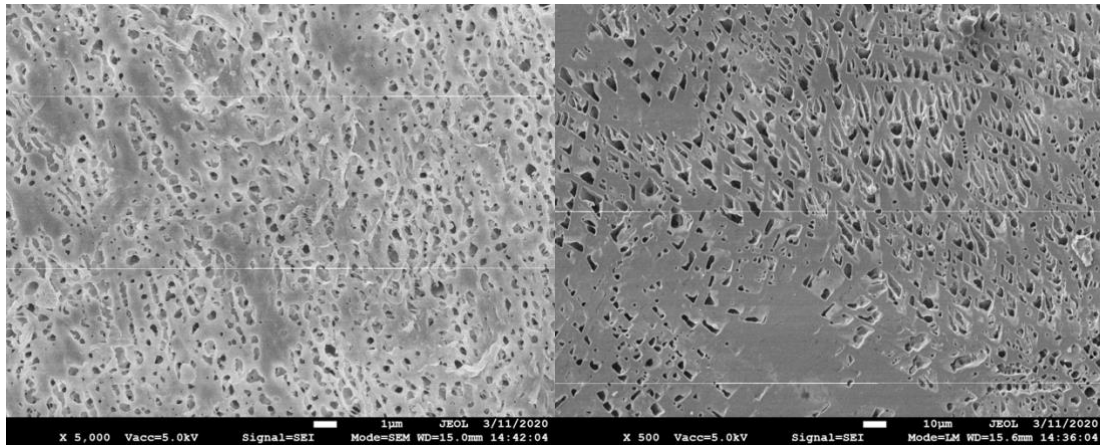
**Figure 4.3 The process of making two temperature gradients**

#### 4.2.1. Mechanical properties of the support layer

The straight pores are necessary to transfer water thru the membrane as fast as possible to avoid ICP. At the same time, the mechanical properties of the membrane have to be measured to determine if it can stand high pressure of water. The membrane has to withstand the water pressure in the RO and FO test. The pressure applied on the membrane in PRO system can be as high as 27 bar (or even more), so the maximum stress that the membrane can maintain is crucial. Compared to the latest work (3.5 MPa)[18], our support layer has a relatively similar behavior (Figure 4.4).

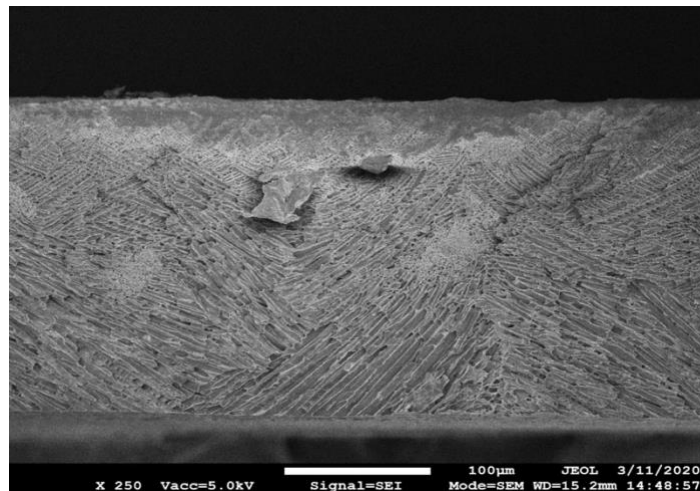


**Figure 4.4 Stress-Strain plot of the PVDF and PVDF – 1% CNT using DMA to measure the strength of the membrane**



**Figure 4.5 A. Glass and B. Steel side of the PVDF membrane**

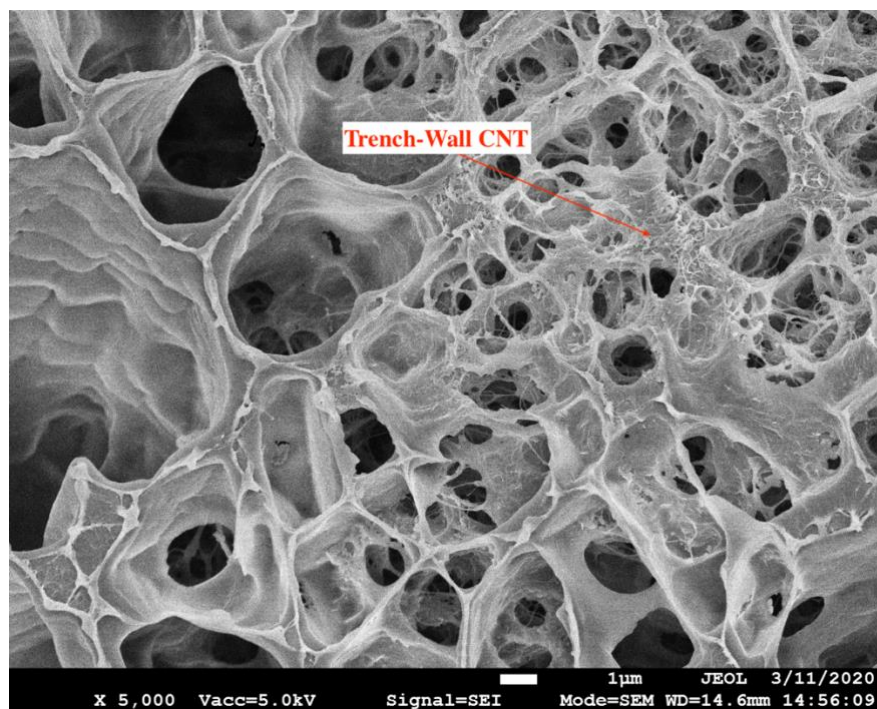
Based on the SEM images at Figure 4.5, the number of wholes on the both surfaces are significantly less than the sample with no CNT. The trench-wall CNT has affected the temperature gradient and the straight pores have gone astray from the desired path. CNT patches can be seen in that have disrupted the growth of DMSO<sub>2</sub>. (Figure 4.6)



**Figure 4.6 Cross section of PVDF with trench-wall**



Figure 4.7 was captured by cutting the membrane with an angle. By doing so, we can see how the wholes look from inside of the membrane, and CNTs can be seen forming around the wholes which can improve the mechanical strength of the membrane.

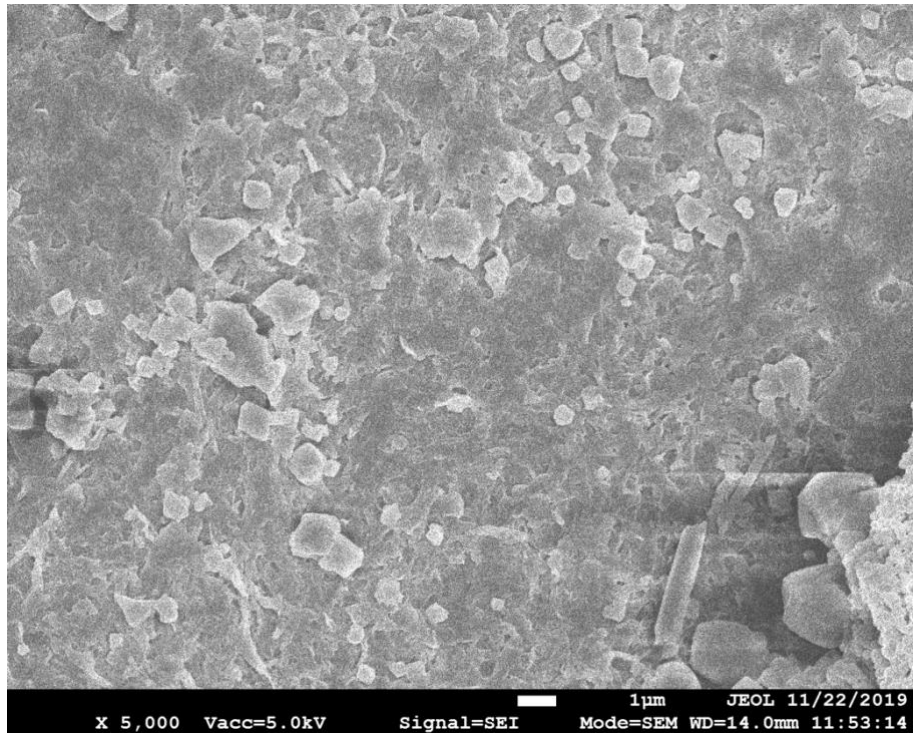


**Figure 4.7** Cross section of the membrane with trench-wall CNTs

### 4.3. Active layer

Coating the surface of the hydrophobic support layer is a challenge; to make sure the active layer has completely covered the surface some preparation has been made.

(Figure 4.8)



**Figure 4.8. Surface of the PA layer**

SEM imaging has shown us that the PA layer covers the membrane with the thickness less than 1 micron, also the MIL-101s are visible as well. (Figure 4.9)



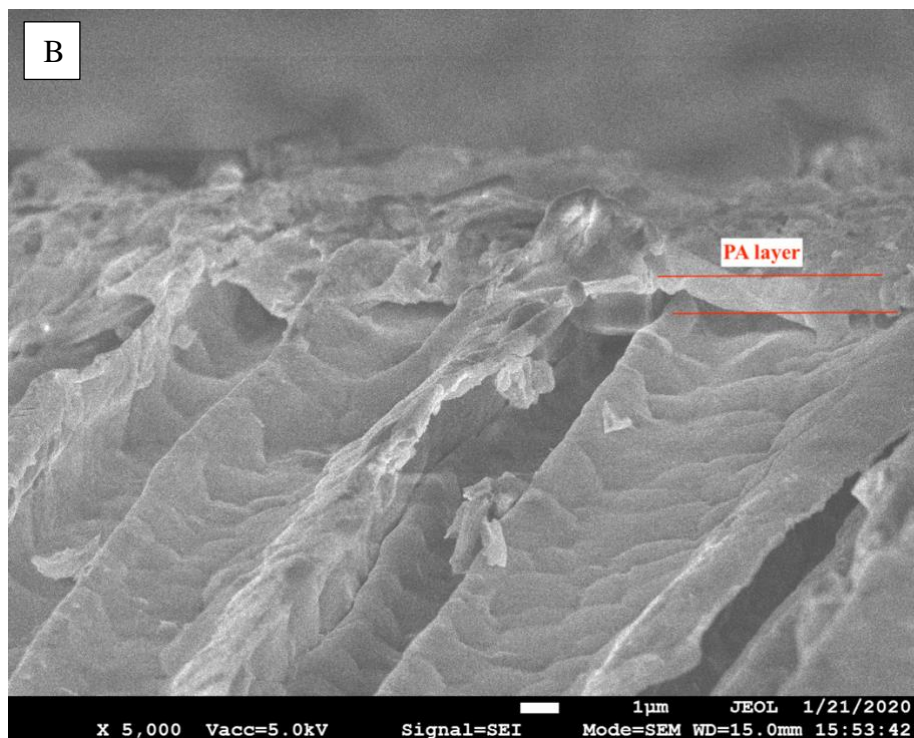
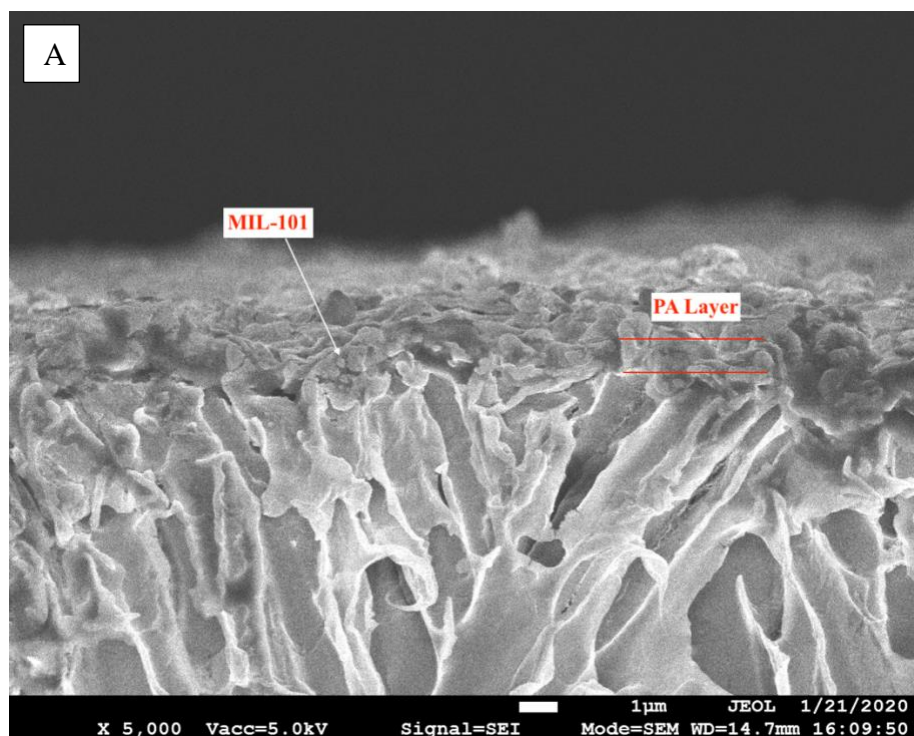
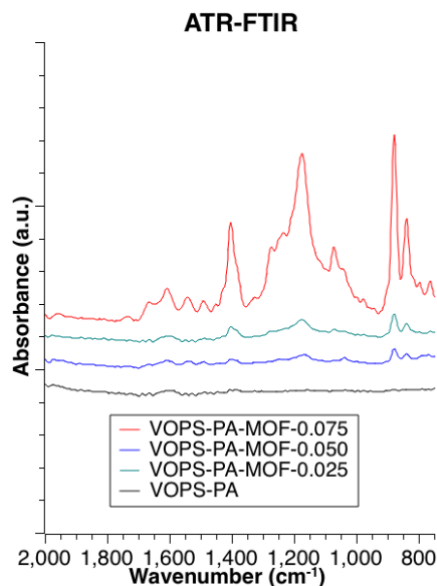


Figure 4.9. Cross section of membrane with the PA + 0.075%v/w MIL-101 layer visible

The MOF-MIL-101 (Cr) was embedded in the active layer. Three combinations of the MOF have been used; samples had 0.025, 0.05 and 0.075% v/w of MOF and were named VOPS-PA-MOF-0.025, VOPS-PA-MOF-0.050 and VOPS-PA-MOF-0.075 respectively. Sample VOPS-PA was produced as the reference sample with only the PA layer and no MOF particles.

For example, UIO-66, and ZIF-8 have been used in multiple research papers. MIL-101 was specifically chosen because of its large 18Å pore diameter compared to the 6 and 11.6 Å pore diameter of UIO-66, and ZIF-8, respectively.

The MOF particles were sonicated for 1 hours using the pin ssonicator with 100% of the power, then the bath sonicator was used to keep the particles afloat before the polymerization process.



**Figure 4.10 ATR-FTIR of VOPS-PA, and three samples with different concertation of MOF MIL-101**

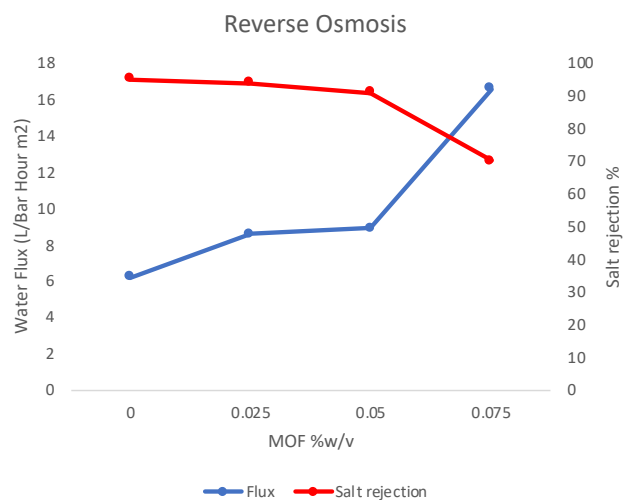
The ATR-FTIR plot (Figure 4.10) shows us the peaks C=O (1660  $\text{cm}^{-1}$ ), C-N (1543  $\text{cm}^{-1}$ ) which indicate the selective layer on the surface of the support layer. In addition, the FTIR shows the bond 1405  $\text{cm}^{-1}$  which are an indication of MIL-101 in the support layer.[5], [18], [19]

#### **4.4. Osmosis testes**

Osmotic pressure is analyzed through the reverse and forward osmosis systems that we have designed.

In the case of RO, with the added 1000 ppm salt to the feed solution, we can measure the salt rejection of the membrane. A bicker is used at the draw solution side to measure the volume of water transferred per hour. The results of the RO test are summarized in Figure 4.11.

As it can be seen in Table 4.2 the water permeability and the salt rejection percentage of our VOPS-PA is higher than the literatures. By adding and increasing MIL-101 to the membrane, the water flux has increased by to 5.6  $\text{L}/\text{Hour} \cdot \text{Bar} \cdot \text{m}^2$ . The VOPS-PA-MOF-0.050 Sample is very close in properties to the VOPS-PA-MOF-0.025 sample but with a lower salt rejection. The continuous PA layer has been disrupted by addition of MOF particles and consequently the salt rejection



**Figure 4.11 Reverse osmosis results**

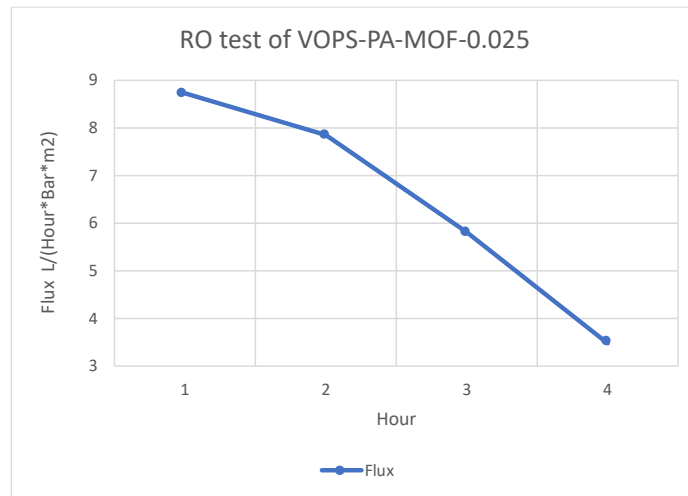
**Table 4.2 RO test results**

	<b>L/(Hour*Bar*m<sup>2</sup>)</b>	<b>Salt rejection %</b>	<b>Citation</b>
<b>VOPS-PA</b>	6.2	95	This work
<b>VOPS-PA-MOF-0.025</b>	8.6	94	This work
<b>VOPS-PA-MOF-0.050</b>	8.9	91	This work
<b>VOPS-PA-MOF-0.075</b>	16.6	70	This work
<b>VOPS-CNT-PA</b>	4.8	95	This work
<b>PVDF-VOPS + PA</b>	4.7	93	[18]
<b>PS + PA</b>	1.6	99	[5]
<b>PS+PA+MIL-101</b>	2.1	99	[5]
<b>Psf + TiO<sub>2</sub> NPs</b>	1.6	97	[20]

The significant advantage of VOPS membrane is apparent in Table 4.2; the PS membrane can only deliver less than half of the flux. It is apparent that the selective layer of the PS membrane is better constructed as it is almost impenetrable by salt. This will be very important in keeping salt on the draw side in the FO process.

Figure 4.14 is showing the same trend of the RO test; by increasing the MOF concentration the flux of water increases. Similarly, the amount of salt transferred from the feed to the draw side has increased by increase of MIL-101.

The membrane containing CNT has a lower flux of water as expected by the SEM images, but at the same time the mechanical strength is apparent.

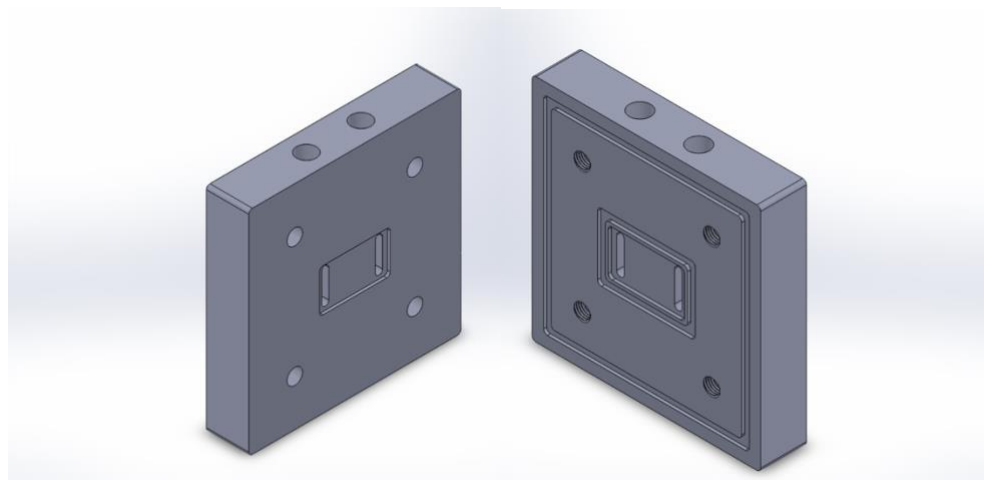


**Figure 4.12 RO test of VOPS-PA-MOF-0.025 for 4 hours**

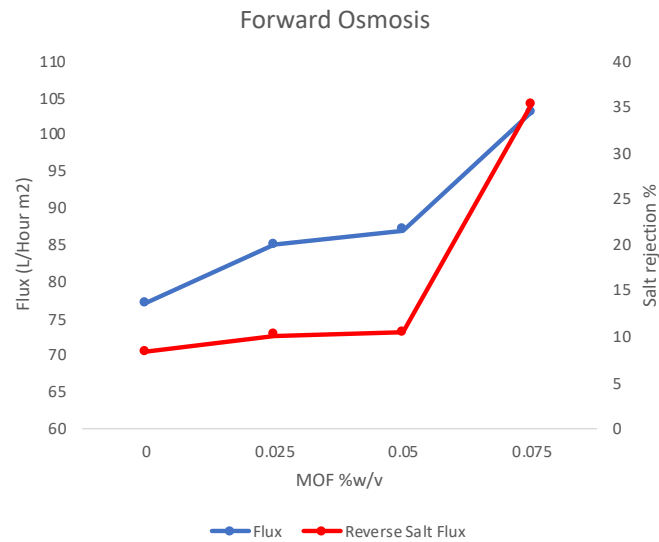
The FO performance was measured by a cell made with stainless steel. The was cell designed (Figure 4.13) and made with help of Computer numerical control (CNC)

machining. 1 Molar of NaCl in DI water was added to the feed side of the FO cell, the only pressure that forces the water to transfer from feed side to the draw side is the osmosis pressure.

The best sample with 0.025% w/v MOF was tested for 4 hours to see how the membrane performs for a long period of time. The sample was not washed between the intervals of 1 hour. (Figure 4.12)



**Figure 4.13 Two sides of the FO cell; the plates are screwed to each other to seal the cell from water leakage**



**Figure 4.14 FO test results**

**Table 4.3 Forward osmosis results with 1 bar on each side and 1 molar of NaCl on the draw solution side**

<b>Name</b>	<b>L/(Hour*m<sub>2</sub>)</b>	<b>Reverse salt flux (g/Hour*m<sub>2</sub>)</b>	<b>Citation</b>
<b>VOPS-PA</b>	77	8.3	This work
<b>VOPS-PA-MOF-0.025</b>	85	10.1	This work
<b>VOPS-PA-MOF-0.050</b>	87	10.4	This work
<b>VOPS-PA-MOF-0.075</b>	103	36	This work
<b>PVDF-VOPS + PA</b>	70.3	7.8	[18]

In Table 4.3, this work has been compared to PVDF-VOPS + PA, they had the same approach of testing and same approach of manufacturing. The results are similar in the base sample, but by adding MOF to the active layer, the flux of water increases by 10 percent. The addition of 0.075% w/v of MIL-101 to the membrane has increased the reverse salt flux to a point that is not efficient.



## 5. CONCLUSION

We have successfully produced a PVDF membrane with straight pores, and MOF MIL-101 imbedded in the PA selective layer. The reverse osmosis test shows that the addition of MIL-101 has achieved an improvement in flux. Still, the salt rejection is lower than the convectional membrane for all VOPS membranes; this problem is solvable by improving the adhesion of the PA layer on the membrane. The salt rejection has been reduced by the addition of MOF; the MIL-101 has disrupted the cautious PA layer and consequently reduced the salt rejection.

The FO test has shown us that MOF particles have been effective in improving the already impressive flux of water. The straight pores have helped water effectively to reduce the ICP, which is a significant issue for FO systems.

Further investigation is needed to improve the salt rejection of the active layer; continuous Polyamide layer is essential to keep the flux of salt to a minimum.

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