SUPERHYDROPHOBIC MODIFICATION OF PVDF MEMBRANES FOR APPLICATION IN MEMBRANE DISTILLATION

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Abstract

Membrane distillation is an emerging technology currently being researched for improvements in order to make it a more competitive separation process. Desalination is the most common application for membrane distillation. During this process, the liquid feed undergoes treatment by directly contacting a porous hydrophobic membrane. Water vapor molecules transfer across the membrane into the permeate feed. This study performed preliminary research on the superhydrophobic modification of polyvinylidene fluoride (PVDF) hydrophobic membranes in order to improve the major disadvantages of this process. Modified membranes were tested on their performance compared to non-modified membranes in direct contact membrane distillation (DCMD). Modification of these membranes were unsuccessful, however, membranes were analyzed in DCMD.

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Chapter 1 Introduction

In the past few decades, China's water scarcity level has increased drastically and continues to increase due to population growth and economic development. This has led China to search for alternative ways to produce fresh water. Seawater desalination proves to be a possible method of renewing its water supply. Unfortunately, the conventional separation processes result in high costs and high energy use. This has led to the need to research alternative desalination processes.

Membrane distillation (MD) is an emerging technology for separation processes that are traditionally completed by conventional methods such as reverse osmosis and multi-stage flash distillation. This developing research has expanded over many decades throughout the world. Membrane distillation proves to be an attractive separation process due to its cost efficiency and ability to use alternative energy sources including solar energy. MD has many applications other than desalination such as wastewater treatment, brine management and food industry. Major drawbacks of MD consist of membrane pore wetting, low permeate flux, high thermal energy consumption and its module design. Due to these disadvantages, the MD process has not yet reached the level of industrialization or even been accepted as a reliable separation process.

During this separation process, only vapor molecules pass through a porous hydrophobic membrane to a permeate stream. The liquid feed, for example, seawater, is in direct contact with a hydrophobic membrane at elevated temperatures. If successfully distillated, none of the liquid feed will be able to penetrate the membrane and contaminate the permeate stream. Recent studies, however, have tried to alleviate this problem. A hydrophobic membrane can separate clean water from the liquid feed to a certain extent; this study investigates how successful this process will be if the surface of the membrane is *superhydrophobic*.

This study will contribute to the preliminary research of the modification on the surface of commercial hydrophobic polyvinylidene fluoride (PVDF) membranes to reach superhydrophobicity. In order to test the performance of the modified membrane, the membrane will be used in direct contact membrane distillation (DCMD). This preliminary research will also contribute to the overall goal of this lab, which is to create PVDF membranes by electrospinning and compare their performance in DCMD to commercial PVDF membranes. This aims to explore the full potential of the MD process and eventually introduce membrane distillation for more promising commercial use. With its many drawbacks, modifying the surface of the membrane is expected to eliminate the main barriers and, as a result, be a competitive separation process for desalination and other water treatments.

Chapter 2 Background

2.1 Water in China

For many years, China, mainly northern China, has struggled with their amount of water supply and water quality leading China to reach severe water conditions. Currently, China's water availability is estimated to be less than 2100 m^3 per capita per year. Table 1 below shows the standards for measuring water scarcity levels [1].

Water availability, m^3 per capita per year	Consequences
<1700	Disruptive water shortage can frequently occur
<1000	Severe water shortage can occur threatening food production and economic development
<500	Absolute water scarcity would result

Table 1. Standards for measuring water scarcity [1].

There are many factors that contribute to China's current water situation including poor water resource management, population growth, rapid economic development and uneven water distribution. Many solutions arise to solve these problems; however, none seem to be effective. China is home to nine major basins that are utilized as water resources [1]. The basins used primarily by northern China are Huang, Huai, Hai and Luan. Table 2 shows the future demand and shortage for these basins. It can clearly be seen that demand will increase and the current means of water supply will not be sufficient.

River	Year	Water Availability	High Growth		Moderate Growth		Low Growth	
			Demand	Shortage	Demand	Shortage	Demand	Shortage
Huang	2030	44.3	57.1	12.8	53.5	9.2	52.3	8
	2050	44.8	60.5	15.7	54.5	9.7	53	8.2
Huai	2030	73.5	85.3	11.8	81.5	8	79.9	6.4
	2050	76.4	89.7	13.3	83.9	7.5	81.6	5.2
Hai & Luan	2030	40.6	56.1	15.5	53.9	133	52.7	12.1
	2050	41.8	58.7	16.9	55.6	13.8	53.7	11.9
Total	2030	158.4	198.6	40.2	188.9	30.5	184.9	26.5
	2050	163	208.9	45.9	194	31	188.2	25.2

Table 2. Water shortage analysis of basins in northern China (km^3/y) [2].

The water supply and quality does not only affect China. These conditions in China have a ripple effect worldwide economically and environmentally. It is pertinent that the water shortage is focused on in order to meet the demands in the future. The Chinese government is well aware of these issues and has improved their water resource management system in order to alleviate their water scarcity and enhance water quality. This includes creating water law and issuing water policy guidance. Unfortunately, certain regulations have not been properly enforced and therefore have made minimal impact to water status in China [1].

This government has also invested time and money to search for new water saving technologies especially in regards to the expansion of irrigated agricultural and increasing demands for urban areas. However, there has been minimal research in water saving technology due to lack of funding [3]. China also tried to spread the water supply equally among China. Hence, the government developed a project called “South- North water transfer project” in 2002. The goal of this project was to transfer water through canals from the Yangtse River to the Yellow River. In Figure 1, the map of the project is shown.

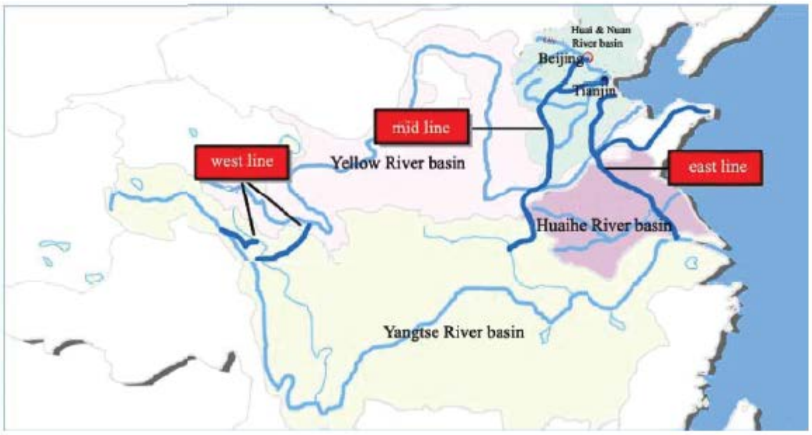


Figure 1. South-North water transfer project [4].

Another solution that seems to have made a breakthrough in China’s water crisis is seawater desalination. China is surrounded by over 18,000 kilometers of coastline which holds over 3,000,000km^2 of ocean seawater [4]. Utilizing this water to create fresh water may hold the potential to rid China of their water shortages.

2.2 Membrane Distillation

The need for clean water has drastically increased. In some parts of the world, as mentioned previously, water supply reaches severe scarcity levels. There are also increases in groundwater salinity and lack of pure drinkable water [5]. Because of this, the demand for water purification rises significantly. Specifically, desalination is the focused means of producing clean and useable water. The process of desalination is the removal of dissolved salts from water, such as seawater and brackish water, therefore producing freshwater. Traditional methods of desalination include reverse osmosis, multi-stage flash distillation, and electrodialysis [6]. Although these separation processes are effective, the need for a more cost- and energy-efficient separation process needs to be researched.

Membrane distillation (MD) is an emerging separation process currently being researched for improvements in the process in order to make it a competitive option for desalination. The MD process proves to be an attractive separation process for many different reasons including the rejection of non-volatile solute by 100%, theoretically, low operating pressure and temperature, and its ability to use solar energy or low-grade heat sources to operate [7]. However, there are many drawbacks to MD that make it unable to be commercialized. These disadvantages include, low permeate flux compared to traditional separation processes, high thermal energy consumption, pore wetting and membrane fouling [8]. All research conducted in regards to membrane distillation strives to eliminate these drawbacks in order for MD to reach its full potential.

2.2.1 History of Membrane Distillation and Past Research

This separation process made its first appearance in 1963. The MD process did not reach the same production level as reverse osmosis, therefore MD was then neglected for many years. In the early 1980's, MD was then noticed again [8]. More advantageous characteristics of MD, including its capability to use alternative energy sources, were discovered which then made this a promising process worth researching [5]. Studies of membrane distillation spread worldwide with an increasing number of published journals in membrane literature.

Research has strived to solve the problems of the main drawbacks of the MD processes. Past research of membrane distillation includes the focus of different microporous polymeric membranes, such as polyvinylidene fluoride, polypropylene, polytetrafluoroethylene and polyethylene, in the MD process, along with different MD configurations including, direct contact membrane distillation, air gap membrane distillation, sweeping gas membrane distillation and vacuum membrane distillation. Generally a hydrophobic membrane is used for the MD process but there has been discoveries made for applications using hydrophilic membranes. However, the new discovery of modifying the surface of a hydrophobic membrane has risen. Research, from A. Razmjou et.al, has concentrated on the modification processes to the surface of different polymeric hydrophobic membranes and their performance in the MD process through various characterization methods. These methods included measurements of the contact angle and liquid entry pressure of the membrane's surface and also microscopic analysis of the membrane by scanning electron microscopy and x-ray photoelectron spectroscopy. [9,10]. Research, from S. Meng et.al, looks into alterative chemicals used in the modification process to deem the most effective solutions. This research also looks into the fouling and crystallization behavior of modified hydrophobic membranes [11,12]. It can easily be seen that the research from MD has increased greatly and there are many prospects for further research in order to commercialize the MD process.

2.2.2 Hydrophobic Membranes in Membrane Distillation

As mentioned previously, hydrophobic membranes are the primary membranes used in membrane distillation. Although hydrophobic membranes are effective in this process, their character does provide several drawbacks in the MD process such as pore wetting which hinders the MD process greatly. Wetting occurs when the feed stream penetrates the pores of the membranes and contaminates the permeate stream. This defeats the purpose of the entire process. In order to prevent this from happening and extending the lifetime of the membrane, current research has focused on modifying the surface of the hydrophobic membrane to reach superhydrophobicity. Superhydrophobicity is expected to alleviate this main disadvantage to make MD a more reliable and attractive separation process. A hydrophobic membrane can separate clean water from the liquid feed to a certain extent; this leads to more research investigating how successful this process will be if the surface of the membrane is *superhydrophobic*.

2.3 Methods of modifying the surface of hydrophobic membranes

In order to properly modify the surface of a porous hydrophobic membrane to reach superhydrophobicity the surface of the membrane can either undergo surface roughening or lower the surface energy material. Either way there are various techniques that can achieve this goal including plasma treatment, sol gel technology and nanoparticle deposition on roughened substrates along with surface fluorosilanization [9]. However, the extent of modifying the surface of membranes is limited due to the many different types of hydrophobic membranes. The processes that are focused on for this study are the roughening of the surface by a low temperature hydrothermal process then reducing the surface free energy of the surface by surface fluorosilanization.

2.3.1 Low Temperature Hydrothermal Process

Using a low temperature hydrothermal (LTH) process to roughen the surface of a polymeric hydrophobic membrane contributes to the modification of membranes to reach superhydrophobicity. The aim of this process is to roughen the surface by creating a hierarchical structure on the surface. LTH processes generate nano-composite coatings that can achieve this structure [10]. A number of nanocomposites materials are considered for roughening the surface of the membrane. Titanium dioxide (TiO_2) nanoparticles are used in this process. The TiO_2 nanoparticles generate self-cleaning surfaces by first turning the surface of the membrane superhydrophilic after exposed to UV light [9]. From this initial step to the overall modification process, the surface of the membrane is able to reach both extremes; superhydrophilicity and superhydrophobicity. The use of TiO_2 in LTH plays a pertinent role in altering and determining the final wettability of the membrane surface [12].

2.3.2 Surface Fluorosilanization

Both the low temperature hydrothermal coating process and surface fluorosilanization need to be used together in order to alter the surface of a hydrophobic membrane to be superhydrophobic. When TiO_2 is bonded to the surface of the membrane, this allows access for fluorosilanization to take place on the surface of the membrane, therefore producing a superhydrophobic surface. Figure 2 below, displays the interactions between these two steps in the modification process. These interactions to the surface of a TiO_2 modified membrane lead to a water repellent layer, hence a more hydrophobic surface [9,10,11].

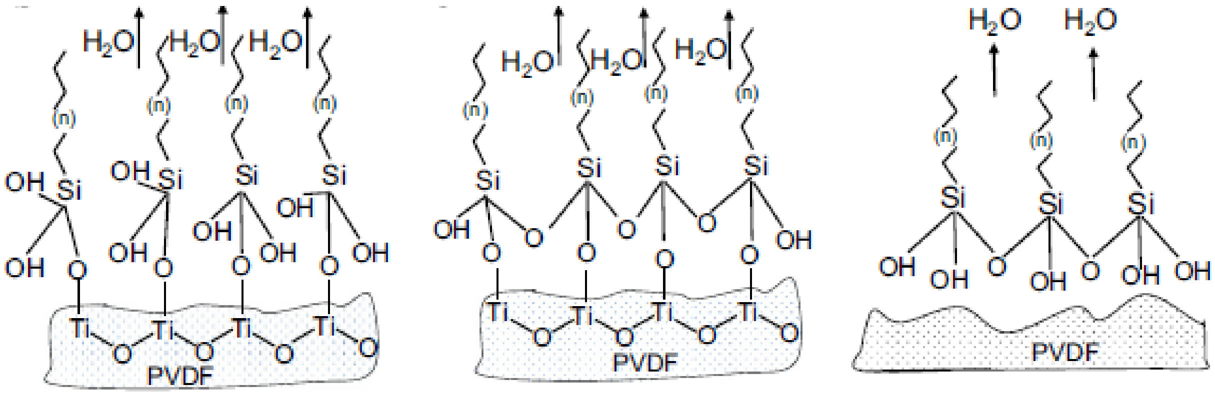


Figure 2. Proposed scheme for the silanization of the PVDF membranes [9].

2.4 Membrane Distillation

Membrane distillation is a thermally driven process, where hydrophobic membranes allow passage of only vapor molecules. The feed stream needs to be treated and is in direct contact with the membrane. Due to the hydrophobicity of the membrane and its surface tension forces, the membrane cannot be penetrated by the feed stream to the permeate stream. Liquid-vapor interfaces are created at the pores of the membrane, therefore, allowing only water vapor molecules to pass through the membrane. The driving force of the membrane is the vapor pressure difference that can be found in four different types of membrane distillation configurations: direct contact membrane distillation, air gap membrane distillation, sweeping gas membrane distillation and vacuum membrane distillation [8,13,14]. These four MD configurations, seen in Figure 3, are all currently under research and each configuration specializes in certain MD applications.

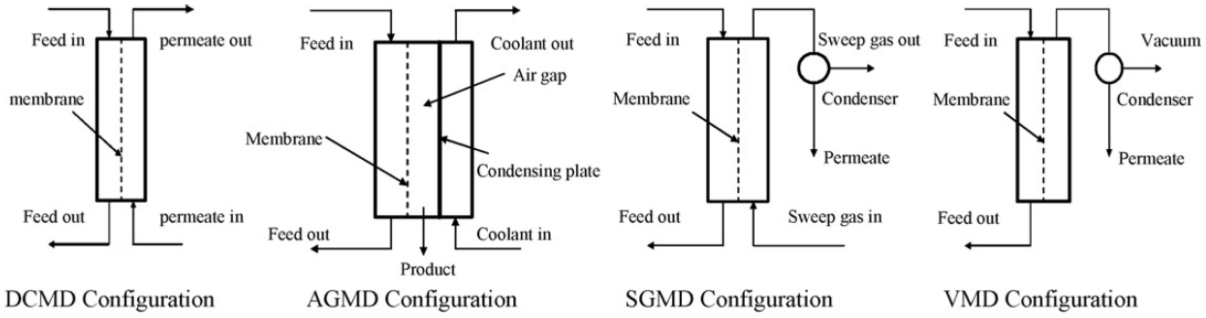


Figure 3. The different types of membrane distillation configurations [8].

2.4.1 Direct Contact Membrane Distillation (DCMD)

In direct contact membrane distillation (DCMD), the hydrophobic membrane is in direct contact with both the feed and the permeate streams. The feed stream operates at high temperatures (50-90C), while the permeate stream is at room temperature. Due to the vapor pressure difference, the vapor molecules evaporate across the membrane and condense in the cold liquid (permeate stream) [8].The DCMD applications include desalination and concentration of aqueous solutions in food industries [13]. The advantage of DCMD is that it is the simplest configuration amongst the four. The disadvantage is its heat lost by conduction.

2.4.2 Air Gap Membrane Distillation (AGMD)

Air gap membrane distillation (AGMD) is similar to DCMD. However, the membrane is only in direct contact with the feed solution and there is stagnant air in between the membrane and the permeate stream [13]. In AGMD, the vapor molecules cross the membrane, from the feed side, and condense over the cold surface inside the membrane module. Because of this air gap, the heat loss by conduction decreases. AGMD can also be applied to desalination and removing volatile compounds from aqueous solutions. The main disadvantage of this configuration is the additional resistance to mass transfer.

2.4.3 Sweeping Gas Membrane Distillation (SGMD)

Inert gas is used in sweeping gas membrane distillation (SGMD) to sweep the vapor molecules at the permeate side of the membrane. The vapor molecules then go through a condenser and enter the permeate solution. The inert gas also reduces the heat loss by conduction. A barrier for SGMD is the need for large condensers due to the small volume of permeate that diffuses in a large sweep gas volume [13]. The main application of SGMD is the removal volatile compounds from aqueous compounds.

2.4.4 Vacuum Membrane Distillation (VMD)

A pump is used in this configuration, vacuum membrane distillation (VMD), to create a vacuum in the permeate side of the membrane. After the vapor molecules cross the membrane, they are condensed in the vacuum and continue onto the cold permeate solution. Like, AGMD SGMD, there is reduced heat lost by conduction. It also operates with a higher permeate flux than any other MD configuration [8]. However, condensation is required to take place outside of the membrane module, which makes it more complex to operate.

2.4.5 Heat and Mass Transfer in DCMD

Direct contact membrane distillation is the focused MD configuration of this study. Looking deeper into how DCMD operates, heat and mass transfer of this MD configuration is analyzed. This can also be applied to other MD configurations. The MD process simultaneously involves both heat and mass transfer. However, heat transfer is believed to be the rate controlling step [8]. Below, Figure 4, is the temperature profile of the MD process that illustrates the heat and mass transfer in DCMD.

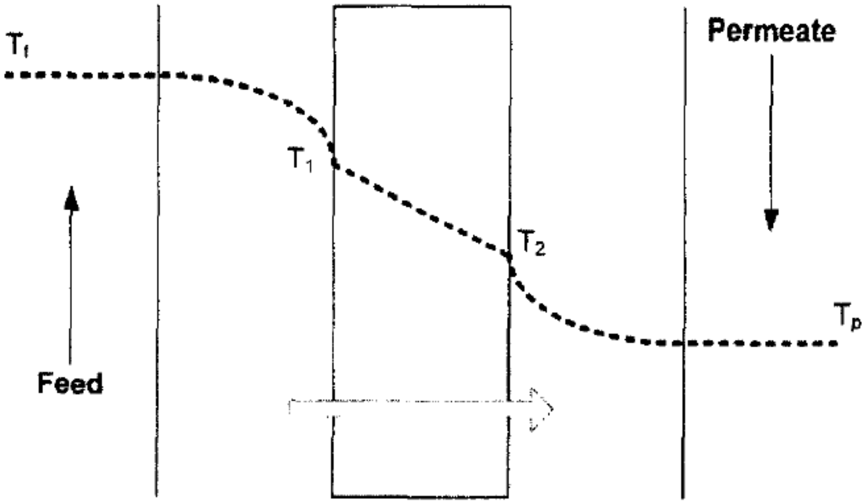


Figure 4. Schematic of the temperature profile across a membrane [14].

The mass transfer in the MD process can be seen as a linear function involving the vapor pressure difference across the membrane [15]. The mass flux, J, is given by:

$$J = C(P_1 - P_2)$$

where, C is the MD coefficient, and P_1 and P_2 are the partial pressures of water vapor determined at the membrane surface temperatures T_1 and T_2 [14]. For heat transfer, there is heat transferred from the feed solution to the permeate stream, seen in Figure 4, when heat crosses through the thermally boundary layer to the permeate stream [8]. This creates temperature polarization effects that occur in the MD process [16]. Using T_1 and T_2 from Figure 4, the temperature polarization coefficient (τ) can be found given by:

$$\tau = \frac{T_1 - T_2}{T_f - T_p}$$

2.5 Characterization of Superhydrophobic Membranes

As mentioned earlier, the modification of hydrophobic membranes to superhydrophobicity is an important research ground for improving the MD process. In order to determine and predict the performance of the modified membrane, a few characterization methods must be used. These include contact angle, x-ray photoelectron spectroscopy and scanning electron microscopy. During the MD process, liquid entry pressure is determined for the membrane which gives information about the parameters the membrane can operate at in MD.

2.5.1 Contact Angle

Contact angle is a measurement that can be used as direct method to characterize the hydrophobicity of a surface. Generally, a goniometer is used in order to measure the contact angle. Depending on the study, any liquid can be used to determine the contact angle of that certain liquid to the surface. In Figure 5, a comparison of images of the contact angle from a hydrophobic and superhydrophobic surface can be seen.

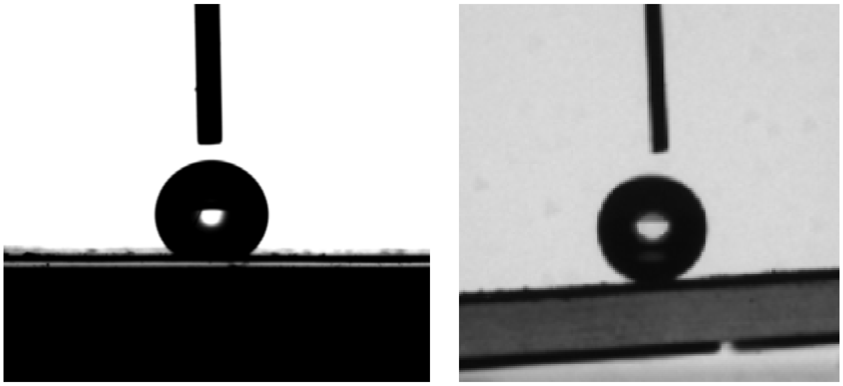


Figure 5. Comparison of the contact angle picture of a hydrophobic surface (left) and a superhydrophobic surface (right) [9].

In order for the surface of a membrane to be superhydrophobic, the contact angle of a liquid must be 150° or greater. At this hydrophobicity, the membrane possess the ability to self-clean the liquid off of itself.

2.5.2 Scanning Electron Microscopy (SEM)

Field emission scanning electron microscopy (SEM) is used in order to observe the surface microstructure of the membrane, which determines the surface topography and pore structure of the membrane. As seen in Figure 6, the thickness of the membrane material is thicker for that of the superhydrophobic membrane compared to the hydrophobic membrane. It is important to view the SEM images of a virgin and modified membrane to determine the effectiveness of the modification process. This can determine if a step in the modification process was not properly completed and if the coating sol-gel and fluoro-silane layer penetrated the membrane [9].

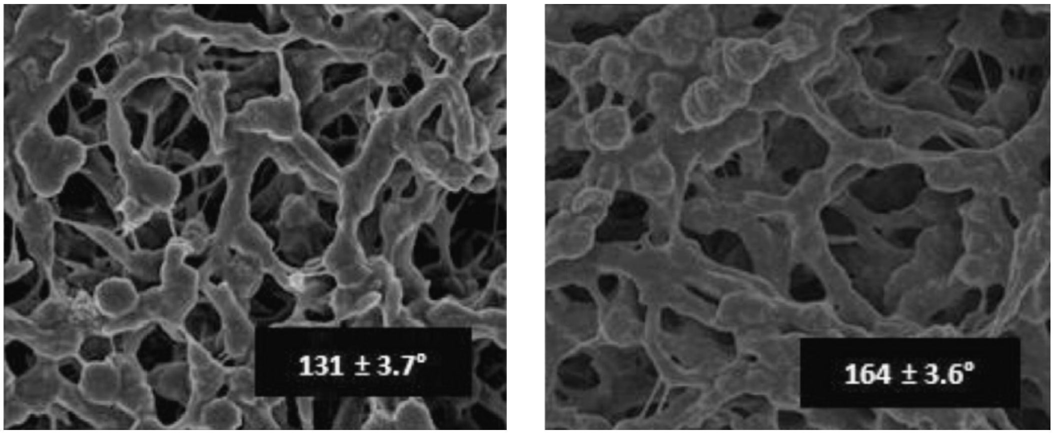


Figure 6. SEM images for hydrophobic and superhydrophobic membranes. The contact angles are on the bottom right side of the images [11].

2.5.3 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) examines the surface chemistry of the PVDF membranes. During this procedure, X-rays are exposed onto the surface of the membrane and eject electrons from the core energy levels of the atoms present. The electrons with lower energies are taken into a vacuum spectrometer to create a spectrum. The spectrum includes detailed peaks that provide the elemental analysis or the surface composition of the membrane surface. This can also be useful in determining the correct methods of a modification process to these membranes. This analysis shows if the coating sol-gel and fluoro-silane are successfully presented on the membrane surface.

3.0 Methodology

The attraction of membrane distillation for water purification has amplified. In order to understand the cost efficient process of the modification of commercial hydrophilic and hydrophobic membranes, membranes will be investigated by direct contact membrane distillation to gauge the success of the modification process.

3.1 Project Objectives

The primary goal of this project was to modify commercial PVDF membranes focusing on the different parameters (including time, speed and volume) of the modification process of PVDF membranes.

Under the direction of Professor Jiahui Shao, from Shanghai Jiao Tong University, the trajectory of this project included creating a modified membrane that would be suitable for the separation processes in real life applications. The performance of the membranes in direct contact membrane distillation, before and after modification, was investigated using sodium chloride as a model foulant.

3.2 Theoretical

In order to determine the performance of virgin and modified membranes in direct contact membrane distillation, membrane flux and conductivity were measured.

3.2.1 Membrane Flux Analysis

To calculate the flux of membrane, the following equation was used:

$$J = \frac{v}{A}$$

$$where : v = \frac{m_p}{\rho \Delta t}$$

J is the volumetric flux of the permeate stream [m/s], v is the volumetric flowrate of the permeate [cm^3/s] and A is the membrane surface area (0.00096 mm^2). The volumetric flowrates were calculated using the mass of the permeate tank throughout a period of time. The density of water [1 g/cm^3] was used. The mass of the permeate sample [grams] was m_p. Lastly, Δt was recorded as the time [seconds] that the sample of the permeate mass was measured.

3.2.2 Membrane Conductivity and Rejection Analysis

An electrical conductivity meter (EC meter) was used to measure the conductivity of the feed and permeate stream. In the results for conductivity, only the permeate stream conductivity was analyzed. However, in order to measure the rejection of the membrane, both the conductivity of the feed and permeate stream were needed. Rejection was measurement by the equation below:

$$Rejection = \frac{F_C - P_C}{F_C}$$

Where F_C is the conductivity of the feed stream and P_C is the conductivity of the permeate stream.

3.3 Materials and Equipment

Commercial hydrophilic and hydrophobic polyvinylidene fluoride (PVDF) flat-sheet membrane HVHP (purchased from Millipore, nominal pore size: 0.45 µm, porosity: 75%) was used in this study. Pluronic F127 and Titanium (IV) iso-propoxide were purchased from Sigma Aldrich. 1H, 1H, 2H, 2H-perfluorododecyltrichlorosilane (FTCS) was purchased from Aladdin. 2,4-pentanedione was purchased from Alfa Aesar. Toulene, Ethanol, and Perchloric acid (70%) were purchased from the SJTU chemistry stock room.

Below are the two pieces of equipment that are vital to characterize the modified PVDF membranes. In Figure 7A, the contact angle of ultrapure water of the membranes was determined by the goniometer. As seen in Figure 7B, the direct contact membrane distillation configuration tests the performance of the modified membranes compared to the virgin PVDF membranes.

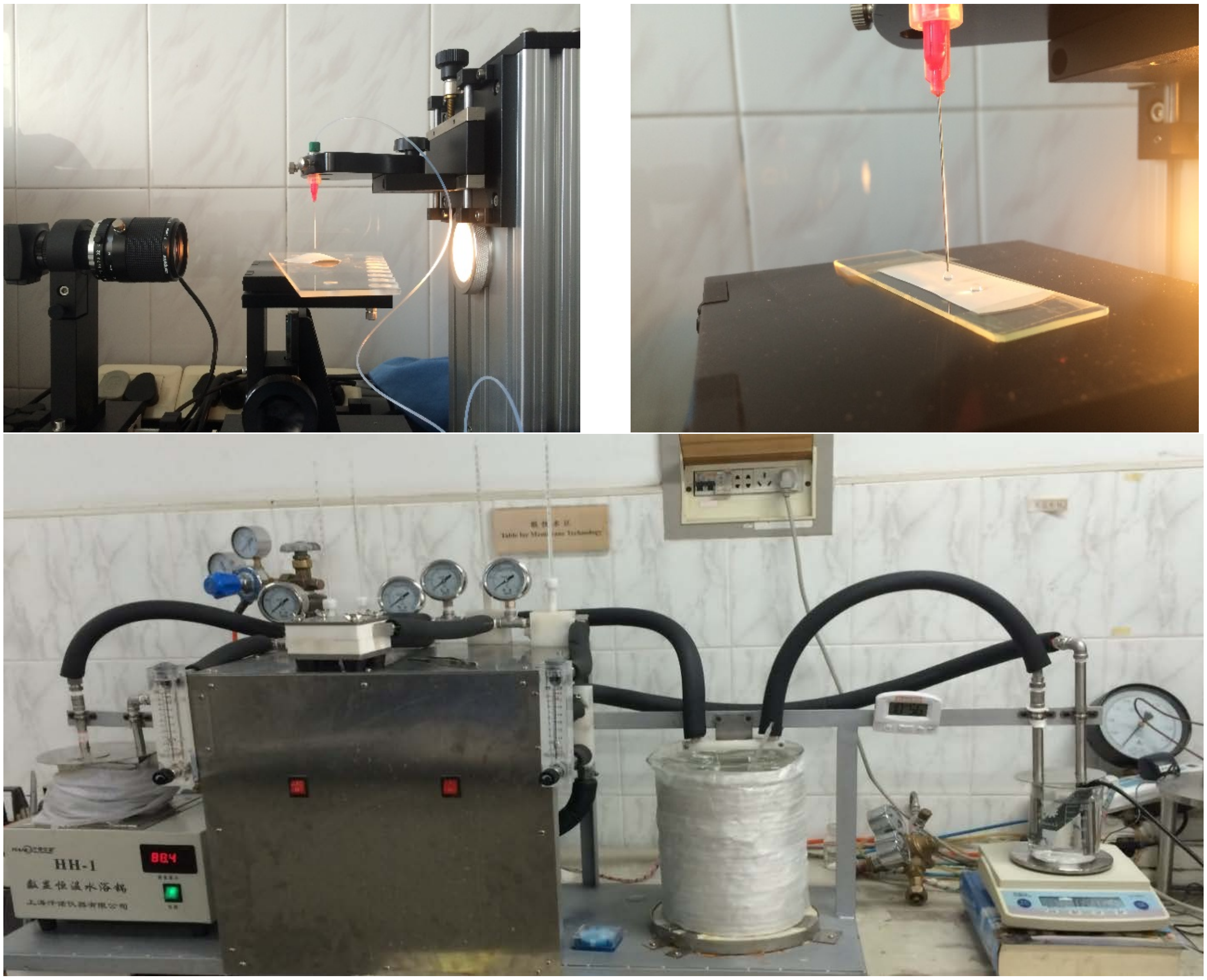


Figure 7A. Goniometer measuring the contact angle of modified and virgin membranes. B. Direct contact membrane distillation configuration.

3.4 Experimental

3.4.1 Superhydrophobic and hydrophobic modification of commercial PVDF membranes

Each membrane was coated with a TiO_2 solution followed by fluorination through vacuum filtration with FTCS solution in order to create a superhydrophobic surface.

Solution Preparation

For the TiO_2 coating sol-gel solution, pluronic F127 (templating agent) was mixed in ethanol (70 vol%) until the solution was completely dissolved. Under the fume hood, 2,4-pentanedione, perchloric acid, and Titanium (IV) iso-propoxide were added to the pluronic F127 and ethanol solution and then mixed with a magnetic stirrer at a speed of 650 rpm. Ultrapure water was added drop-wise (to avoid the creation of foam at the surface of the solution) while the solution was still stirring. This solution remained stirring for one hour. The pH of this solution was 1.2.

For the 1H, 1H, 2H, 2H-perfluorododecyltrichlorosilane (FTCS) solution, an ice bath was needed in order to decrease the temperature of toluene down to 0°C and -5°C. The toluene had to remain at this temperature and be sealed for the duration of the experiment. Once toluene reached the desired temperature, FTCS was added to the toluene. FTCS was mixed with toluene until it was completely dissolved using a magnetic stirrer and a speed of 650 rpm [1].

Modification Process

TiO_2 nanoparticles were coated onto the PVDF membranes by a low temperature hydrothermal process, explained previously in section 2.3.1. The membranes were dip-coated in the TiO_2 sol-gel solution under the conditions seen below in Table 3. The time correlates to the duration the membrane remained submerged in the solution. The speed represents how fast the membrane was retracted from the solution. After, the coated membranes were dried in the oven for 1 hour at a temperature of 120°C in order to remove solvent and any other volatile chemicals in the sol-gel. Following the heat treatment, the membranes were transferred into a beaker filled with ultra-pure water for a hot bath treatment for 2 hours at 90 °C. During the bath treatment, the templating agent, Pluronic F127, detached from the membrane. This was seen as floating particulates in the bath along with weakly bonded TiO_2 [12]. After the hot bath treatment, the membranes were rinsed with UP water and placed under a UV light for 6 hours in order to decompose any remaining organic residuals [12]. These membranes were labeled TiO_2-PVDF.

Time Speed	4 sec	8 sec	12 sec	16 sec	20 sec	30 sec
4 mm/min						
8 mm/min						
12 mm/min						
16 mm/min						
20 mm/min						
30 mm/min						

Table 3. Parameters for withdrawal speed and dip coating time of PVDF membranes.

The fluorination, explained in section 2.3.2, of TiO_2-coated PVDF membranes was accomplished by a vacuum filtration. The TiO_2-coated PVDF membranes were fixed to a Buchner Funnel attached to a conical flask vacuum pump. For wetting purposes, the membranes were first filtered with minimum volume of toluene (~5mL). Following the toluene, the FTCS solution (~30mL) was then filtered through the membranes. At the end of the filtration, the membranes were removed and rinsed with 10mL of fresh toluene to remove any residuals on the surface of the membrane. The fluorinated membranes were then transferred into a covered petri-dish and placed in an oven for two hours at 120°C. Lastly, backwashing of each membrane with ethanol (30vol%) was performed for five minutes (~200mL) to open the plugged pores by residuals for fluorosilanization. Membranes were placed in individual bags after the ethanol evaporated completely. These membranes are labeled FTCS-TiO_2-PVDF.

3.4.2 Membrane Characterization Using Contact Angles

In order to characterize each membrane, the hydrophobicity of the surface was determined by contact angle measurement. The sessile drop method was used in the contact angle goniometer. Other parameters are located in Table 4 below. A syringe would release a droplet of water on the surface of the membrane. A high speed camera simultaneously captured the initial contact between the membrane surface and the droplet. The contact angle would then be calculated by using the "Conic" computation program with the software of the goniometer. In order for the surface of the membrane to be superhydrophobicity, the contact angle needed to be >150°. The average of at least five measurements was recorded. The effects of dip coating time and withdrawal speed of the modification process were studied.

Contact Angle Goniometer Parameters	
Camera Settings	
Brightness	53
Contrast	255
Gamma	0.53
Droplet Settings	
Type	Sessile Drop
Volume	5
Rate	100
Computation Settings	
Method	Conic

Table 4. Goniometer operating parameters.

3.4.3 Direct Contact Membrane Distillation

Direct contact membrane distillation (DCMD) was used in order to determine the performance of both the virgin and FTCS-TiO_2-PVDF hydrophobic membranes. The feed solution used in this experiment was sodium chloride (3.5wt%) to model seawater as a foulant. The permeate solution was ultrapure water. The DCMD, a schematic shown in Figure 8, operated in a counter current flow to reach the highest temperature driving force. In this membrane distillation process, virgin PVDF hydrophobic membranes were fouled at different temperatures to determine the effects of rising temperature on the performance of the membranes. FTCS-TiO_2-PVDF membranes were tested at the optimized temperature found with virgin membranes, thus temperature was a controlled variable. The parameters of the DCMD can be seen in Table 5.

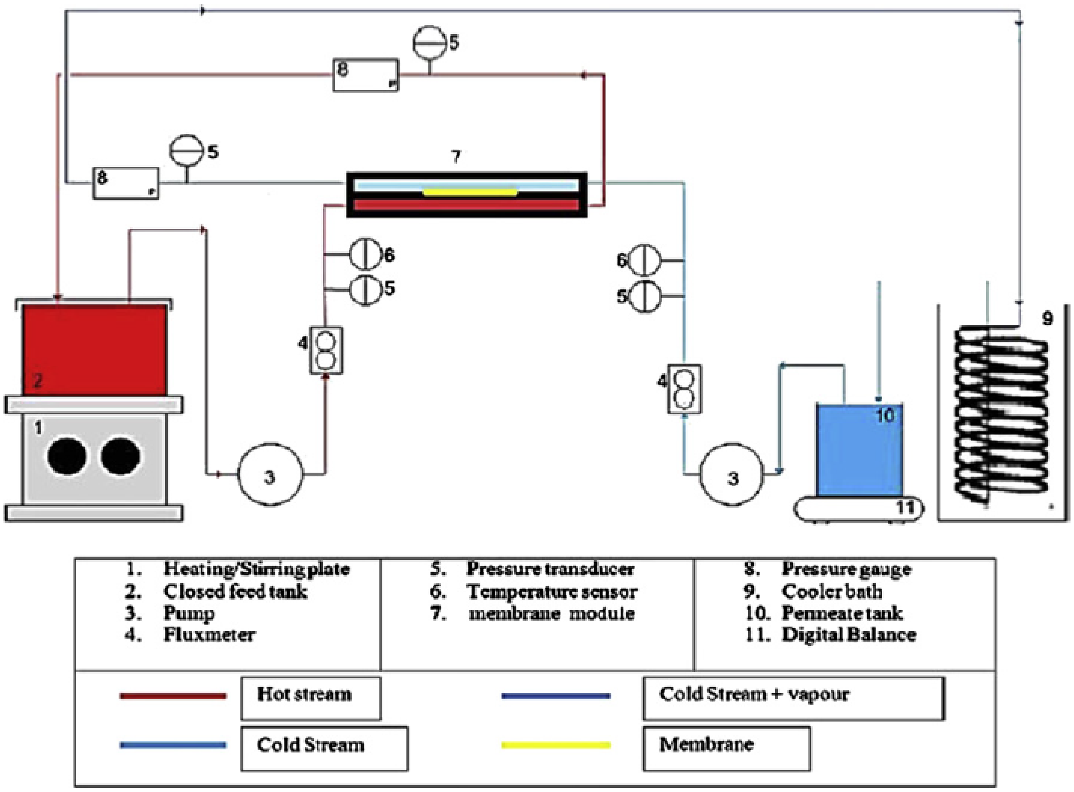


Figure 8. Schematic diagram of the lab scale direct contact membrane distillation setup [9].

Feed inlet temperature	70C (for virgin membrane different temperatures were tested on the membrane)
Permeate inlet temperature	25C
Feed flow rate	500 mL/min
Permeate flow rate	500 mL/min
Feed volume	1.3 L

Table 5. Direct contact membrane distillation operating parameters.

Chapter 4 Results and Discussion

The commercial PVDF membranes were characterized by studying the contact angles of ultrapure water on the surface of the membranes. The effects of dip coating time and withdrawal speed of the TiO_2 coating modification step and the volume amount of FTCS filtered through the membrane were studied to determine the best parameters for superhydrophobicity. In order for the modified membrane to reach superhydrophobicity, the contact angle had to be greater than 150°. Overall, the contact angle of ultrapure water on the surface of commercial PVDF membranes increased from 89.7° ± 1° for virgin membranes to 133.4° ± 3° for FTCS-TiO_2-PVDF membranes. This indicates that these experiments were not successful in modifying a commercial PVDF membrane to reach superhydrophobicity. In previous work, A. Razmjou et al. [9], virgin PVDF membranes were initially hydrophobic with a starting contact angle of 125° ± 1°, and were modified, using the same procedures, to reach a contact angle of 163° ± 3°. The membranes that were modified in that lab were hydrophobic, whereas, the commercial membranes used in this paper were *hydrophilic*. It can be noted that the hydrophilic membranes increased in contact angles by 43.7°, in this study, and 38° for the hydrophobic membranes in previous work. Due to the similarities in the increased contact angles, it was assumed that trends in the parameters studied can be applied to the hydrophobic PVDF membranes. Due to time constraints, commercial hydrophobic PVDF membranes were not modified at different modification parameters.

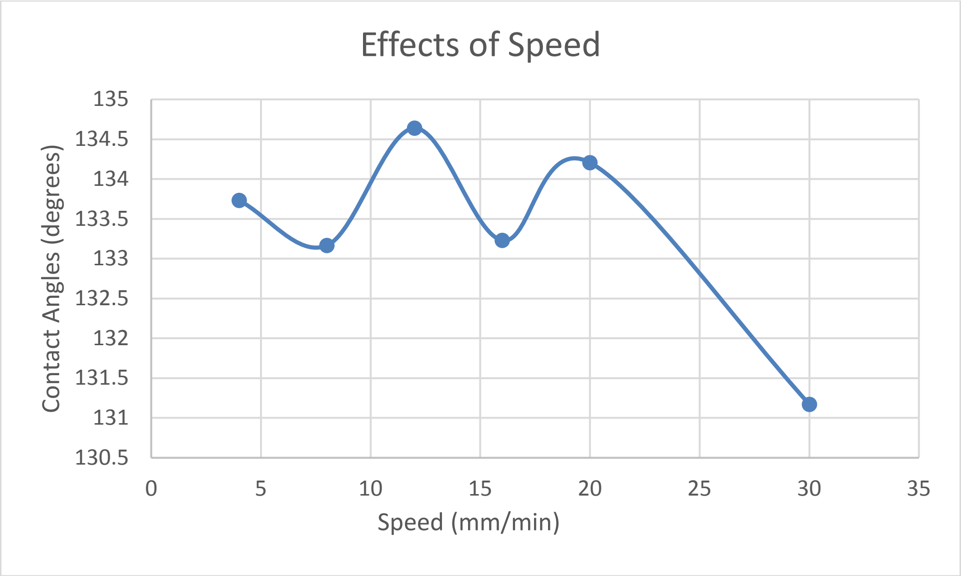
4.1 Effects of Coating Parameters on PVDF Membranes

TiO_2 coating parameters. The modification process of PVDF membranes contains two steps. The first step was coating the membrane with a TiO_2 coating sol-gel. The coating parameters of dip coating time and withdrawal speed were studied. The second step, FTCS filtration, remained constant at 30 mL of the FTCS solution filtered through each membrane. The contact angles at the different parameters can be seen below in Table 6.

Average FTCS-TiO_2-PVDF membrane contact angles						
Time/Speed	4 sec	8 sec	12 sec	16 sec	20 sec	30 sec
4 mm/min	133.2167	128.8	130.8667	137.1167	135.1667	137.22
8 mm/min	130.48	132	129.8	134.74	135.9333	136.0333
12 mm/min	133.1333	134.88	131.76	135.46	133.9333	138.66
16 mm/min	134.05	133.46	133.86	136.06	134.24	127.7
20 mm/min	134.3333	135.3667	131.6333	135.46	135.92	132.52
30 mm/min	128.75	132.8667	132.1333	133.62	133.9333	125.72

Table 6. Average contact angles of FTCS-TiO_2-PVDF membranes. At least 5 contact angles were measured for every membrane.

The graphs shown below in Figure 9A and 9B show the results of the contact angles for modified PVDF membranes. There were no apparent changes to the adjustment of dip coating time and withdrawal speed of the TiO_2 coating process. However, seen in Figure 9A, there may be a decrease in hydrophobicity with an increasing withdrawal speed over 20 mm/min. Although, with changing speed, there was minimal fluctuation of contact angles, the difference from 20 mm/min to 30 mm/min was significant and led research to the conclusion that high withdrawal speeds for the TiO_2 coating process may result in a decrease of the hydrophobicity.



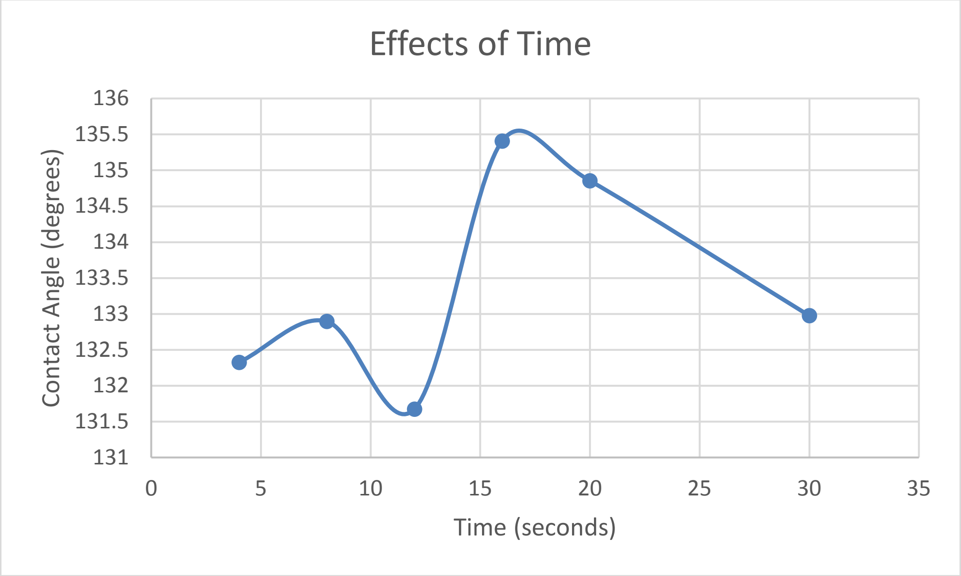


Figure 9. A. The average effects of withdrawal speed on the contact angles of the PVDF membranes. B. The average effects of dip coating time on the contact angles of the PVDF membranes.

FTCS filtration parameters. The second step of the modification process was filtering an FTCS solution through each membrane. After determining that dip coating time and coating speed of the TiO_2 process did not significantly impact the hydrophobicity of the, these parameters were held constant at 8 sec holding time and 12mm/min coating time as found in previous work [1,2,3]. The changing parameter was the volume, milliliters, of FTCS solution filtered through each membrane.

As seen in Figure 10, increasing the amount of FTCS filtered through the membrane will decrease the contact angle. This was expected because in previous work [1,2],the amount of FTCS depended on the size of the membrane. With these results, it was determined that 30 mL of FTCS would optimize the hydrophobicity of these PVDF membranes.

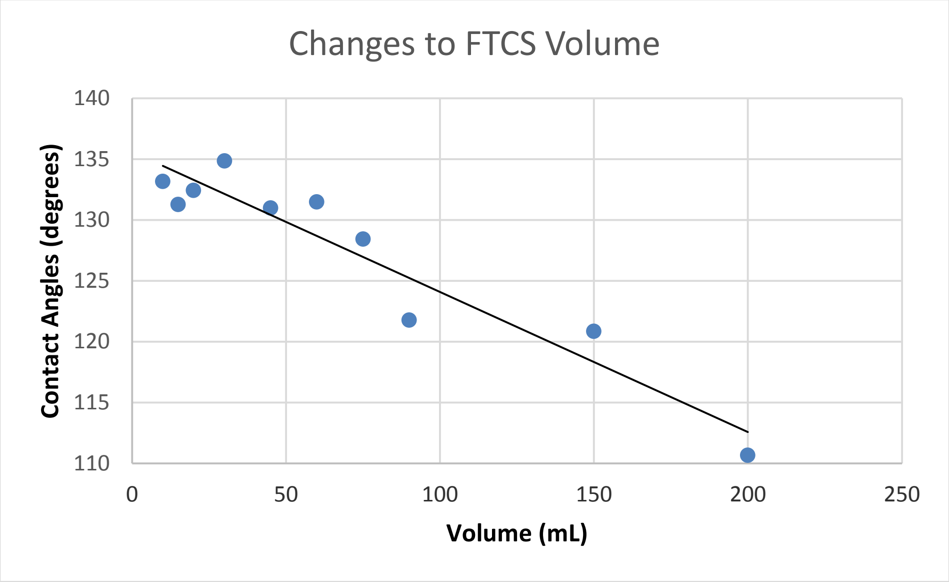


Figure 10. Changes to FTCS volume on PVDF hydrophilic membranes.

Physical changes on the membrane. With the naked eye, the effect of different volumes of FTCS could be seen in Figure 11 below. When increasing the volume of the FTCS solution there would be a thick layer formed on the surface of the membrane. It is clearly seen in Figure 11 at 200 mL of FTCS solution, where there is to be a small ship of the layer at the bottom of the membrane.


10 ml


35 ml

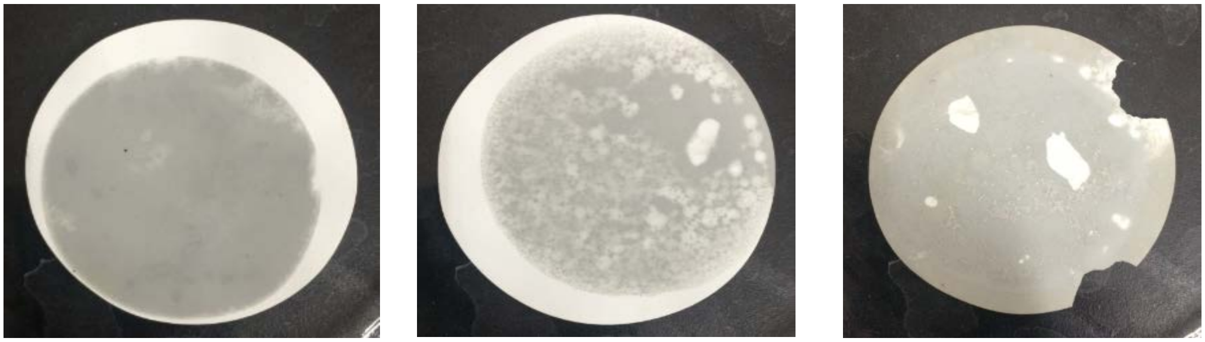

75 ml

90 ml 150 ml 200 ml

Figure 11. Effects of manipulating the volume of FTCS solution filtered through PVDF membranes. Photos taken immediately after FTCS vacuum filtration.

After the filtration and heat treatment, the membranes were backwashed with ethanol and left to dry. As seen in Figure 12, the FTCS had an impact on the physical characteristics of the membrane. As FTCS volume increased, the membrane became more transparent. This possibly ruined the integrity and stability of the membrane. Further research was not completed at this time.

10 ml 35 ml 75 ml



90 ml 150 ml 200 ml

Figure 12. Physical effects of changing the volume of FTCS filtered through PVDF membrane.

Contact angle measurements using a goniometer. As mentioned earlier, the contact angle was vital in these experiments in determining the characterization of the modified membranes. Below, Figure 13, are the pictures that can clearly represent the different stages of the modification process on the surface of the membrane. After the TiO_2 coating process, the membrane did reach a superhydrophilicity in order to later reach superhydrophobicity after the FTCS process.

Virgin PVDF TiO$_2$-PVDF FTCS-TiO$_2$-PVDF

Figure 13. Effect of super hydrophobic modification on the surface of the hydrophilic PVDF membranes.

4.2 Hydrophilic versus Hydrophobic PVDF Membranes

Initially, the conducted experiments consisted of the modification of PVDF *hydrophobic* membranes. However, the modification of *hydrophilic* PVDF membranes took place. It was assumed that the degree of modification of both hydrophobic and hydrophilic membranes could be compared. After many experiments, it was determined that this could not be assumed. As seen in Table 7 below, previous work using the similar methods were successful in modifying a PVDF membrane to reach superhydrophobicity. Although, mentioned earlier, the hydrophilic membranes were able to increase their hydrophobicity to the same degree as in previous work, the hydrophobic membranes were unsuccessful in increasing its hydrophobicity to superhydrophobicity. In fact, the hydrophilic membranes were more hydrophobic than the modified hydrophobic membranes.

In order to determine the source of the problem in the modification process, TiO$_2$-PVDF and FTCS-PVDF modified membranes were compared to previous work. Both steps of the modification process proved to be unsuccessful in altering the membrane surface to superhydrophophilicity and superhydrophobicity. New chemicals were used to purify the modification process and results remained similar. Solving the problem of this modification process remains inconclusive. Further research and analysis needs to be conducted in order to continue the projected research.

Contact Angles			
	Prev. Work	Hydrophilic	Hydrophobic
Virgin	125° ± 1°	89° ± 1°	125° ± 1°
TiO$_2$-PVDF	98° ± 13°	56° ± 18°	117° ± 5°
FTCS-PVDF	146° ± 5°	137° ± 1°	134° ± 2°
FTCS-TiO$_2$-PVDF	163° ± 3°	133° ± 3°	131° ± 3°

Table 7. Comparison of modification processes in previous work with hydrophilic and hydrophobic PVDF membranes.

4.3 Direct Contact Membrane Distillation (DMCD)

In order to determine the performance of PVDF membranes, direct contact membrane distillation was performed. However, the main focus of these results was the effect of the feed (3.5wt% of sodium chloride water) temperature on the flux of the membrane. Because the PVDF membranes were not successfully modified, virgin hydrophobic membranes were fouled in the DCMD to determine these temperature effects. In Figure 14, it is clear that the temperature increase of the feed solution was proportional to the flux of the virgin membranes. However, due to fluctuations of temperature at 75°C, the chosen optimized temperature for the DCMD runs on modified membranes was 70°C.

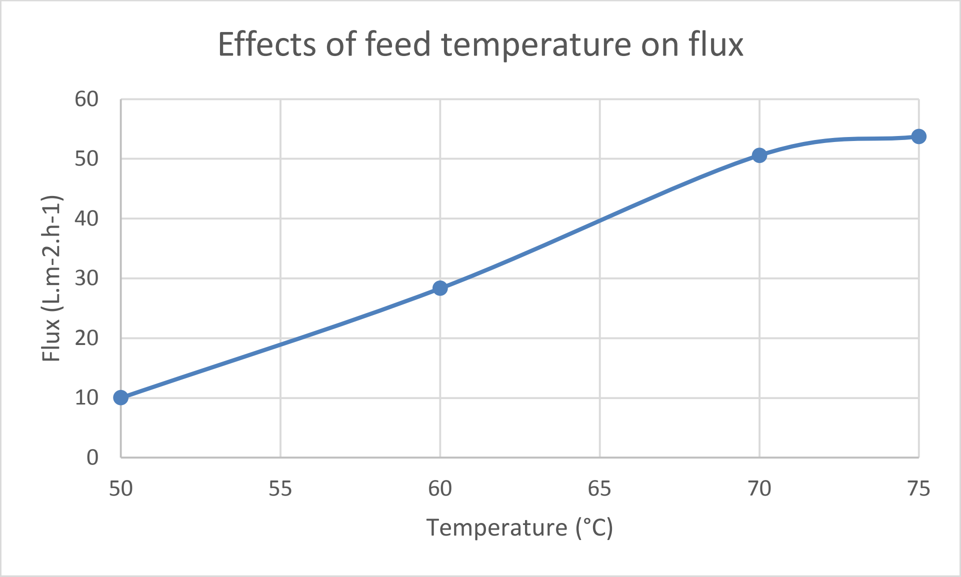


Figure 14. The effects of the feed temperature versus the flux of the membrane.

After the modification of hydrophobic PVDF membranes, the modified membranes were compared to the virgin PVDF membranes at 70°C with respect to the flux and conductivity. As can be seen in Figure 16A, the flux of the FTCS-TiO_2-PVDF membranes was significantly lower than the virgin membranes. These results were expected, however, the flux of the modified membranes were lower than that of the modified membranes in previous work. Again, the reason for this is the result of the unsuccessful modification process to the surface of PVDF membranes. Flux is expected to be higher for virgin membranes as a result of liquid penetration. This can be made clear by looking at Figure 16B. The conductivity measurements indicated the ability of the water to conduct electricity. Since the virgin membranes conductivity of the permeate side increases with time, it was determined the NaCl particulates penetrated the membrane and entered the permeate stream. This can also be the reason for an increased flux. The FTCS-TiO_2-PVDF membrane was successful in maintaining a low steady conductivity. However, the modification process must be altered in order to successfully test the performance of the membrane through DCMD.

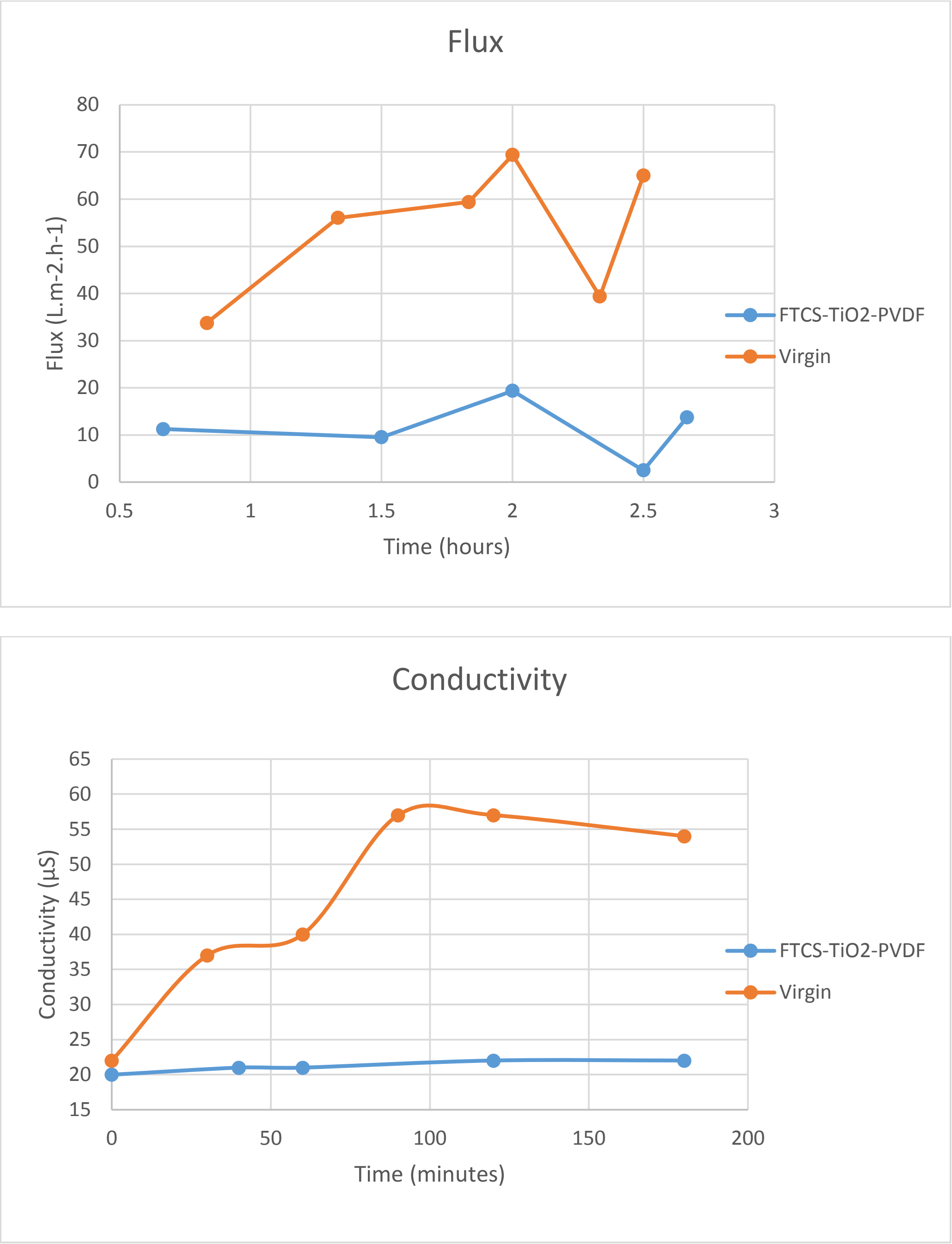


Figure 15 A. Comparison of the flux and B. conductivity of FTCS-TiO_2-PVDF membranes and the virgin hydrophobic PVDF membranes.

The rejection of both the virgin and modified membranes was calculated. It was expected for both membranes to have a rejection near 100%. The rejection for FTCS-TiO_2-PVDF membranes was 99.92% ± 0.0194%. The rejection for virgin PVDF membranes was also 99.92% ± 0.0194%.

As mentioned, such a high rejection from these membranes was expected. Thus being one of the many advantages of membrane distillation. The modified membranes were predicted to reach a rejection of 100% if modified properly to superhydrophobicity.

Chapter 5 Conclusions and Recommendations

In conclusion, the modification process used in this study was unsuccessful in altering the surface of a PVDF hydrophobic membrane to be superhydrophobic. Both parts of the two step modification process were analyzed to determine the source of the problem. The modification of these membranes did affect their performance in DCMD. The modified membrane had a significantly lower flux then that of FTCS-TiO_2-PVDF membranes in previous works.

As this project continues, it is recommended that different modification processes be considered. In this project, the only way of characterizing the modified membranes was by measuring their contact angles. It is also recommended that other means of characterization be utilized to better understand and predict the behavior of the membrane. By characterizing the membrane in various ways, including liquid entry pressure, x-ray photoelectron spectroscopy and scanning electron microscopy, using the current modification process, it can help determine what is problematic about the modification process that hinders the membrane from reaching superhydrophobicity.

Moving forward, it can be predicted that, after determining a successful modification process and creating a superhydrophobic surface, the modified membranes will perform better than the virgin PVDF membranes. After, this study can continue with its overall goal of creating hydrophobic membranes by electrospinning, modifying them and testing their performance in DCMD compared to commercial modified membranes. If this study is successful in these steps, membrane distillation will be seen as a more competitive and reliable means of a separation process.

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Appendix

Appendix 1 TiO$_2$ contact angles on PVDF hydrophilic membranes

Virgin Membranes				
	Theta (M)	Theta (L)	Theta (R)	Drop CD (mm)
PVDF Membrane	88.8	89.3	88.3	2.537
	88.8	89.3	88.3	2.521
	90.5	89.3	91.7	2.578
	90.5	87.2	93.7	2.549

TiO$_2$-PVDF membranes contact angles				
Type of Membrane	Theta (M)	Theta (L)	Theta (R)	Drop CD (mm)
4 sec; 4mm/min	64.3	58.9	69.8	2.739
4 sec; 8mm/min	28.8	28.4	29.1	3.021
	35.7	31.8	39.5	3.272
4 sec; 12mm/min	59.4	59.6	59.2	2.79
4 sec; 16mm/min	45.2	44.7	45.8	2.914
4 sec; 20mm/min	45.7	49.7	41.7	3.267
4 sec; 30mm/min	72	77.5	66.6	2.441
	68.4	70.2	66.5	2.707
8 sec; 4mm/min	23.7	23.9	23.5	3.195
	29	31.7	26.2	2.889
8 sec; 8mm/min	58.9	60	57.8	2.582
8 sec; 12mm/min	56	56.1	56	2.546
8 sec; 16mm/min	18.6	19.5	17.6	4.637
	17.9	18.2	17.5	4.618
8 sec; 20mm/min	35.1	32.8	37.4	3.292
	52.6	53.4	51.7	2.605
8 sec; 30mm/min	14.2	13.1	15.4	4.376
	22.6	23.3	22	3.507
12sec; 4mm/min	57.2	58	56.4	3.679
	63.1	61.2	65	3.319
12sec; 8mm/min	52.1	52.3	52	3.518
	54.6	51.9	57.4	3.529
12sec; 12mm/min	57.5	61.5	53.4	3.62
	55	54.2	55.8	3.28

12sec; 16mm/min	63.6	63.8	63.5	3.277
	62.4	62.4	62.4	3.153
12sec; 20mm/min	68.5	74.2	62.7	3.071
	65.1	64.8	65.4	2.937
12sec; 30mm/min	70.4	72.8	67.9	2.987
	64.6	64.8	64.5	2.908
	73.8	72.7	75	2.333
16sec; 4mm/min	73.5	76.6	70.4	2.381
	75.7	69.7	81.8	3.569
	77.2	72.8	81.5	2.384
16sec; 8mm/min	79.2	78.9	79.5	2.337
	80.7	76.8	84.7	2.353
16sec; 12mm/min	69.9	67.8	72.1	2.429
	62.2	63.1	61.3	2.773
16sec; 16mm/min	77.7	80.4	75	2.409
	76.5	72	80.9	2.518
16sec; 20mm/min	64.3	63.5	65.1	2.652
	68.6	65.6	71.6	2.705
16sec; 30mm/min	78.1	76.2	80	2.59
	76.9	75.2	78.6	2.62
20sec; 4mm/min	59.5	59.6	59.4	2.685
	65.2	71.6	58.8	2.74
20sec; 8mm/min	71.8	75.2	68.4	2.909
	70.1	69.3	71	3.001
20sec; 12mm/min	79.8	80.1	79.4	2.656
	72.2	72.3	72.1	2.687
20sec; 16mm/min	63.9	56.6	71.1	2.812
	46.6	47.7	45.6	2.978
20sec; 20mm/min	40.1	42.9	37.3	3.245
	74	75.9	72	2.562
	47.7	45.4	50	3.436

20sec; 30mm/min	55.9	56.7	55.1	3.081
	58.1	53.8	62.5	3.03
30sec; 4mm/min	51.4	49.5	53.3	3.062
	53.1	57	49.3	3.089
30sec; 8mm/min	56	60.1	51.8	3.234
	49.5	45.2	53.8	3.534
30sec; 12mm/min	27.6	23.9	31.2	4.088
	24.6	30.5	18.6	4.226
30sec; 16mm/min	41.5	36.6	46.4	3.488
	63.3	64.5	62.2	3.075
	50.8	41.1	60.4	3.257
30sec; 20mm/min	20.8	19.3	22.2	3.02
	25.1	27.8	22.4	3.611
30sec; 30mm/min	73.3	73.6	73	2.864
	34.6	33.1	36	3.119
	55.4	59.9	50.9	2.984

Averages of TiO_2 Contact Angles on Commercial PVDF membranes						
Time/Speed	4 sec	8 sec	12 sec	16 sec	20 sec	30 sec
4mm/min	64.3	26.35	60.15	75.46667	62.35	52.25
8mm/min	32.25	58.9	53.35	79.95	70.95	52.75
12mm/min	59.4	56	56.25	66.05	76	26.1
16mm/min	45.2	18.25	63	77.1	55.25	51.86667
20mm/min	45.7	43.85	66.8	66.45	53.93333	22.95
30mm/min	70.2	18.4	69.6	77.5	57	54.43333

FTCS-TiO_2-PVDF membranes contact angles							
	Theta (M)	Theta (L)	Theta (R)	Vol (µl)	Area (mm²)	Drop CD (mm)	Drop Height (mm)
4 sec; 4mm/min	127.8	128	127.6	3.103	8.856	1.499	1.49
	133.5	133.4	133.5	2.804	8.434	1.338	1.468
	135.7	135.7	135.6	2.809	8.518	1.288	1.485
	133.6	133.5	133.6	2.699	8.223	1.323	1.446
	133.9	134	133.9	2.707	8.268	1.302	1.465
	134.8	134.8	134.8	2.774	8.441	1.285	1.492

4 sec; 8mm/min	132.6	132.5	132.7	2.809	8.41	1.363	1.457
	129.1	128.8	129.3	2.766	8.209	1.439	1.418
	131.6	131.6	131.6	2.826	8.413	1.389	1.453
	129	128.8	129.2	2.794	8.268	1.441	1.426
	130.1	130.2	130	2.836	8.397	1.417	1.451
4 sec; 12mm/min	132.6	132.8	132.4	2.79	8.391	1.348	1.467
	133.1	133.4	132.8	2.743	8.297	1.339	1.451
	131.9	131.9	131.8	2.824	8.443	1.365	1.473
	133.5	133	133.9	2.74	8.273	1.354	1.428
	133.9	134.2	133.5	2.734	8.313	1.313	1.464
	133.8	133.8	133.8	2.704	8.213	1.338	1.426
4 sec; 16mm/min	132.3	132.4	132.3	2.687	8.154	1.353	1.43
	132.8	132.7	132.9	2.787	8.381	1.347	1.464
	135.6	135.9	135.3	2.81	8.518	1.288	1.486
	136.3	136.4	136.2	2.766	8.437	1.276	1.471
	132.9	132.9	132.8	2.724	8.25	1.344	1.443
	134.4	134.5	134.3	2.721	8.29	1.309	1.454
4 sec; 20mm/min	135.5	135.8	135.2	2.792	8.485	1.282	1.488
	133.2	133.1	133.3	2.738	8.291	1.334	1.453
	134.3	134.1	134.5	2.79	8.432	1.313	1.477
	133.7	133.7	133.7	2.726	8.292	1.315	1.462
	135.1	135.2	135.1	2.89	8.662	1.311	1.497
	134.2	134.2	134.1	2.802	8.451	1.32	1.474
4 sec; 30mm/min	129.7	129.8	129.6	2.789	8.276	1.428	1.428
	129	128.7	129.4	2.824	8.332	1.444	1.434
	131.9	132.1	131.8	2.791	8.361	1.368	1.457
	125.9	126	125.8	2.825	8.263	1.494	1.428
	125	125.3	124.7	2.671	7.923	1.497	1.383
	131	131.6	130.5	2.961	8.661	1.424	1.47
8 sec; 4 mm/min	129.9	130.2	129.7	2.816	8.345	1.423	1.44
	129.5	129.7	129.4	2.665	8.018	1.414	1.401
	129.5	129.5	129.4	2.692	8.099	1.4	1.428
	126.2	126.4	126	2.752	8.127	1.476	1.417
	128.9	129.2	128.5	2.852	8.383	1.454	1.436
8 sec; 8 mm/min	129.4	129.4	129.3	2.77	8.24	1.423	1.432
	131.6	131.6	131.5	2.743	8.249	1.374	1.44
	132.5	132.6	132.4	2.729	8.255	1.346	1.449
	130.9	131.3	130.5	2.751	8.272	1.369	1.458
	134.8	135.1	134.6	2.922	8.722	1.321	1.503
	132.8	132.8	132.8	2.755	8.336	1.33	1.47
8 sec; 12 mm/min	135.1	135.2	135	2.705	8.285	1.285	1.461

	136.7	136.9	136.6	2.775	8.472	1.265	1.478
	135.2	135.5	135	2.545	7.969	1.25	1.44
	132.3	132.4	132.3	2.903	8.579	1.393	1.462
	135.1	135.1	135.1	2.664	8.166	1.307	1.423
8 sec; 16 mm/min	135.9	135.9	135.9	2.781	8.465	1.28	1.48
	131.5	131.6	131.4	2.751	8.263	1.377	1.44
	133.2	133.6	132.9	2.886	8.593	1.352	1.484
	133	133.1	133	2.763	8.317	1.36	1.438
	133.7	133.6	133.7	2.793	8.382	1.36	1.437
8 sec; 20 mm/min	135.3	135.3	135.2	2.799	8.462	1.313	1.462
	135.4	135.9	134.9	2.751	8.395	1.282	1.476
	136.1	136.3	135.9	2.667	8.242	1.25	1.468
	133.5	133.8	133.1	2.911	8.677	1.336	1.507
	137.1	137.4	136.7	2.739	8.415	1.25	1.477
	134.8	135.1	134.4	2.755	8.405	1.283	1.488
8 sec; 30 mm/min	135.8	136	135.7	2.736	8.375	1.271	1.474
	132.5	132.7	132.4	2.744	8.305	1.334	1.466
	130.9	131.6	130.2	2.925	8.601	1.408	1.477
	135.2	135.1	135.2	2.763	8.408	1.293	1.472
	131.1	131.3	131	2.762	8.276	1.384	1.443
	131.7	131.7	131.6	2.778	8.335	1.367	1.457
12 sec; 4 mm/min	131.3	132.4	130.3	2.368	7.486	1.303	1.379
	128.9	129	128.7	2.597	7.872	1.408	1.392
	128.4	129	127.8	2.764	8.202	1.441	1.425
	132.4	132.4	132.3	2.617	8.014	1.338	1.42
	133	132.4	133.6	2.756	8.328	1.34	1.457
	131.2	131.2	131.2	2.739	8.235	1.377	1.441
12 sec; 8 mm/min	132.7	133	132.3	2.751	8.309	1.344	1.456
	131.7	131.8	131.6	2.737	8.252	1.362	1.448
	133.3	133.2	133.4	2.785	8.389	1.341	1.461
	126.6	126.8	126.4	2.692	8.014	1.462	1.404
	128.4	128.3	128.4	2.542	7.765	1.397	1.392
	126.1	126	126.3	2.742	8.112	1.472	1.419
12 sec; 12 mm/min	125.6	125.6	125.6	2.664	7.928	1.48	1.39
	131.9	132.1	131.6	2.784	8.338	1.377	1.446
	134.7	135.3	134.2	2.781	8.441	1.298	1.48
	133.2	133.6	132.8	2.744	8.297	1.34	1.45
	133.4	133.6	133.2	2.692	8.195	1.326	1.443
12 sec; 16 mm/min	131.5	131.8	131.2	2.725	8.221	1.363	1.445

	134.8	134.8	134.9	2.783	8.433	1.306	1.471
	134.2	134.2	134.1	2.783	8.424	1.312	1.476
	134.6	134.3	134.8	2.756	8.373	1.306	1.466
	134.2	134.3	134.1	2.838	8.523	1.329	1.476
12 sec; 20 mm/min	132	131.9	132.1	2.743	8.262	1.365	1.442
	130.6	130.9	130.3	2.786	8.308	1.396	1.447
	135.1	134.9	135.3	2.767	8.411	1.297	1.47
	130.7	130.4	131	2.779	8.331	1.37	1.471
	129.3	129.4	129.3	2.66	8.032	1.393	1.425
	132.1	132.3	131.9	2.81	8.416	1.362	1.468
12 sec; 30 mm/min	132.5	132.7	132.3	2.767	8.342	1.345	1.464
	131.4	131.8	131.1	2.814	8.403	1.377	1.464
	131.4	131.7	131.1	2.809	8.387	1.375	1.465
	133.4	132.9	133.9	2.799	8.443	1.327	1.48
	133.1	133.2	133.1	2.787	8.388	1.345	1.46
	131	131.2	130.9	2.805	8.37	1.386	1.457
16 sec; 4 mm/min	136.2	136.3	136.2	2.13	7.098	1.162	1.358
	135	135.1	134.8	2.632	8.138	1.272	1.452
	136.8	137	136.7	2.716	8.337	1.271	1.451
	139.1	139.3	138.9	2.725	8.418	1.228	1.457
	138.6	138.6	138.6	2.733	8.457	1.209	1.49
	137	136.9	137.1	2.799	8.556	1.242	1.507
16 sec; 8 mm/min	136	136.2	135.9	2.702	8.311	1.263	1.468
	133.7	133.8	133.5	2.475	7.77	1.276	1.413
	135.6	135.7	135.6	2.711	8.309	1.278	1.462
	134.5	134.5	134.5	2.839	8.538	1.322	1.479
	133.9	133.9	133.9	2.735	8.339	1.296	1.482
16 sec; 12 mm/min	135.6	135.6	135.7	2.749	8.386	1.286	1.467
	135.9	136	135.8	2.795	8.51	1.271	1.495
	136.5	136.7	136.4	2.78	8.487	1.262	1.487
	134.8	135	134.7	2.672	8.212	1.285	1.455
	134.5	134.4	134.6	2.764	8.405	1.296	1.482
16 sec; 16 mm/min	136.2	136.3	136.1	2.634	8.165	1.259	1.446
	135.6	135.6	135.5	2.873	8.638	1.304	1.491
	137.8	137.9	137.7	2.786	8.535	1.233	1.497
	135.1	135.1	135.1	2.703	8.273	1.291	1.454
	135.6	135.6	135.6	2.768	8.442	1.275	1.486

16 sec; 20 mm/min	134.2	134.3	134.2	2.819	8.469	1.339	1.459
	133.8	134.3	133.3	2.708	8.23	1.327	1.44
	136.9	137	136.8	2.785	8.502	1.261	1.483
	135.7	135.6	135.8	2.824	8.551	1.287	1.49
	136.7	136.8	136.6	2.509	7.933	1.216	1.439
16 sec; 30 mm/min	134.3	134.5	134.2	2.775	8.394	1.323	1.459
	132.7	133	132.4	2.715	8.239	1.333	1.454
	132.7	132.7	132.7	2.77	8.334	1.354	1.452
	136.8	137	136.7	2.754	8.445	1.251	1.484
	131.6	131.6	131.5	2.729	8.222	1.369	1.44
20 sec; 4 mm/min	134.7	135	134.4	2.826	8.514	1.317	1.477
	134.5	134.6	134.5	2.723	8.304	1.303	1.459
	136.8	136.8	136.8	2.896	8.73	1.274	1.509
	137	137.1	137	2.712	8.364	1.239	1.479
	132.3	132.3	132.4	2.734	8.263	1.349	1.451
	135.7	135.8	135.7	2.711	8.311	1.278	1.46
20 sec; 8 mm/min	136.6	136.9	136.3	2.591	8.102	1.231	1.453
	135.1	135.3	135	2.747	8.377	1.289	1.472
	135.9	135.8	135.9	2.775	8.463	1.272	1.486
	136	136.1	136	2.562	8.008	1.252	1.43
	135.4	135.5	135.3	2.816	8.516	1.3	1.479
	136.6	136.8	136.4	2.792	8.498	1.276	1.474
20 sec; 12 mm/min	137.1	137.1	137.1	2.921	8.786	1.273	1.512
	135	135.2	134.7	2.852	8.577	1.314	1.484
	133.2	133.3	133.2	2.777	8.369	1.342	1.458
	132.7	132.5	132.9	2.773	8.335	1.361	1.445
	131.7	131.8	131.5	2.731	8.23	1.366	1.441
	133.9	134	133.9	2.918	8.698	1.33	1.507
20 sec; 16 mm/min	134.5	134.3	134.6	2.75	8.355	1.309	1.463
	134.3	134.8	133.9	2.808	8.465	1.318	1.476
	134.8	134.9	134.8	2.781	8.439	1.3	1.477
	133.6	133.8	133.5	2.44	7.684	1.281	1.394
	134	134	134	2.743	8.329	1.318	1.459
20 sec; 20 mm/min	135.4	135.7	135	2.818	8.512	1.308	1.472
	136	135.9	136.2	2.691	8.274	1.266	1.462
	135.6	135.8	135.3	2.788	8.45	1.303	1.463

	136.3	136.5	136.2	2.697	8.29	1.273	1.451
	136.3	136.3	136.3	2.756	8.402	1.288	1.456
20 sec; 30 mm/min	133.6	133.7	133.5	2.683	8.185	1.324	1.438
	134.2	134.2	134.2	2.72	8.271	1.322	1.443
	134.1	134.1	134	2.813	8.465	1.331	1.468
	135.9	136	135.7	2.768	8.427	1.286	1.469
	133.8	134.1	133.4	2.781	8.404	1.325	1.468
	132	132.1	131.9	2.744	8.267	1.361	1.446
30 sec; 4 mm/min	139.1	138.9	139.2	8.224	17.633	1.743	2.14
	136.9	136.8	136.9	8.037	17.227	1.798	2.11
	135.8	135.8	135.8	7.5	16.486	1.737	2.111
	135.7	135.9	135.5	8.041	17.204	1.809	2.128
	138.6	138.6	138.7	7.653	16.803	1.704	2.1
30 sec; 8 mm/min	137.1	137.3	137	7.947	17.151	1.765	2.123
	139	139	138.9	7.797	17.058	1.69	2.131
	135	135.1	135	8.189	17.358	1.851	2.125
	133.9	134	133.9	7.915	16.876	1.877	2.077
	136.6	136.7	136.5	7.505	16.429	1.772	2.053
	134.6	134.7	134.5	7.266	16.029	1.778	2.054
30 sec; 12 mm/min	137.5	137.7	137.4	8.016	17.26	1.763	2.126
	138.8	138.9	138.7	7.537	16.648	1.688	2.093
	140.4	140.5	140.3	6.853	15.74	1.57	2.058
	139.9	140.1	139.8	7.553	16.727	1.658	2.098
	136.7	136.8	136.6	7.783	16.851	1.783	2.086
30 sec; 16 mm/min	129.7	129.8	129.6	7.47	16.086	1.917	2.055
	126.6	126.6	126.7	8.661	17.584	2.099	2.137
	133.4	133.4	133.4	8.144	17.233	1.877	2.13
	136.2	136.5	135.9	8.045	17.251	1.792	2.136
	127.7	127.9	127.5	8.26	17.078	2.044	2.104
	128.8	128.8	128.7	7.991	16.775	1.984	2.098
30 sec; 20 mm/min	130.9	131	130.8	2.279	7.284	1.297	1.358
	132.9	132.9	132.8	2.877	8.561	1.364	1.476
	132.1	132.2	132.1	2.959	8.689	1.399	1.477
	133.6	133.8	133.4	2.827	8.499	1.328	1.484
	133.1	133.2	133	2.327	7.437	1.269	1.373
30 sec; 30 mm/min	120.6	120.6	120.5	2.812	8.062	1.629	1.357

	127.9	127.9	127.9	3.046	8.726	1.506	1.461
	127.5	127.9	127.1	2.873	8.391	1.478	1.438
	129.2	129.2	129.2	2.748	8.202	1.415	1.435
	123.4	123.7	123.1	2.784	8.086	1.562	1.379

Average FTCS-TiO$_2$-PVDF membrane contact angles						
Time/Speed	4 sec	8 sec	12 sec	16 sec	20 sec	30 sec
4 mm/min	133.2167	128.8	130.8667	137.1167	135.1667	137.22
8 mm/min	130.48	132	129.8	134.74	135.9333	136.0333
12 mm/min	133.1333	134.88	131.76	135.46	133.9333	138.66
16 mm/min	134.05	133.46	133.86	136.06	134.24	127.7
20 mm/min	134.3333	135.3667	131.6333	135.46	135.92	132.52
30 mm/min	128.75	132.8667	132.1333	133.62	133.9333	125.72

Averages of TiO$_2$-PVDF and FTCS-TiO$_2$-PVDF		
Membrane	TiO$_2$-PVDF	FTCS-TiO$_2$-PVDF
4 sec; 4mm/min	64.3	133.2166667
4 sec; 8mm/min	32.25	130.48
4 sec; 12mm/min	59.4	133.1333333
4 sec; 16mm/min	45.2	134.05
4 sec; 20mm/min	45.7	134.3333333
4 sec; 30mm/min	70.2	128.75
8 sec; 4 mm/min	26.35	128.8
8 sec; 8 mm/min	58.9	132
8 sec; 12 mm/min	56	134.88
8 sec; 16 mm/min	18.25	133.46
8 sec; 20 mm/min	43.85	135.3666667
8 sec; 30 mm/min	18.4	132.8666667
12 sec; 4 mm/min	60.15	130.8666667
12 sec; 8 mm/min	53.35	129.8

12 sec; 12 mm/min	56.25	131.76
12 sec; 16 mm/min	63	133.86
12 sec; 20 mm/min	66.8	131.6333333
12 sec; 30 mm/min	69.6	132.1333333
16 sec; 4 mm/min	75.466667	137.1166667
16 sec; 8 mm/min	79.95	134.74
16 sec; 12 mm/min	66.05	135.46
16 sec; 16 mm/min	77.1	136.06
16 sec; 20 mm/min	66.45	135.46
16 sec; 30 mm/min	77.5	133.62
20 sec; 4 mm/min	62.35	135.1666667
20 sec; 8 mm/min	70.95	135.9333333
20 sec; 12 mm/min	76	133.9333333
20 sec; 16 mm/min	55.25	134.24
20 sec; 20 mm/min	53.933333	135.92
20 sec; 30 mm/min	57	133.9333333
30 sec; 4 mm/min	52.25	137.22
30 sec; 8 mm/min	52.75	136.0333333
30 sec; 12 mm/min	26.1	138.66
30 sec; 16 mm/min	51.866667	127.7
30 sec; 20 mm/min	22.95	132.52

30 sec; 30 mm/min	54.433333	125.72

FTCS-TiO_2-PVDF membrane contact angle of different FTCS volumes

Amount of FTCS (mL)	Theta (M)	Theta (L)	Theta (R)	Vol (µl)	Area (mm²)	Drop CD (mm)	Drop Height (mm)
10	134.6	134.7	134.5	3.116	9.105	1.347	1.542
	131.7	131.7	131.7	3.145	9.065	1.417	1.527
	135.7	135.9	135.6	3.2	9.303	1.333	1.563
	130.4	130.4	130.5	3.217	9.199	1.431	1.558
	132.9	133	132.9	3.405	9.588	1.436	1.566
	133.9	133.8	134	3.134	9.107	1.372	1.533
20	131.5	131.4	131.6	3.238	9.232	1.44	1.536
	133	133.1	132.9	3.143	9.104	1.388	1.534
	131.4	131.4	131.4	3.266	9.298	1.432	1.555
	131.6	131.6	131.7	3.208	9.193	1.422	1.543
	134.8	134.8	134.9	3.127	9.14	1.34	1.548
25	119.2	119.1	119.3	3.172	8.744	1.69	1.438
	123.9	123.9	123.9	3.27	9.062	1.602	1.495
	125.8	125.7	125.8	3.084	8.784	1.523	1.49
	124.3	124	124.7	3.056	8.672	1.561	1.463
	124.4	124.5	124.4	3.446	9.386	1.631	1.513
30	132.6	132.8	132.4	2.79	8.391	1.348	1.467
	133.1	133.4	132.8	2.743	8.297	1.339	1.451
	131.9	131.9	131.8	2.824	8.443	1.365	1.473
	133.5	133	133.9	2.74	8.273	1.354	1.428
	133.9	134.2	133.5	2.734	8.313	1.313	1.464
	133.8	133.8	133.8	2.704	8.213	1.338	1.426
35	121.2	121.1	121.4	3.204	8.856	1.654	1.459
	122.5	122.3	122.7	3.057	8.597	1.616	1.43
	121.2	121	121.5	2.777	8.048	1.579	1.388
	121.3	121.3	121.3	3.04	8.56	1.619	1.44
	122.8	122.6	123.1	3.221	8.902	1.647	1.448
45	128.1	128.1	128.2	2.884	8.445	1.456	1.456
	131.9	131.8	131.9	2.977	8.763	1.373	1.517
	135.6	135.6	135.7	2.949	8.794	1.312	1.506
	131.7	131.7	131.7	3.039	8.848	1.41	1.5
	127.7	127.4	127.9	3.019	8.714	1.473	1.492
50	121.2	121.2	121.3	3.332	9.091	1.676	1.477
	127.1	127.3	126.8	3.317	9.245	1.545	1.523
	120.5	120.6	120.5	3.129	8.707	1.649	1.449

	121.1	121.4	120.7	3.122	8.684	1.656	1.431
	119.8	119.7	119.9	2.891	8.224	1.635	1.39
	120.1	120.1	120.1	3.539	9.43	1.735	1.498
60	131.5	131.1	131.8	3.038	8.859	1.4	1.514
	131.7	131.4	132	2.978	8.743	1.391	1.501
	132.3	132.1	132.4	2.814	8.416	1.369	1.459
	133	132.9	133.1	2.924	8.679	1.354	1.499
	129.1	129	129.3	2.992	8.701	1.439	1.496
75	128.6	128.5	128.7	3.189	9.052	1.49	1.515
	131	130.7	131.3	3.133	9.014	1.435	1.516
	124.8	124.7	125	2.981	8.543	1.539	1.453
	126.2	126.2	126.2	3.079	8.77	1.525	1.48
	131.4	131.4	131.4	3.066	8.882	1.426	1.497
	128.7	128.5	128.8	3.161	9.008	1.479	1.516
90	122.4	122.6	122.1	3.251	8.966	1.645	1.467
	123.2	123.3	123.1	3.097	8.728	1.584	1.468
	119.9	119.9	119.9	3.028	8.472	1.667	1.403
	122	122.1	122	3.255	8.963	1.653	1.465
	125.6	125.4	125.9	3.228	9.031	1.561	1.499
	122.8	122.6	123	3.042	8.603	1.589	1.45
90	116	115.9	116.1	2.881	8.122	1.699	1.369
	123.5	124	123.1	3.136	8.814	1.58	1.48
	122.5	122.6	122.4	2.887	8.284	1.58	1.409
	120.1	120.3	119.9	3.06	8.56	1.651	1.429
150	121.5	121.4	121.5	3.154	8.777	1.634	1.459
	118.2	118.1	118.2	3.039	8.47	1.687	1.41
	121.5	121.2	121.8	2.986	8.458	1.608	1.428
	123.8	123.7	123.8	3.344	9.183	1.625	1.497
	119.3	119.2	119.4	3.044	8.51	1.662	1.422
200	113.9	114.2	113.5	2.792	7.883	1.746	1.313
	110	110.2	109.8	2.874	7.985	1.813	1.321
	109.5	109.4	109.5	3.089	8.36	1.872	1.343
	109.3	109	109.6	3.177	8.511	1.898	1.349

Appendix 2 Modification of PVDF hydrophobic membranes

Virgin Membranes							
Membrane	1	2	3	4	5	6	AVG
Contact Angle	125.1	127	123.8	124	125.4	126.7	125.3333

TiO$_2$-PVDF membranes contact angles

Membrane	Theta (M)	Theta (L)	Theta (R)	Vol (µl)	Area (mm^2)	Drop CD (mm)	Drop Height (mm)
B3	106.3	107.5	105.2	5.004	11.369	2.366	1.449
	119.3	119.6	119.1	4.968	11.726	2.006	1.622
	120.9	121	120.9	4.482	11.002	1.901	1.581
	120.3	120.3	120.3	4.169	10.467	1.868	1.541
	120.3	120.4	120.1	4.669	11.285	1.942	1.598
C3	119.5	119	120	4.633	11.205	1.953	1.589
	109.3	109.4	109.2	5.116	11.629	2.286	1.518
	118.1	118.1	118.1	4.479	10.904	1.968	1.555
	116.5	117.2	115.7	4.339	10.612	1.993	1.514
	120.2	120.4	120.1	4.799	11.489	1.963	1.61

FTCS-PVDF membranes contact angles

Membrane	Theta (M)	Theta (L)	Theta (R)	Vol (µl)	Area (mm^2)	Drop CD (mm)	Drop Height (mm)
I	132.9	132.9	132.8	4.489	11.55	1.56	1.735
	138.7	138.7	138.6	4.922	12.525	1.467	1.817
	130.2	130.2	130.2	4.7	11.76	1.674	1.717
	134.8	134.8	134.9	4.61	11.828	1.533	1.754
	135.7	135.7	135.6	4.716	12.032	1.529	1.766
	133.2	133.2	133.2	4.539	11.611	1.582	1.717
II	133.2	133.2	133.2	4.676	11.866	1.584	1.748
	133.1	133.2	133	4.724	11.949	1.589	1.757
	133.3	133.4	133.3	4.642	11.821	1.573	1.749
	133.2	133.2	133.2	4.497	11.546	1.573	1.716
	133.1	133.2	132.9	4.752	11.992	1.592	1.761
III	138.4	138.2	138.6	4.816	12.354	1.45	1.817
	136.3	136.3	136.3	4.617	11.882	1.508	1.752
	132.9	133	132.8	4.576	11.661	1.594	1.718
	133.7	133.8	133.7	3.842	10.433	1.467	1.646
	134	134.2	133.9	4.638	11.833	1.561	1.747
IV	134.2	134	134.3	4.656	11.867	1.559	1.75
	132.8	132.7	132.9	4.868	12.166	1.62	1.765
	132.7	132.7	132.7	4.382	11.339	1.564	1.707
	131.4	131.4	131.4	4.313	11.142	1.606	1.669
	135.7	135.7	135.7	4.786	12.17	1.527	1.785
V	134.9	134.9	134.8	4.757	12.078	1.546	1.775
	129.2	129.1	129.3	4.745	11.866	1.659	1.763
	133.7	133.5	133.9	4.697	11.948	1.556	1.774

	133.8	133.8	133.8	4.731	12.016	1.554	1.783
	134.7	134.7	134.6	4.422	11.519	1.501	1.745
VI	136.3	136.4	136.3	4.884	12.372	1.514	1.81
	136.7	136.7	136.6	4.6	11.885	1.485	1.764
	135.1	135.3	134.8	4.734	12.074	1.524	1.789
	134.1	134.3	133.8	4.686	11.916	1.566	1.752
	133.2	133	133.4	4.708	11.933	1.581	1.759

FTCS-TiO_2-PVDF membranes contact angles

Membrane	Theta (M)	Theta (L)	Theta (R)	Vol (µl)	Area (mm²)	Drop CD (mm)	Drop Height (mm)
A.1	133.4	133.5	133.2	4.603	11.729	1.584	1.728
	132.3	132.2	132.4	4.728	11.892	1.629	1.732
	133.6	133.8	133.4	4.666	11.859	1.578	1.745
	129.9	130.1	129.8	4.487	11.378	1.665	1.677
	132.1	132	132.1	4.652	11.759	1.623	1.724
A.2	129.9	130.1	129.8	5	12.251	1.714	1.753
	132.3	132.3	132.2	4.748	11.95	1.615	1.752
	132	132	132.1	3.843	10.369	1.508	1.633
	132.5	132.6	132.3	4.641	11.764	1.604	1.733
	132.6	132.5	132.7	4.757	11.969	1.615	1.748
A.3	126.5	126.7	126.4	4.678	11.561	1.774	1.674
	133.6	133.4	133.8	4.748	11.99	1.59	1.751
	128.4	128.5	128.3	4.197	10.865	1.637	1.66
	127.6	127.7	127.6	4.613	11.511	1.728	1.685
	126.5	126.4	126.6	4.621	11.476	1.759	1.674
A.4	132.7	132.7	132.7	5.004	12.364	1.651	1.766
	134.2	134.3	134.1	4.66	11.872	1.562	1.748
	135	134.9	135	4.335	11.369	1.49	1.728
	130.4	130.5	130.4	4.922	12.133	1.698	1.742
	131.6	131.6	131.6	4.825	12.067	1.63	1.768
A.5	134	133.8	134.3	4.912	12.331	1.57	1.804
	130.1	129.8	130.4	4.753	11.909	1.644	1.766
	128.6	128.9	128.2	3.893	10.374	1.57	1.644
	127.4	127.7	127.1	4.439	11.235	1.696	1.678
	129.4	129.6	129.2	4.64	11.65	1.672	1.719
	122.1	121.9	122.2	4.909	11.784	1.899	1.676
A.6	132.6	132.6	132.5	4.798	12.023	1.627	1.745
	131.8	131.6	132	4.364	11.261	1.591	1.69
	131.2	131.4	131.1	4.891	12.146	1.654	1.765

	133.1	133.1	133.1	4.647	11.8	1.591	1.735
	132.7	132.7	132.6	4.749	11.953	1.613	1.745
A.7	133.9	133.8	134.1	4.712	11.947	1.576	1.751
	130.1	130.1	130	4.573	11.531	1.672	1.691
	132.3	132	132.7	4.836	12.077	1.637	1.749
	132.3	132.1	132.4	4.622	11.695	1.626	1.708
	132.6	132.4	132.8	4.607	11.706	1.603	1.723
	132.6	132.4	132.8	4.607	11.706	1.603	1.723
A.8	131.1	131	131.1	11.002	20.813	2.189	2.294
	131.5	131.6	131.4	10.294	19.938	2.127	2.248
	130.3	130.2	130.4	10.419	20.038	2.164	2.258
A.9	128.2	128	128.3	4.702	11.692	1.718	1.709
	127.5	127.4	127.7	4.768	11.779	1.741	1.712
	129.2	129.5	129	4.486	11.379	1.661	1.694
	130.5	130.5	130.4	4.624	11.653	1.653	1.715
	128.2	128.1	128.4	4.625	11.575	1.7	1.707
A.10	128.7	128.2	129.1	4.792	11.818	1.746	1.692
	135.6	135.3	135.8	4.723	12.054	1.523	1.777
	133.6	133.7	133.6	4.608	11.742	1.583	1.724
	135.4	135.4	135.4	4.517	11.678	1.516	1.738
	135.8	135.7	135.8	4.663	11.95	1.519	1.762
	136.6	136.6	136.6	4.792	12.206	1.512	1.784
B1	135.6	135.7	135.5	4.69	11.992	1.526	1.766
	135.6	135.7	135.4	4.482	11.589	1.533	1.707
	135.7	135.6	135.8	4.582	11.796	1.52	1.743
	135	135.1	134.8	4.696	11.979	1.539	1.766
	134	133.9	134	4.65	11.844	1.565	1.748
B2	127.7	128	127.5	4.778	11.808	1.734	1.718
	128.5	128.7	128.4	4.357	11.129	1.667	1.668
	134.7	134.7	134.7	4.664	11.872	1.568	1.732
	133.6	133.7	133.5	4.557	11.671	1.567	1.729
	132.4	132.5	132.3	4.473	11.49	1.579	1.72
C1	132	132.1	132	4.729	11.899	1.624	1.742
	134.8	135	134.6	4.647	11.884	1.539	1.757
	139	139.1	138.9	4.83	12.409	1.431	1.826
	132.7	132.8	132.5	4.646	11.788	1.597	1.738
	135.3	135.3	135.3	4.551	11.737	1.521	1.742
C2	133.8	133.8	133.8	4.716	11.955	1.576	1.755
	134.4	134.3	134.5	4.773	12.054	1.579	1.752
	132.2	132.2	132.1	4.323	11.199	1.581	1.683
	136	136.1	135.9	4.737	12.087	1.521	1.772

	131.2	131.2	131.3	4.616	11.684	1.623	1.73

Appendix 3 Direct Contact Membrane Distillation (DCMD) results

DCMD of virgin hydrophobic PVDF membrane at 50C									
Minute	Seconds	Time (secs)	Weight (g)	Area (m2)	Time (hr)	Delta time	Delta weight	Flux	
0	0	0	632.3	0.00096	0	0	0	0	x
10	0	600	631.5	0.00096	0.166667	0.166666667	-0.8	-5	x
20	0	1200	633.3	0.00096	0.333333	0.166666667	1.8	11.25	
30	0	1800	634.1	0.00096	0.5	0.166666667	0.8	5	
40	0	2400	641.7	0.00096	0.666667	0.166666667	7.6	47.5	
60	0	3600	646	0.00096	1	0.333333333	4.3	13.4375	
80	0	4800	657.4	0.00096	1.333333	0.333333333	11.4	35.625	x
90	0	5400	655.7	0.00096	1.5	0.166666667	-1.7	-10.625	
100	0	6000	658	0.00096	1.666667	0.166666667	2.3	14.375	
110	0	6600	660.8	0.00096	1.833333	0.166666667	2.8	17.5	
120	0	7200	662.5	0.00096	2	0.166666667	1.7	10.625	
130	0	7800	679.5	0.00096	2.166667	0.166666667	17	106.25	x
140	0	8400	679.9	0.00096	2.333333	0.166666667	0.4	2.5	
150	0	9000	677.8	0.00096	2.5	0.166666667	-2.1	-13.125	
160	0	9600	679.2	0.00096	2.666667	0.166666667	1.4	8.75	
170	0	10200	686.8	0.00096	2.833333	0.166666667	7.6	47.5	
180	0	10800	689.9	0.00096	3	0.166666667	3.1	19.375	
200	0	12000	697.8	0.00096	3.333333	0.333333333	7.9	24.6875	x
210	0	12600	698.6	0.00096	3.5	0.166666667	0.8	5	
220	0	13200	700	0.00096	3.666667	0.166666667	1.4	8.75	
230	0	13800	700.6	0.00096	3.833333	0.166666667	0.6	3.75	
240	0	14400	708.7	0.00096	4	0.166666667	8.1	50.625	x

DCMD of virgin hydrophobic PVDF membrane at 60C									
Minute	Seconds	Time (secs)	Weight (g)	Area (m2)	Time (hr)	Delta time	Delta weight	Flux	
0	0	0	686.6	0.00096	0	0	0	0	
8	0	480	688	0.00096	0.133333	0.1333333	1.4	10.9375	
11	45	705	690.5	0.00096	0.195833	0.0625	2.5	41.66667	
15	30	930	691	0.00096	0.258333	0.0625	0.5	8.333333	
17	30	1050	692	0.00096	0.291667	0.0333333	1	31.25	
24	41	1481	698.3	0.00096	0.411389	0.1197222	6.3	54.81439	
25	0	1500	698	0.00096	0.416667	0.0052778	0.3	59.21053	

26	0	1560	699	0.00096	0.433333	0.0166667	1	62.5	
27	0	1620	700	0.00096	0.45	0.0166667	1	62.5	
28	0	1680	699.8	0.00096	0.466667	0.0166667	0.2	12.5	
29	0	1740	701.4	0.00096	0.483333	0.0166667	1.6	100	x
36	15	2175	706.4	0.00096	0.604167	0.1208333	5	43.10345	
37	15	2235	707.2	0.00096	0.620833	0.0166667	0.8	50	
39	0	2340	707.9	0.00096	0.65	0.0291667	0.7	25	
40	0	2400	708.7	0.00096	0.666667	0.0166667	0.8	50	
41	0	2460	709.3	0.00096	0.683333	0.0166667	0.6	37.5	
42	0	2520	709.6	0.00096	0.7	0.0166667	0.3	18.75	
43	0	2580	710.6	0.00096	0.716667	0.0166667	1	62.5	
44	0	2640	711.4	0.00096	0.733333	0.0166667	0.8	50	
46	0	2760	712.2	0.00096	0.766667	0.0333333	0.8	25	
47	0	2820	712.9	0.00096	0.783333	0.0166667	0.7	43.75	
48	0	2880	713.7	0.00096	0.8	0.0166667	0.8	50	
50	0	3000	715.3	0.00096	0.833333	0.0333333	1.6	50	
51	0	3060	715.8	0.00096	0.85	0.0166667	0.5	31.25	
59	0	3540	719.8	0.00096	0.983333	0.1333333	4	31.25	x
71	0	4260	724.8	0.00096	1.183333	0.2	5	26.04167	
80	0	4800	729.2	0.00096	1.333333	0.15	4.4	30.55556	
90	0	5400	734.3	0.00096	1.5	0.1666667	5.1	31.875	
100	0	6000	739.1	0.00096	1.666667	0.1666667	4.8	30	
110	0	6600	744.4	0.00096	1.833333	0.1666667	5.3	33.125	x
130	0	7800	751.9	0.00096	2.166667	0.3333333	7.5	23.4375	
140	0	8400	756.5	0.00096	2.333333	0.1666667	4.6	28.75	
150	0	9000	760.6	0.00096	2.5	0.1666667	4.1	25.625	
160	0	9600	764.7	0.00096	2.666667	0.1666667	4.1	25.625	
170	0	10200	769.3	0.00096	2.833333	0.1666667	4.6	28.75	x
190	0	11400	776.4	0.00096	3.166667	0.3333333	7.1	22.1875	
200	0	12000	779.6	0.00096	3.333333	0.1666667	3.2	20	
210	0	12600	782.8	0.00096	3.5	0.1666667	3.2	20	
220	0	13200	785.3	0.00096	3.666667	0.1666667	2.5	15.625	
230	0	13800	788.5	0.00096	3.833333	0.1666667	3.2	20	
240	0	14400	794.6	0.00096	4	0.1666667	6.1	38.125	x
260	0	15600	799.5	0.00096	4.333333	0.3333333	4.9	15.3125	
280	0	16800	809.7	0.00096	4.666667	0.3333333	10.2	31.875	x
300	0	18000	818.7	0.00096	5	0.3333333	9	28.125	
310	0	18600	824.5	0.00096	5.166667	0.1666667	5.8	36.25	
320	0	19200	828.4	0.00096	5.333333	0.1666667	3.9	24.375	
340	0	20400	837.1	0.00096	5.666667	0.3333333	8.7	27.1875	
360	0	21600	847.8	0.00096	6	0.3333333	10.7	33.4375	

370	0	22200	647.4	0.00096	6.166667				
380	0	22800	653.2	0.00096	6.333333	0.1666667	5.8	36.25	x
390	0	23400	658.4	0.00096	6.5	0.1666667	5.2	32.5	
400	0	24000	662.6	0.00096	6.666667	0.1666667	4.2	26.25	
410	0	24600	667.6	0.00096	6.833333	0.1666667	5	31.25	
420	0	25200	672.1	0.00096	7	0.1666667	4.5	28.125	x

DCMD of virgin hydrophobic PVDF membranes at 70C									
Minute	Seconds	Time (secs)	Weight (g)	Area (m2)	Time (hr)	Delta time	Delta weight	Flux	
0	0	0	537.7	0.00096	0	0	0	0	
20	0	1200	544.5	0.00096	0.333333	0.333333	6.8	21.25	x
40	0	2400	557	0.00096	0.666667	0.333333	12.5	39.0625	
50	0	3000	562.4	0.00096	0.833333	0.166667	5.4	33.75	
80	0	4800	589.3	0.00096	1.333333	0.5	26.9	56.04167	
100	0	6000	610.5	0.00096	1.666667	0.333333	21.2	66.25	x
110	0	6600	620	0.00096	1.833333	0.166667	9.5	59.375	
120	0	7200	631.1	0.00096	2	0.166667	11.1	69.375	x
130	0	7800	641.3	0.00096	2.166667	0.166667	10.2	63.75	
140	0	8400	647.6	0.00096	2.333333	0.166667	6.3	39.375	
150	0	9000	658	0.00096	2.5	0.166667	10.4	65	x
160	0	9600	664.4	0.00096	2.666667	0.166667	6.4	40	
170	0	10200	669.9	0.00096	2.833333	0.166667	5.5	34.375	
180	0	10800	680.5	0.00096	3	0.166667	10.6	66.25	x
190	0	11400	684.2	0.00096	3.166667	0.166667	3.7	23.125	
200	0	12000	694.9	0.00096	3.333333	0.166667	10.7	66.875	
210	0	12600	703	0.00096	3.5	0.166667	8.1	50.625	x
221	0	13260	711.9	0.00096	3.683333	0.183333	8.9	50.56818	
230	0	13800	720.8	0.00096	3.833333	0.15	8.9	61.80556	
240	0	14400	727.6	0.00096	4	0.166667	6.8	42.5	x
270	0	16200	751.7	0.00096	4.5	0.5	24.1	50.20833	
280	0	16800	749.7	0.00096	4.666667	0.166667	-2	-12.5	
290	0	17400	759	0.00096	4.833333	0.166667	9.3	58.125	
300	0	18000	766.8	0.00096	5	0.166667	7.8	48.75	
320	0	19200	783.7	0.00096	5.333333	0.333333	16.9	52.8125	x
330	0	19800	796.5	0.00096	5.5	0.166667	12.8	80	
340	0	20400	802.2	0.00096	5.666667	0.166667	5.7	35.625	
355	0	21300	804.5	0.00096	5.916667	0.25	2.3	9.583333	
360	0	21600	804.7	0.00096	6	0.083333	0.2	2.5	x

DCMD of virgin hydrophobic PVDF membranes at 75C

Minute	Seconds	Time (secs)	Weight (g)	Area (m2)	Time (hr)	Delta time	Delta weight	Flux	
2	0	120	494.7	0.00096	0.033333	0	0	0	
10	0	600	502.8	0.00096	0.166667	0.133333	8.1	63.28125	
20	0	1200	511.7	0.00096	0.333333	0.166667	8.9	55.625	
30	0	1800	519.1	0.00096	0.5	0.166667	7.4	46.25	
40	0	2400	528.3	0.00096	0.666667	0.166667	9.2	57.5	
50	0	3000	536.5	0.00096	0.833333	0.166667	8.2	51.25	
60	0	3600	544.1	0.00096	1	0.166667	7.6	47.5	x
70	0	4200	551.4	0.00096	1.166667	0.166667	7.3	45.625	
80	0	4800	561.1	0.00096	1.333333	0.166667	9.7	60.625	
90	0	5400	570.9	0.00096	1.5	0.166667	9.8	61.25	
100	0	6000	579.6	0.00096	1.666667	0.166667	8.7	54.375	
110	0	6600	588.4	0.00096	1.833333	0.166667	8.8	55	
120	0	7200	597.5	0.00096	2	0.166667	9.1	56.875	x
130	0	7800	606.3	0.00096	2.166667	0.166667	8.8	55	
140	0	8400	615.2	0.00096	2.333333	0.166667	8.9	55.625	
150	0	9000	623.2	0.00096	2.5	0.166667	8	50	
160	0	9600	631	0.00096	2.666667	0.166667	7.8	48.75	
170	0	10200	639.1	0.00096	2.833333	0.166667	8.1	50.625	
180	0	10800	646.6	0.00096	3	0.166667	7.5	46.875	
190	0	11400	652.5	0.00096	3.166667	0.166667	5.9	36.875	x
200	0	12000	660	0.00096	3.333333	0.166667	7.5	46.875	
210	0	12600	669.9	0.00096	3.5	0.166667	9.9	61.875	
220	0	13200	677.6	0.00096	3.666667	0.166667	7.7	48.125	
230	0	13800	683.6	0.00096	3.833333	0.166667	6	37.5	
240	0	14400	695.2	0.00096	4	0.166667	11.6	72.5	x

Rejection of Virgin Membrane at 70°C

Feed	Permeate	Time (mins)		Rejection (%)
54900	22	0	0.999599	99.95992714
57700	37	30	0.999359	99.93587522
58000	40	60	0.99931	99.93103448
60900	57	90	0.999064	99.90640394
63200	57	120	0.999098	99.90981013
63500	57	150	0.999102	99.91023622
65500	54	180	0.999176	99.91755725
65900	63	210	0.999044	99.90440061

67500	74	240	0.998904	99.89037037
68500	59	310	0.999139	99.91386861
77800	78	360	0.998997	99.89974293

*Feed and permeate are conductivity measurements in µS

Rejection of FTCS-TiO_2-PVDF Membranes at 70°C

Feed	Permeate	Time (mins)		Rejection (%)
54900	22	0	0.999599	99.95992714
57700	37	30	0.999359	99.93587522
58000	40	60	0.99931	99.93103448
60900	57	90	0.999064	99.90640394
63200	57	120	0.999098	99.90981013
63500	57	150	0.999102	99.91023622
65500	54	180	0.999176	99.91755725
65900	63	210	0.999044	99.90440061
67500	74	240	0.998904	99.89037037
68500	59	310	0.999139	99.91386861
77800	78	360	0.998997	99.89974293

*Feed and permeate are conductivity measurements in µS