AMERICAN UNIVERSITY OF BEIRUT

UNSUPPORTED HYDROPHOBIC ELECTROSPUN MEMBRANES FOR WATER DESALINATION USING DIRECT CONTACT MEMBRANE DISTILLATION

by
GHADEER AMER JALLOUL

A thesis
Submitted in partial fulfillment of the requirements
for the degree of Master of Engineering
to the Department of Chemical and Petroleum Engineering
of the Maroun Semaan Faculty of Engineering and Architecture
at the American University of Beirut

Beirut, Lebanon
May 2019

AMERICAN UNIVERSITY OF BEIRUT

Unsupported Hydrophobic Electrospun Membranes for Water Desalination Using Direct Contact Membrane Distillation

by
GHADEER AMER JALLOUL

Approved by:

Ali Tehrani

Dr. Ali Tehrani, Professor — Advisor
Department of Chemical and Petroleum Engineering

Dr. Mohammad N. Ahmad, Professor, Chairman — Co-Advisor
Department of Chemical and Petroleum Engineering

Dr. Kamel Aboughali, Professor, Chairman — Member of Committee
Department of Mechanical Engineering

Date of thesis defense: May 28, 2019

iii

AMERICAN UNIVERSITY OF BEIRUT

THESIS, DISSERTATION, PROJECT RELEASE FORM

Student Name: Jalloul (Last) Ghadeer (First) Amer (Middle)

☑ Master's Thesis ○ Master's Project ○ Doctoral Dissertation

☐ I authorize the American University of Beirut to: (a) reproduce hard or electronic copies of my thesis, dissertation, or project; (b) include such copies in the archives and digital repositories of the University; and (c) make freely available such copies to third parties for research or educational purposes.

☑ I authorize the American University of Beirut, to: (a) reproduce hard or electronic copies of it; (b) include such copies in the archives and digital repositories of the University; and (c) make freely available such copies to third parties for research or educational purposes
after:

One ---- year from the date of submission of my thesis.
Two ---- years from the date of submission of my thesis.
Three ---- years from the date of submission of my thesis.

Signature 15/8/2019 Date

iv

ACKNOWLEDGEMENTS

My sincere appreciation and deep regards go to my advisors: Dr. Ali Tehrani**,** Dr. Mohammad N. Ahmad, and Dr. Belal Abu Tarboush for their unwavering support, encouragements, and patience throughout the research. It was a great privilege and honor to work under their guidance, and I am grateful for what they offered me. I would like to also thank Dr. Kamel Aboughali for his valuable comments as a member of the committee.

Not least of all, I owe so much to my whole family for their undying support, and unwavering belief. Had it not been for all their prayers, benedictions, and sincere love, I would have never completed this research so thank you!

AN ABSTRACT OF THE THESIS OF

Ghadeer Amer Jalloul for Master of Engineering
Major: Chemical Engineering

Title: Unsupported Hydrophobic Electrospun Membranes for Water Desalination Using Direct Contact Membrane Distillation

Water is the most fundamental element of life. However, the boost in economic development, industrialization, and uncontrolled population growth are causing a severe threat to fresh water finite resources that are naturally available on earth, especially in the Middle East and North Africa (MENA) region. Due to limited accessibility to fresh water, desalination is believed to be a promising method to supply the continuously increasing fresh water needs. Desalination is a process that removes the excess amount of salts and minerals from seawater to make it drinkable. Over the last few decades, membrane-based technologies have gained considerable popularity due to their high separation efficiencies, relatively low costs, and ease of operation.

In this project, we developed an unsupported electrospun hydrophobic poly(vinylidene fluoride)-co-hexafluoropropylene (PVDF-HFP) membrane for direct contact membrane distillation (DCMD) for seawater desalination. The driving force of separation in DCMD is a partial vapor pressure difference on both sides of the hydrophobic membrane that is imposed by the temperature difference between liquid feed and permeate flows. The hydrophobic porous membrane acts as a barrier and separates the hot salty water (liquid feed) from the cold water (permeate). The electrospinning effective parameters were found to be polymer's concentration, applied voltage, and tip to collector distance. The fabricated membranes were characterized using various techniques such as SEM, capillary flow porometry, and contact angle measurement. The electrospun membrane was heat pressed and treated in ethanol at 65 C to improve its performance. The modified electrospun membrane showed very high permeate flux (>15 $Kg/m^2.hr$) and salt rejection rate of 99.99%. The proposed modified PVDF-HFP electrospun membrane was found to be a good candidate in the DCMD process. The performance of the electrospun membrane was compared to that of a commercially available PTFE membrane for benchmarking.

Keywords: Desalination, membrane distillation, electrospun, pore, membrane.

CONTENTS

FIGURES

Figures Page

TABLES

Table page

CHAPTER I

INTRODUCTION

In many regions of the world, reported fresh water demand exceeded 2% annually and such projections are almost double the population growth rates of these countries. If this trend continues, it is predicted that water scarcity will threaten some regions of the world, affecting more than 1.8 billion people by 2025, as compared to 0.25 billion presently in 2010 [1]. In fact, global water demand is forecasted to increase by 55% between 2000 and 2050. Agriculture accounts for the highest percentage of this demand about 70% of global freshwater use while food production will need to grow by 69% by 2035 to feed the growing population. On the other hand, water withdrawal for heating and cooling in industrial sectors is also expected to increase by over 20% [2]. Surprisingly, 2.1 billion people lack access to safely managed drinking water services while water scarcity already affects four out of every ten people [3].

Seawater is available on earth in large quantities, whereby 96.5 % of total water is found in the World's natural Oceans [4]. Unfortunately, the water resources that can supply freshwater are scarce while freshwater is unexceptional to satisfy the drinking water needs of the world's continuously increasing population. Due to the fact that traditional freshwater resources such as lakes, rivers and groundwater are no longer capable of satisfying the current and growing demand, a new method such as water

desalination had to be developed. Nowadays, desalination has already become an important part of the freshwater provision [2].

However, some desalination technologies like membrane distillation are not fully industrialized due to the high cost of fabricating robust and anti-wetting porous membranes to produce very pure fresh water. Based on this, we can observe the importance of developing and optimizing such desalination processes especially those that are less energy consuming. And here comes the importance of this particular project in fabricating and modifying electrospun polymeric membranes to be practically used in the Direct Contact Membrane Distillation (DCMD) technology for seawater desalination. Specifically, these membranes can play role in decreasing the overall cost of the operation and increasing its efficiency.

In this work we were able to produce an unsupported electrospun hydrophobic polymeric membrane that showed excellent performance in the DCMD process. After fabricating the membrane, we modified it using two steps thermal modification in order to eliminate the possibility of pore wetting and to maintain stable flux and salt rejection percentage. The obtained results show that the modified membrane showed a stable high permeate flux (15 $kg/m^2.hr$) and excellent stable salt rejection (>99.99%). Besides, it is shown that this membrane can compete with commercially available supported membranes with similar average pore size.

CHAPTER II

LITERATURE REVIEW

A. Membrane Distillation

Membrane distillation (MD) is a promising and competitive thermally driven separation and purification technology that has been recently used for many water treatment application and mainly desalination [5-8]. Once it is fully optimized and developed to be industrially used in large scale, this technique is believed to replace the conventional separation methods. These traditional high-energy consuming techniques include (i) Phase change processes: multi-stage flash distillation, vapor compression, and multiple effect distillation; (ii) membrane filtration processes: nano-filtration, reverse osmosis, and forward osmosis. [5, 6, 8-10]. The configuration, operating conditions, and membranes' properties in the MD process have been intensively studied for a full commercialization. Accordingly, MD may be an alternative purification technique that lacks the severe fouling problem and huge energy requirements for heating, cooling, or compression [6, 8, 10, 11].

Membrane distillation is a new thermally driven purification method that combines both the traditional heat application for water evaporation as well as membrane separation [12]. It is simply described by the passage of vapor from the hot feed side to cold permeate side through a porous and hydrophobic membrane [6]. The mass transfer driving force of this separation process is the difference in vapor pressure

between the hot and cold sides (across the membrane); this variation is caused by the temperature difference imposed by the operating conditions [5, 8, 12].

Due to the hydrophobic nature of the used micro-porous membranes, only vapor molecules of the volatile feed constituents can be transported across the membrane's pores while liquid diffusion is blocked [5, 8, 12]. Accordingly, the non-volatile feed contaminants are trapped in the hot side while only pure water is collected in the permeate side [5].

1. Types

There exist six different configurations of the membrane distillation in which the condensation medium vary [6]. These modes include: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD), vacuum membrane distillation (VMD), permeate gap membrane distillation (PGMD), and material gap membrane distillation (MGMD) [10]. In the direct contact membrane distillation the membrane is put in direct contact of both sides with the hot feed and the cold permeate respectively, and for the air gap membrane distillation the air gap plays a role of a cold surface to condense and collect the pure water. While in the sweeping gas membrane distillation, an inert cold gas is circulated at the permeate side to help move the vapor out the membrane by condensing it. On the other hand, vacuum is applied in the permeate channel in the vacuum membrane distillation to enhance the mass transfer across the membrane [12].

2. Advantages

MD possesses interesting advantages over other separation methods; it requires lower operating heating temperature and vapor spaces than traditional distillation techniques; as well as lower operating pressure than other separation methods whose driving force is the pressure of the flow like reverse osmosis and ultrafiltration [5, 8]. Therefore, it is considered to be low energy consuming technology which can be integrated with either low-grade thermal waste energy resources like waste heat from electric power plants (heat transfer fluid and boiler gases), high temperature by-products from industrial applications, or renewable energy sources like solar and geothermal energy [10, 11]. On the other hand, MD is characterized by 100% theoretical retention of non-volatile water-soluble species like ions, colloids, macromolecules, cells, salts, heavy metals [8-10]. Moreover, MD is capable of purifying brine solutions with high salt concentration while eliminating the traditional evaporator corrosion problem as well as the concentration polarization effect [5, 8, 9].

3. Limitation

Despite the attractive advantages of MD or DCMD, MD has some limitations that hindered its large-scale industrial application. The most important drawback of MD is its low permeate flux compared to other techniques like reverse osmosis and nano-filtration [5]. Besides, the performance of MD is susceptible to heat loss, mass transfer resistance, temperature polarization between the membrane's sides, and entrapped vapor molecules in the membrane's pores [6]. Now, although fouling or scaling in MD is less significant than in other separation methods, it is still of some concern especially when

it causes pore wetting. In fact, pore wetting not only affects the productivity of the MD system and the flux degradation with time, but it also negatively affects the permeate quality [6, 13, 14]. Whereby, foulants can be either organic (natural organic matter) or inorganic (sulfate, carbonate, chloride salts) species [11]. Moreover, although MD's equipment and operation costs are believed to be lesser than other traditional technologies, there exist uncertainties about its energy and economic costs [6, 14].

B. Direct Contact Membrane Distillation

1. Definition

Among the various modes of MD, direct contact membrane distillation (DCMD) is the simplest, easiest to be operated, and most efficient [5, 7]. Whereby, in (DCMD) the solution to be purified is heated continuously while the pure permeate solution is kept at a much lower temperature and supposed to play the role of condensing the vapor that passes through the membrane. While both streams are kept in continuous circulation on both sides of the membrane to impose a temperature difference for feed evaporation on the membrane's surface to occur, there is no need for a separate condenser [11]. A scheme of DCMD is shown in (Fig.1) .In fact, DCMD has its own advantages including: its resistance to the precipitation of organic and inorganic molecules due to its operation at atmospheric pressure, and its non-significant membrane fouling and scaling problems for a salt concentration less than 4.5 wt% [10].

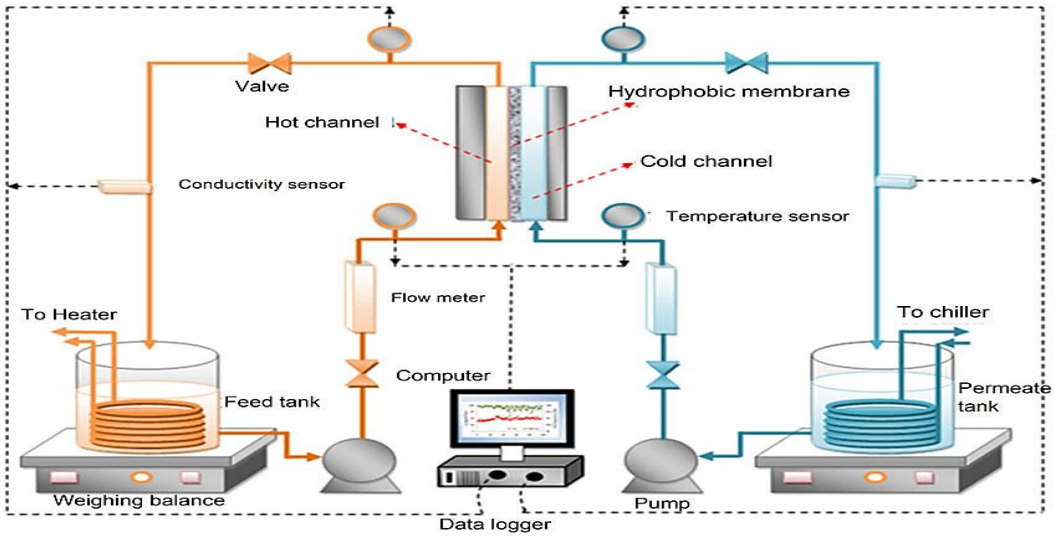

Figure 1-Direct Contact Membrane Distillation Scheme showing all components

2. *Membrane Importance and Characteristics*

The hydrophobic porous membrane is the most crucial part of the DCMD process and controls its efficiency [15]. Whereby, not only does it play the role of the physical separation medium between the concentrated feed and the pure permeate, but also it provides the interface for the water evaporation and contributes in the mass and heat transfer [9]. The main required properties of the membrane to be used in MD are: porosity, high hydrophobicity, resistance to heat conduction, mechanical stability, and affordability [15, 16].

For the MD to be competitive technology the used membrane should possess specific porosity (>75%) and pore diameter (100-300 nm) [9]. However, lower pore size lowers the permeate and deteriorates the membrane's strength flux; but the low pore size should be used for DCMD because it imposes a higher liquid entry pressure (LEP) of the membrane [9, 17]. LEP is used to evaluate the anti-wetting properties of the membrane and is given by the Laplace's equation (Eq.1) [18, 19]. Therefore, a better

performance occurs with a membrane having a higher LEP that is either achieved with smaller maximum pore size that should typically range between 0.5 and 0.6 (μm) or with high contact angle. In fact, pore wetting is described by the penetration of liquid molecules in the membrane's pores resulting in a deterioration in the quality of the permeate, this happens by a decrease in the rejection efficiency due to an increase in the permeate concentration of the contaminant [16]. Specifically, the narrow the pore size distribution is, the average pore diameter is close to the maximum pore diameter, the better wetting resistance is [20].

$$LEP = \frac{-2B \times \gamma_l \times \cos\theta}{r_{max}} \qquad \text{Eq. (1)}$$

Where LEP is the liquid entry pressure (bar), B is a geometric factor, γ_l is the surface tension (N/m), r_{max} is the maximum pore size (μm), and θ is the contact angle (°).

Besides, the contact angle is determined by the hydrophobicity of the membrane; the more hydrophobic the membrane is the higher its water contact angle is and the higher its LEP will become. A membrane is said to be hydrophobic if its water contact angle is ≥90˚, and superhydrophobic if the water contact angle is ≥ 120˚. In fact, the contact angle is a function of the membrane's fabricating material where a material with low surface energy shows a higher contact angle and the surface roughness that is a function of the fabrication technology and/or the post-fabrication treatment. Also, a higher hydrophobicity results in a better fouling resistance. Where, fouling occurs when contaminants in the feed build up on the membrane's surface

leading to pore blocking thus decreasing the rejection percentage and permeate's quality [20].

Another important property of the membrane is its thickness that affects the heat and mass transfer through the membrane. Whereby, a thinner membrane is believed to possess lesser mass transfer of the vapor molecules transported through it but shows lower heat efficiency due to the heat loss it causes [17]. Accordingly, the three membranes properties: porosity, pore size, and thickness should be optimized to come up with robust membrane that possesses a high contact angle as well as a high LEP with a relatively high flux that should be maintained for a long operating time. Specifically, sufficient LEP is obtained with a maximum pore diameter between 0.1 and 1 (μm) with a contact angle above 90˚ and a thickness between 30 and 60 μm with porosity above 75% [9, 19].

3. Available Membranes and Fabrication techniques

The most commonly used membranes in the DCMD are commercially-available membranes that are initially fabricated for micro-filtration applications using phase inversion, stretching, sintering or thermally-induced phase separation fabrication techniques. These polymeric membranes include: Poly(vinylidene fluoride) (PVDF), polytetrafluoroethylene (PTFE), and polypropylene (PP) [16]. The specific reasons for using these membranes are their lower surface energy and better processability than other materials (ceramics) [21].

However, most of the commercially hydrophobic membranes are expensive and suffer some performance drawbacks like wetting problems and possess limiting properties like low permeability [15, 21]. Therefore, researchers have been trying to use different fabrication methods that allow them to fabricate and engineer the desired membrane that ensures the optimum performance of the DCMD by possessing the best characteristics that result in high flux as well as high rejection efficiency at a low cost. The most used fabrication methods are electrospinning and phase-inversion. By using either of these methods the fabrication technique should be optimized in terms of operating conditions, type of hydrophobic polymer or blend of polymers, and additives to come up with a membrane having the best selectivity, permeability, LEP, contact angle, porosity, and thickness.

Electrospinning is a promising technique for production of micro-fibrous and micro-porous hydrophobic membrane by applying a high voltage difference between the tip of the feeding nozzle and the membrane collector drum. This method results in many membrane's characteristics that are important for DCMD such as high surface roughness, high mechanical properties, high contact angle, high porosity, low tortuosity, and high surface area-to-volume ratio [21]. The operating conditions such as the voltage difference, polymeric solution flow rate and concentration, tip to collector distance, and time of electrospinning can all be optimized to get the best desired membrane. Moreover, several modifications have been done to this traditional method to create hollow fiber mesh or tri-bore hollow fibrous membranes [9]. Also, due to its flexibility of operation, this technology is considered attractive to include any solution additives that improve the membrane's properties like nano-particles by simply dissolving these

particles in the dope solution or by depositing them on the fibers by dusting the electrospinning chamber by these solid particles [22].

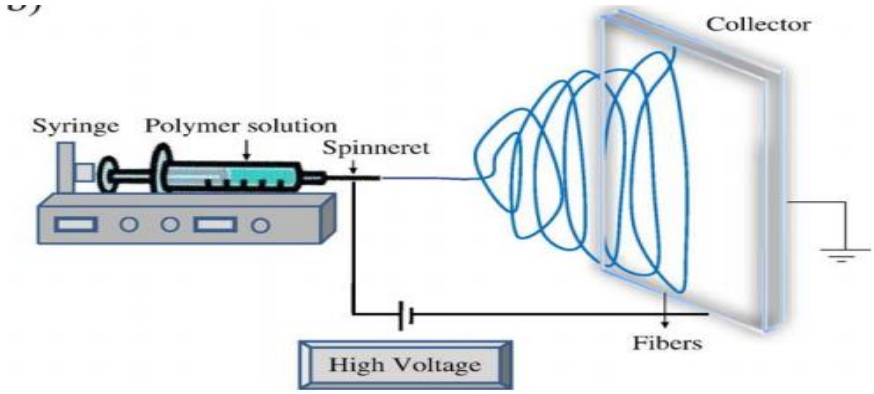

Figure 2-Electrospinning scheme showing the main components

Phase-inversion method is based on casting the polymeric solution on a glass plate by using a knife then moving the plate to a coagulation bath containing a non-solvent of the polymer but is miscible with the polymer solvent for the membrane to peel of the plate. After that, this film-like membrane is kept in a new bath to remove the remaining solvent and left to dry afterward. In this method, the dope solution concentration, the type of solvent, the time in the coagulation bath and its temperature, the solvent exchange bath's temperature and duration, and the non-solvent chemicals are all parameters that should be controlled and varied in order to fabricate the most robust membrane possessing all the adequate properties needed for the DCMD application. This method is capable of fabricating strong membranes with very small pore diameters and very good anti-wetting properties. Pore opening additives are very important in this technology because they play an essential role in determining the pore structure as well as the pore size. Therefore, the concentration of the theses additives and their type should be studied just like all previously mentioned parameters.

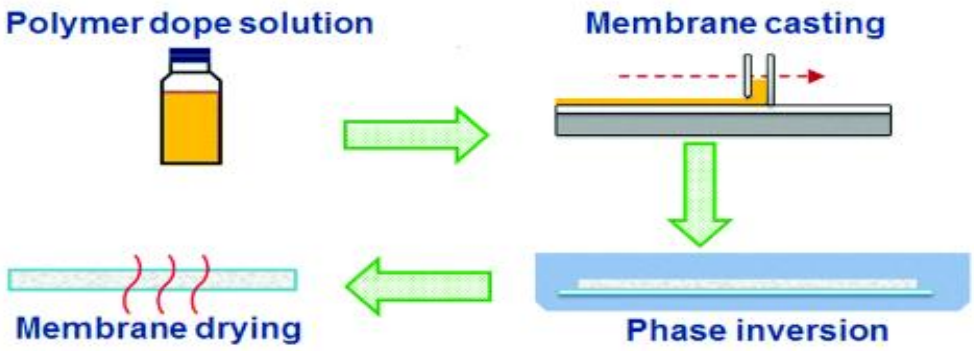

Figure 3-Casting Scheme showing all components and steps

The most used hydrophobic polymers are Polyvinylidene fluoride (PVDF), polyvinylidene fluoride-co-hexafluoro propylene (PVDF-HFP), and polypropylene (PP). But in some recent studies hydrophilic polymers like Polyethersulfone (PES), and polyamide (PA) as base polymers have been used. These layers have been hydrophobized by surface coating or surface grafting of hydrophobic additives [10, 15]. While most of the times a single method is applied for the fabrication of the desired membrane, the engagement of both methods is also possible. More specifically, the electrospun membrane can be used as a substrate on which the dope solution can be casted or vice versa.

4. Membrane Modifications

Researchers have tried to improve the performance of DCMD by applying different modifications to the overall system, membrane module, and membrane's properties. Specifically, different modifications have been applied to the commercial and non-commercial membranes to improve their anti-fouling characteristics (high LEP and super-hydrophobicity), as well as their thermal and mechanical properties. The

contact angle as well as LEP of the membrane have been improved by many methods including the impregnation of nano-particles or nano-tubes in the dope solution for electrospinning or casting or coating them on the membrane's surface for other commercial membranes (silicon oxide, zinc oxide, carbon nanotubes, MOFs, silica, iron, Teflons, graphene oxide, fluorosilanes, aluminum oxide, Zirconium dioxide …), plasma treatment, surface coating by water repellent chemical, and chamber dusting by nano-particles while electrospinning [9, 15, 16, 18, 22-30]. Moreover, to achieve ultra-low surface tension of the hydrophobic membranes researchers have used silanization and fluorination [31, 32].

On the other hand, a dual layer hydrophobic–hydrophilic membrane has been of great interest in recent studies where it showed better performance at the level of flux enhancement; as a result hydrophilization has been applied to the permeate side of the membrane using acid treatment [6, 16, 33]. Besides, special DCMD membranes have been developed in an attempt to create membranes with anti-wetting properties against organic molecules (oils, alkanes, alcohols, surfactants, biomass humic acid) like fabricating omniphobic membranes using a charged electrospun nanofiber scaffold, oleophobic under water membranes, and membranes with hierarchical reentrant structures [18, 26, 34]. Post-fabrication treatment (i.e., heat pressing) can enhance the performance of the membranes and improve its mechanical properties [35].

Not only were the modifications applied to the hydrophobic membranes but also to the DCMD process to enhance its energy efficiency as well as its performance and energy consumption. Energy efficiency as shown in equation (2) is a function of not

only the permeate flux but also the operating temperatures [19]. To increase this efficiency we can either apply modifications (module design or flow design) to increase the flux at the same operating conditions (temperature and flow rate), or lower the operating temperature by using higher feed flow rates using renewable energy resources. In addition to this, energy consumption (flow rates and temperature) can be saved by applying heat integration and using low-grade thermal waste energy resources and renewable energy resources.

$$EE = \frac{N \times \Delta H \times A}{F \times C_p \times (T_{in} - T_{out})} \quad \text{Eq. (2)}$$

Where N is the permeate flux (Kg/m^2.h), ΔH (J/kg) is the enthalpy of evaporation, F is the mass flow rate through the membrane's pores (Kg/s), A is the effective area of the used membrane (m^2), C_p is the specific heat capacity of the hot feed (J/Kg.℃), T_{in} and T_{out} are the temperature at the inlet and outlet of the membrane module.

Multi-stage module has been applied to both air gap membrane distillation (AGMD), vacuum membrane distillation (VMD) and a recent study showed that applying two and three stage DCMD has resulted in a daily water recovery increase by 1.92 and 2.72 times. In a multi-stage DCMD the same feed stream flows continuously from the first membrane module to the last module, each containing a hydrophobic membrane, while a counter-current permeate stream flows from the last module to the first one [14]. Besides, renewable energy especially solar water heaters have been investigated in the DCMD performance to decrease its energy costs and promising

results were obtained with a maximum productivity of 40.587 kg and a daily efficiency of 60.06 % [36].

5. Process Parameters

The operating parameters of the DCMD process play a great role in determining its performance and efficiency. As the feed temperature increases while keeping a fixed permeate temperature, the vapor pressure difference increases as well as the mass transfer coefficient leading to an increase in the flux. The flux also increases when increasing the feed's flow rate because more turbulence will be induced in the module channel. However, increasing the concentration of the salts or any contaminant to be removed from the feed stream generally decreases the obtained permeate flux [7, 8, 15, 25, 27, 37, 38]. On the other hand, the increase in the permeate temperature results in a decrease in the driving force which is the vapor pressure difference thus leads to a decrease in the flux just like the decrease in the permeate flow rate. Specifically, the effects of the permeate's operating conditions (temperature and flow rate) have lesser significant effects on the performance of the DCMD than those of the feed stream.

Another important factor to study in the performance of the DCMD other than the obtained flux is the salt or contaminant rejection percentage. As shown in equation (5) the rejection efficiency R is a function of both the concentration in the feed as well as the permeate [39], and the goal is to obtain an experimental rejection percentage as close as possible to the theoretical 100% rejection. The same operating conditions, flow rates, temperatures, and the contaminant concentration should be studied to come up

with highest possible rejection efficiency. In general, the rejection efficiency decreases as the concentration of the contaminant in the feed increases [7, 27]; however, in other cases the rejection efficiency increased as the feed concentration increased [37].

Concerning the temperature effect, some results have shown a decrease in the rejection efficiency with an increase in the feed temperature [36, 40]. While the effect of the flow rate is relative to the operating temperature and the contaminant to be removed; whereby, for sodium chloride the rejection increased with the flowrate increase [15] while the rejection decreased and increased in the case of phosphorus based on the operating temperature [40].

6. DCMD Applications

DCMD is widely used for seawater and brackish water desalination due to its 100% theoretical salt rejection capability [8]. However, desalination is not the only practical application of DCMD due to its lesser significant fouling and scaling problems at specific contaminant concentrations compared to other separation methods such as microfiltration or reverse osmosis [10]. The other applications include the treatment of wastewater from textile industries, olive mills, gas and oil production fields, pharmaceutical industries, metal plating industries, ground water decontamination, radioactive waste water, human urine, acid-containing water, anaerobic digestion, and nano-particle water suspensions [8, 32, 38, 40-49]. Examples about the pollutants from dye industries are water containing methylene blue, crystal violet, acid red 18, acid yellow 36, phenol, aniline, sulfanilic acid, 3,4-dihydroxybenzoic acid, and p-chloroaniline [50, 51]. While metal contaminants include: boron, arsenic, copper,

nickel, and zinc whereas pharmaceutical compounds include antibiotic [7, 52, 53]. On the other hand, the digestate from anaerobic digestion contains nitrogen, phosphorous, and ammonia while the acid pollutants include sulfuric acid and humic acid. Also, highly saline radioactive waste water was treated in the DCMD and contained: cobalt, strontium, cesium, and boron [40, 47].

CHAPTER II

EXPERIMENTAL PROCEDURE

A. Materials

Dimethylformamide (DMF) with ≥99.8% purity purchased from Sigma Aldrich, Tetrahydrofuran (THF) with ≥99.8% purity purchased from Sigma Aldrich, polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) purchased from Sigma Aldrich with an average molecular weight of 455,000 g/mol and a density of 1770 kg/m^3 ,ethanol with ≥99.8% purity purchased from Sigma Aldrich commercial PTFE membranes with 0.45 micron pore size purchased from Sterli-Tech, deionized water , sodium chloride, two jacketed beakers, PVC pipes, two water circulators, two conductivity meters, two peristaltic pumps, Polypropylene membrane holder purchased from Sterli-Tech, and a balance.

B. Process Installation

A lab-scale DCMD process was installed and a picture of the setup is shown in (fig.4). The setup consists of two water circulators one used for cooling and another for heating. Each of the circulators was connected using pipes to a jacketed beaker. Where, one beaker was used for the permeated and the second for the salty solution. Also, a conductivity meter was immersed in each beaker in order to monitor the change in the conductivity. On the other hand, each peristaltic pump was connected to one side of the membrane holder. In which two pipes were used on each side of the membrane holder; one for feed inlet and another for feed exit. Two pumps were installed; one for the hot feed and another for the cold permeate. More specifically, a pipe had to be pumping

water from the beaker through the pump to the membrane holder and another pipe had to return the remaining water from the holder to the beaker. Besides, the flow of water from the circulator to the jacket of each beaker was necessary to maintain a constant pre-determined temperature.

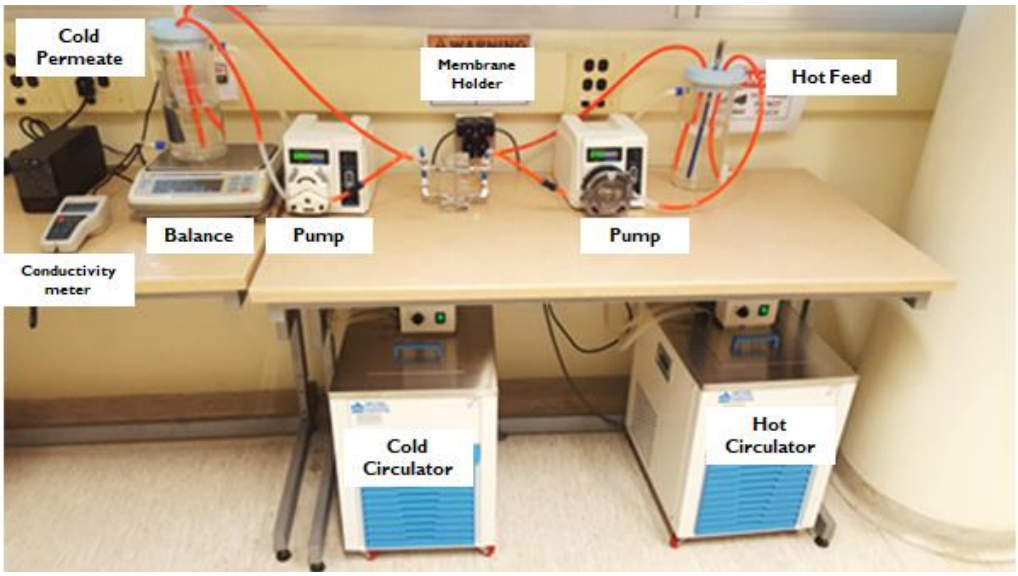

Figure 4-Lab scale DCMD

C. Membrane Fabrication

The steps to fabricate the electrospun membrane included the preparation of the polymeric solution as follows; we dissolved a pre-determined amount of this polymer in a mixture of solvents DMF-THF 50:50 by volume to form an 18 wt% polymeric solution. This solution was kept on a stirrer for around 24 hours with no additional heat at 600 rpm. After making sure the solution was totally transparent with no polymer pellets remained un-dissolved, the solution was transferred to a 20 ml syringe to be installed in the electrospinning machine. Before turning on the electrospinning machine provided by (FLUIDNATEK LE-10, BIOINICIA, Spain), the collector was covered with aluminum foil then polyester substrate. After that, the

voltage was set at 20 kV, the flow rate at 0.5 ml/h, the tip to the collector distance at 15 cm, and the collector's speed at 600 rpm. The duration of electrospinning was set as 24 hours.

D. Membrane Modification

1. Heat pressing

After drying the membrane for 2 hours in the oven at 70 ˚C, the membrane was heat pressed in the oven. Heat pressing includes the use of two aluminum plates that were covered with aluminum foil and iron standard weights. Where, the membrane was put between the metal plates and transferred to a pre-heated oven at a pre-determined temperature. Standard weights around 20 kg (equivalent to 6.5 kPa pressure) were put over the plates. Where, the upper surface of the membrane, being fluffy due to the electrospinning, was placed to be directly beneath the standard weights. Knowing the melting temperature of the PVDF-HFP polymer is around 160 ˚C, three different heat pressing temperatures were tried. Where, the temperature of heat pressing was varied from 150 ˚C to 160 ˚C while the duration of heat pressing in kept 8 hours. A summary of the conditions is shown in Table (1).

Table 1-Heat pressing conditions

Temperature (˚C)	150	155	160
Duration (h)	8	8	8
Pressure (kPa)	6.5	6.5	6.5

2. Ethanol treatment

The heat-pressed membrane was rolled and transferred to glass jar filled with ethanol at room temperature. The membrane was treated at 65 ˚C in a water bath shaker for 24 h.

E. Membrane Characterization

The following techniques were used for characterization of the membranes:

1. SEM

Scanning Electron Microscope (SEM MIRA 3 LMU Tescan, Czech Republic) was used to study the morphology of the membranes and to measure the fiber diameter. Samples were coated with gold using Q150 T Turbo - Pumped Sputter Coater (Quorum Technologies). Then, samples were placed into the SEM sample holder. The working distance between the lenses and the sample is 10 mm to 16 mm, with an acceleration voltage of 20 kV and using an in-beam detector at a magnification range from 20K to 50K.

2. Contact Angle and Surface Energy Measurements

The contact angle of the electrospun or modified membranes will be measured through the optical contact angle measurement. This is the angle formed between the liquid-vapor interface and the liquid-solid interface. This instrument contains a high-resolution camera and data-physics software that are used to analyze this dimension. Whereby, a membrane is considered hydrophobic if its contact angle is higher than 90° and super hydrophobic if higher than 120°.

3. Porosity and Water Resistance Measurements

A capillary flow porometer from Porous Material Inc. (PMI) apparatus is used to analyze the porosity and water resistance of the electrospun and modified membranes. The procedure starts with inserting the membrane into the machine, then wetting the membrane pores with a wetting agent (Galwick). After that, saturated air will be pressured to pass through the membrane's pores. The machine records the volume of the liquid that passed through the membrane's pores as well as the experimental gas pressure. Based on (Eq. 1), the pressure and the maximum pore diameter are inversely proportional so smaller pores require higher pressures to let pass the liquid because they have higher capillary attraction. This fact will allow the software to generate the pore size distribution and the mean pore size diameter. Moreover, this machine is also used to measure water resistance that can be defined as the amount of water in mm that can be mounted above the membrane before any droplet can penetrate it.

4. Thickness

To measure the thickness of the different membranes, a Brunswick machine that has a probe tip and a floating stand anvil. Where, a membrane is placed beneath the probe contact tip that is lifted by squeezing a hand vacuum pump. Once the sample is placed in the right position the hand vacuum pump is released and a measure is shown on the screen.

F. DCMD Testing

To assess the effectiveness of the fabricated membranes these membranes are tested on a DCMD lab setup that we installed. The evaluation of the membrane is done by monitoring the performance of the desalination process. More specifically, this is done by calculating the permeate flux which is reported in (Kg/m^2 hr) which is the increase in mass recorded on balance divided by the surface area of the membrane in contact with the feed or permeate inside the membrane holder and time as shown in (Eq.3). Where, a balance is used to monitor the increase in the permeate mass by recording the apparent mass each pre-specified time lapse and saving them on a connected computer. In addition to the flux, we also calculate the salt rejection using the variation in the conductivity of both feed sides with the help of (Eq.4). In which, a conductivity meter is immersed in each beaker to record the values of the salt concentration.

$$F = \frac{\Delta m}{A.t} \qquad \text{Eq.(3)}$$

With F, Δm, A, and t representing the water flux in (kg/m^2h), increase in the mass of permeate in (L or kg), effective membrane surface area in (m^2), and the sampling time duration in (h) respectively.

$$R(\%) = \frac{C_f - C_p}{C_f} \times 100 \qquad \text{Eq. (4)}$$

Where R is the rejection percentage (%), C_f is the concentration of the contaminant in the feed stream, and C_p is the concentration of the contaminant in the permeate side.

CHAPTER IV

RESULTS AND DISCUSSION

Due to many interesting properties of electrospun membranes like high surface roughness, high mechanical properties, high contact angle, high porosity, low tortuosity, and high surface area-to-volume ratio, electrospinning has been widely used as a fabrication technique to make hydrophobic membranes for DCMD. Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) polymer which was widely used for MD processes due to its attractive chemical and physical properties like low surface energy and hydrophobicity [21], was chosen to be used for our application. This polymer was electrospun to produce a hydrophobic membrane which was further modified. The change in the properties of each membrane after each modification step is monitored as well as the membrane's performance in DCMD.

A. Membrane Electrospinning

To produce the electrospun membrane we had to choose the best electrospinning conditions that result in the minimum possible pore size that is a result of minimum fiber diameter. For this reason, we used the following conditions stated in Table (2) to produce the desired membrane.

Table 2-Electrospinning conditions

Concentration (wt%)	Tip to collector distance (cm)	Collector's speed (rpm)	Voltage (kV)	Flow rate (ml/h)	Duration (h)
18	15	600	20	0.	24

1. *Membrane's Properties*

To check the different properties of the membrane many characterization tests were done. The obtained results are shown in table (3) and Fig. 5

Table 3-Properties of electrospun membrane

Average Pore size (μm)	Contact Angle (˚)	Thickness (μm)	Maximum Pore size (μm)	Average Fiber Diameter (nm)
0.6025	136.6	250	1.72	369

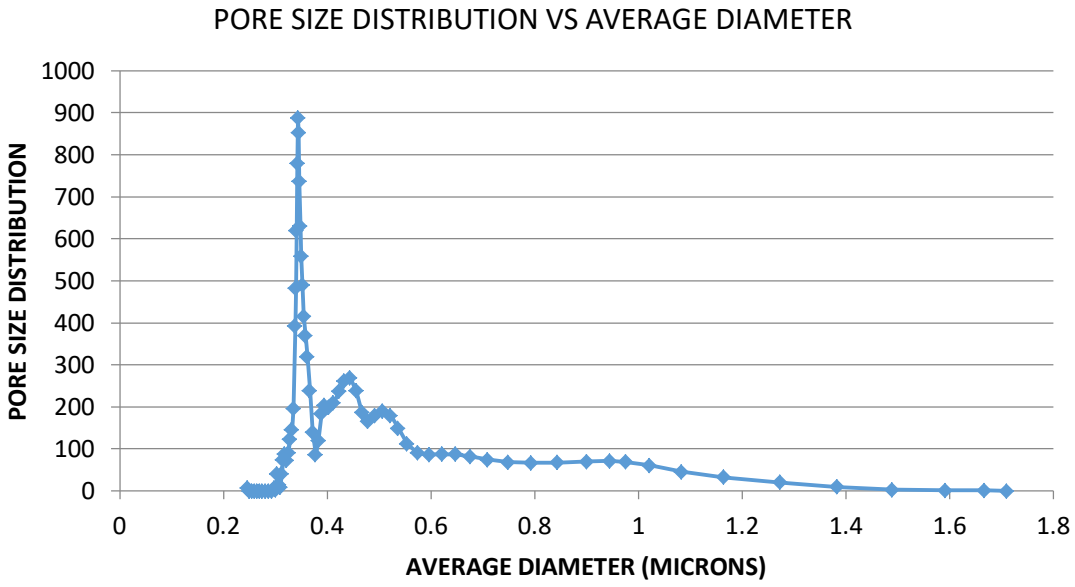

Figure 5-Pore Distribution for electrospun membrane

As can be seen in (fig. 5) the membrane has a wide distribution of pore diameters (0.2 μm-1.7 μm). This is due to the non-uniform distribution of the fiber diameter throughout the membrane area. Where, high fiber diameter impose higher pore diameter while smaller fibers form smaller pores. On the other hand, the presence of

pores with a diameter >1 μm will increase the risk of pore wetting and might lead to entrapment of condensed water vapor inside the membrane pores [9, 19].

2. SEM Pictures

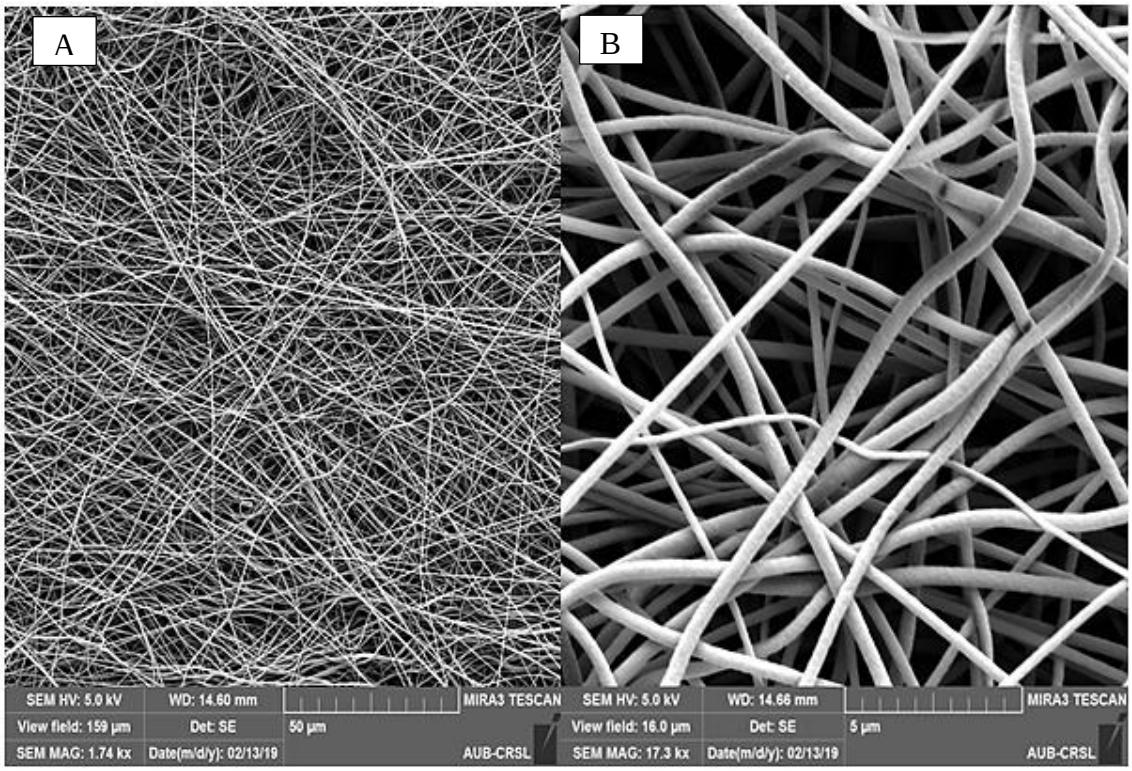

Figure 6-SEM pictures of the electrospun membrane. A: Magnification distance of 50 µm and B: Magnification distance of 5 µm.

The SEM pictures shown in (Fig. 6), shows the randomly distributed nano-fibers that are entangled to form the micro-pores of the membrane. Also, the fibers appear to have slightly different diameters and stacked randomly on top of each other to make a range of pore sizes as shown in (Fig.5). Moreover, it is also seen that the fibers are loosely connected, and this explains the very high surface water contact angle.

The performance of this membrane was tested in DCMD process and both the obtained flux and the salt rejection percentage are shown in the figures below.

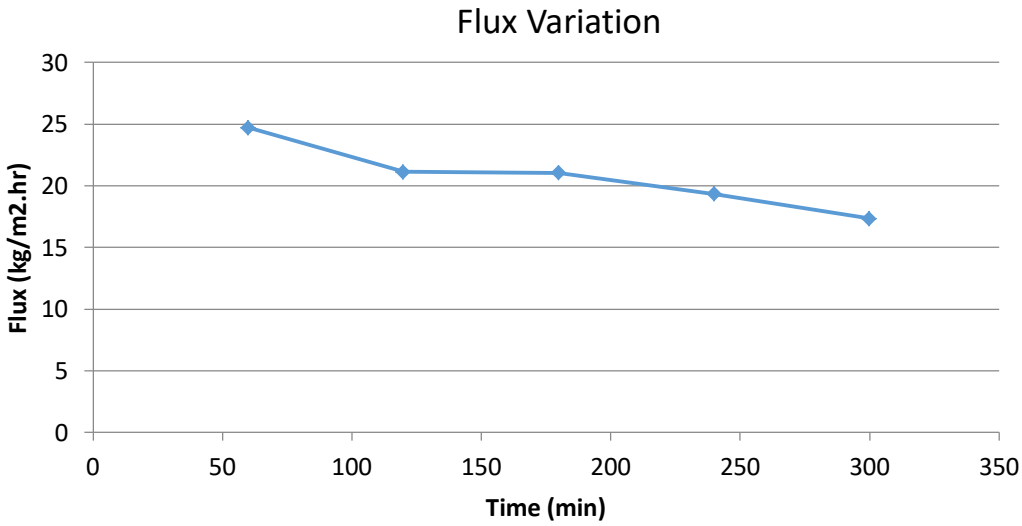

Figure 7-Flux Variation of the Permeate given by an electrospun membrane

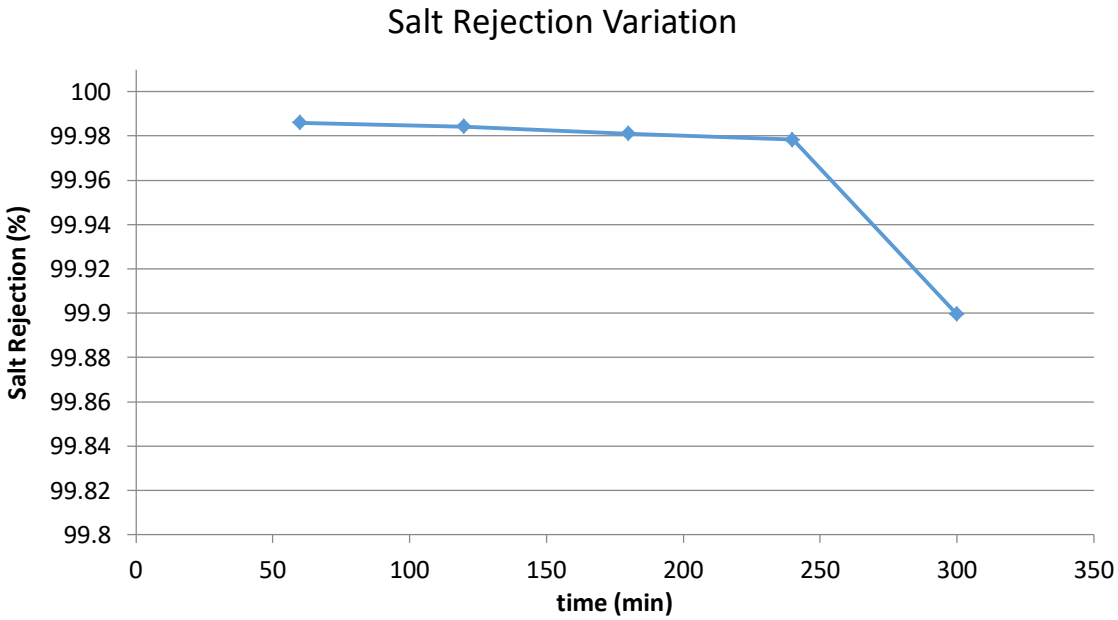

Figure 8-Variation of Salt Rejection of an electrospun membrane

The water desalination flux through the non-modified electrospun membrane was not stable with time and decreased from 25 to less 17 Kg/m^2/h in 5 h (Fig.7). On the other hand, the salt rejection percentage was around 99.99% at the beginning of the operation but decreased to reach 99.89% after 300 min (Fig. 8). The results suggested the membrane wetting during this process.

B. Membrane Modification

1. Heat Pressing

Based on (Eq.1) the greater the maximum pore size the lower the liquid entry pressure the membrane will possess. In other words, when the maximum pore diameter of the membrane is higher than 1 μm it will handle a low pressure before it allows water to penetrate through its pores. Besides, the loose fluffy surface fibers that give the membrane an additional hydrophobicity will be moved and modified due to the harsh conditions in the membrane holder (i.e., high flow rate and high temperature). Therefore, in an attempt to decrease the maximum pore diameter, strengthen the membrane, and improve its surface properties, heat pressing at different temperatures was applied.

a. Change in Properties

The change in the properties of the membrane was observed and the results are shown in the figures below. Besides, the heat pressing conditions and names of each membrane are shown in the table below.

Table 4 Names of modified membranes

Name	ES/ electrospun	M150	M155	M160
Heat pressing temperature (˚C)	---	150	155	160
Duration (h)	---	8	8	8

i. Average Pore size

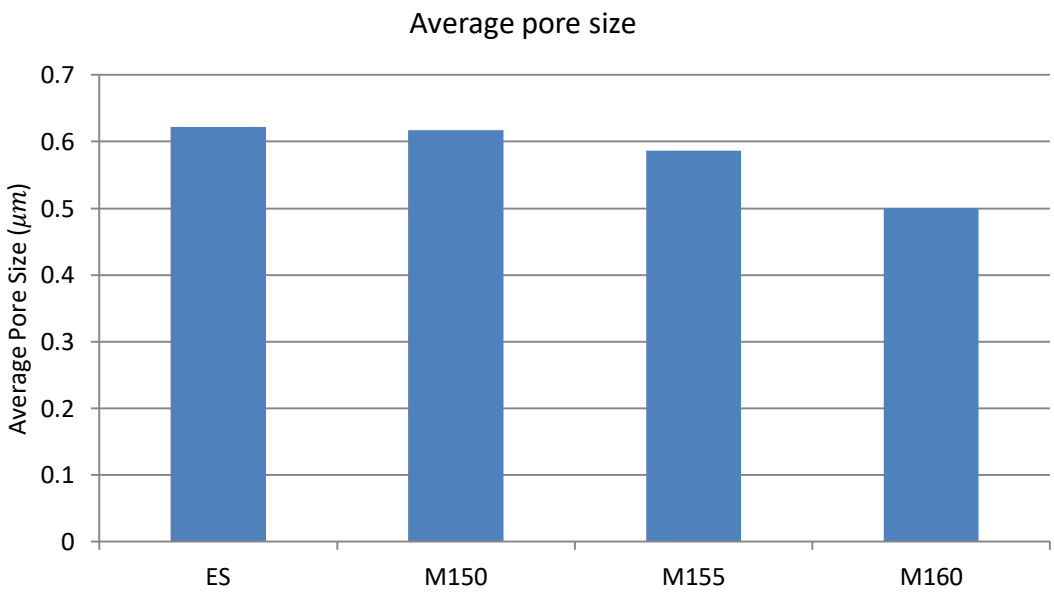

Figure 9-Variation of the Average Pore Diameter After Heat pressing

ii. Contact Angle

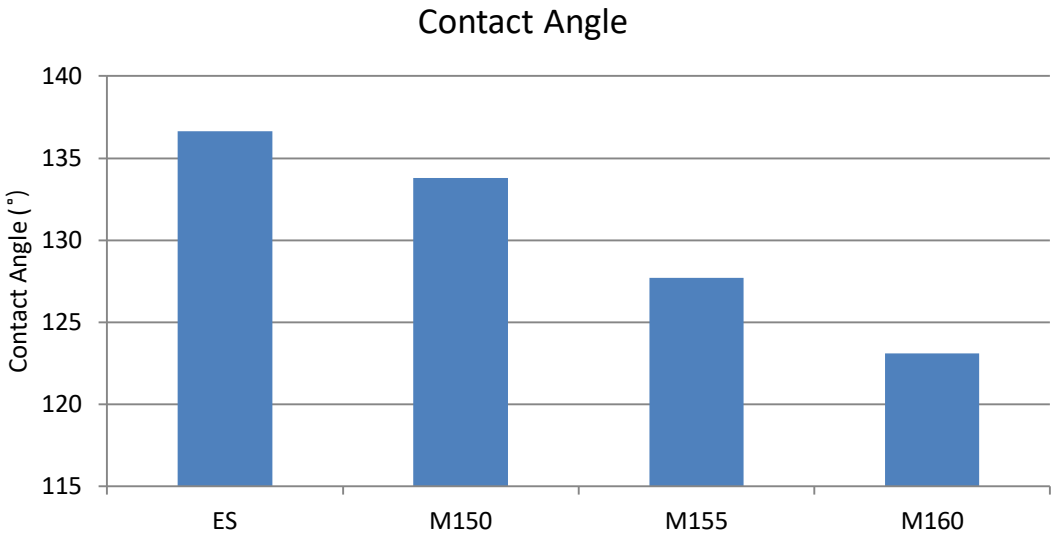

Figure 10-Variation of Contact Angle after Heat Pressing

iii. Thickness

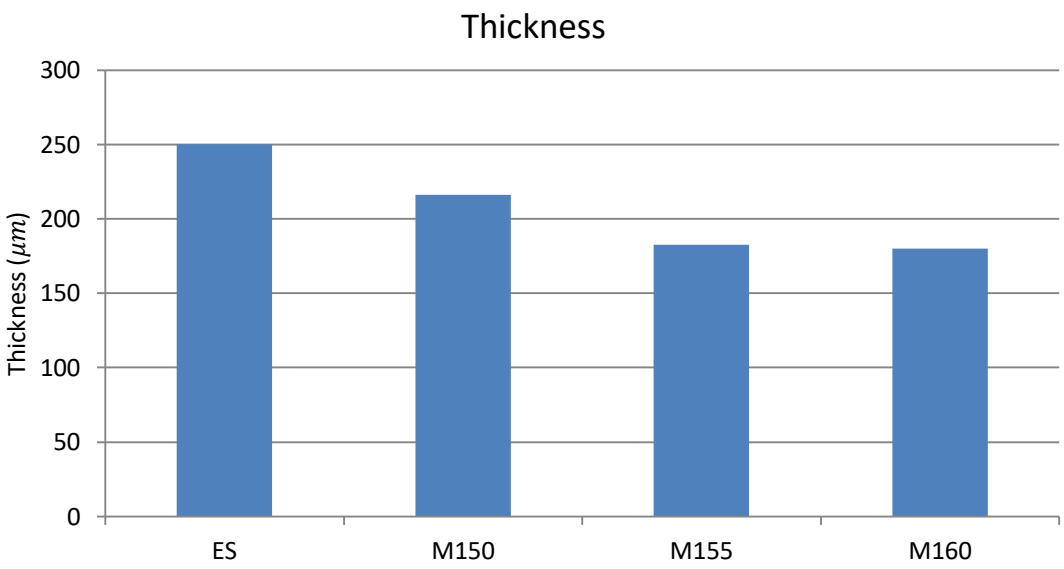

Figure 11-Thickness Variation after Heat Pressing

iv. Pore Size Distribution

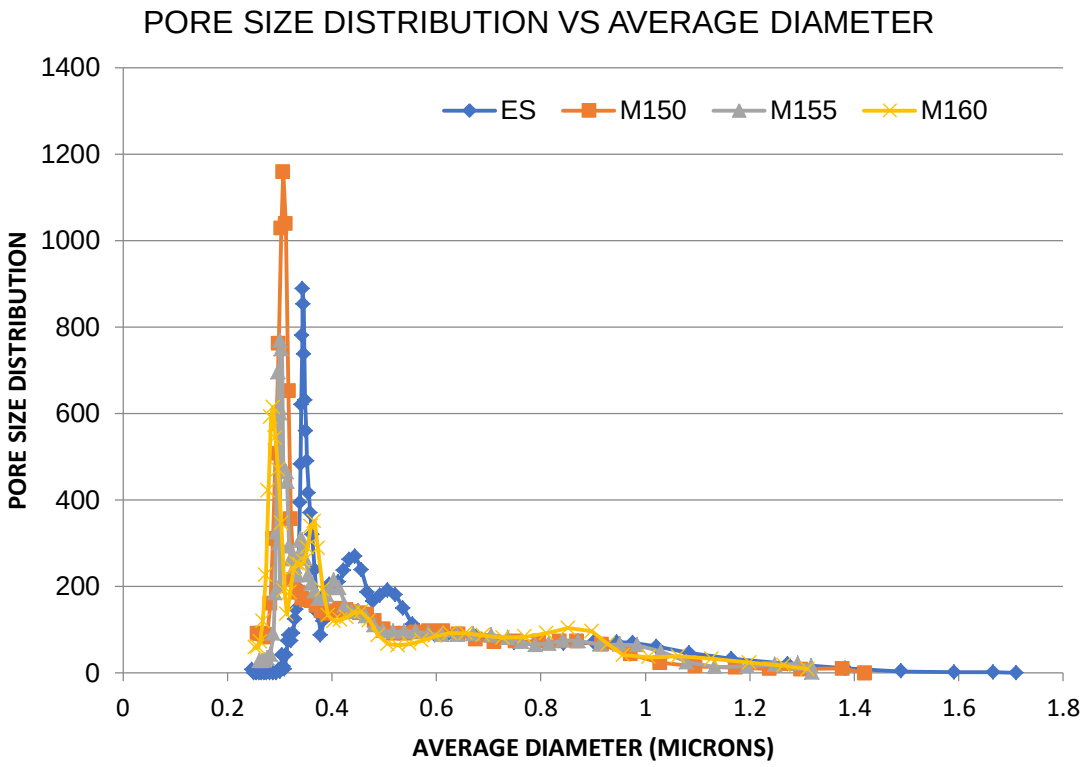

Figure 12-Pore Distribution of the heat pressed membranes

The average pore diameter decreased from 0.62 μm to around 0.5 μm by increasing the heat pressing temperature (Fig. 9). This was expected because the membrane's fibers will be slightly melting and many large and small pores will be closed.

Besides, the contact angle of the membrane was also decreasing with an increase in the heat pressing temperature (Fig.10). Where, it was around 136 ˚ before any heat pressing and decreased to as low as 123˚. This contact angle decrement was due to the decrease in the surface roughness due to both the pressure by standard weights as well as the heat applied.

The thickness of the membrane also decreased with an increase in the heat pressing temperature (Fig.11). The thickness of the unmodified membrane was around 250 μm and decreased to be 180 μm after heat pressing at 160 ˚C. This was due to the melting of fibers and fusion in the vertical direction under the effect of high temperature and pressure.

Figure 12 showed that the pore size distribution also narrowed down as a result of the heat pressing temperature. This is accompanied by a left shift in the peak of the plot indicating a decrease in the average pore diameter of the modified membrane. This result was due to the effect of temperature on fiber melting and fusion that caused pore closing.

b. DCMD Performance

To test the performance of the membrane in the desalination process the three membranes were tested in the DCMD process and the results are shown in the figures below.

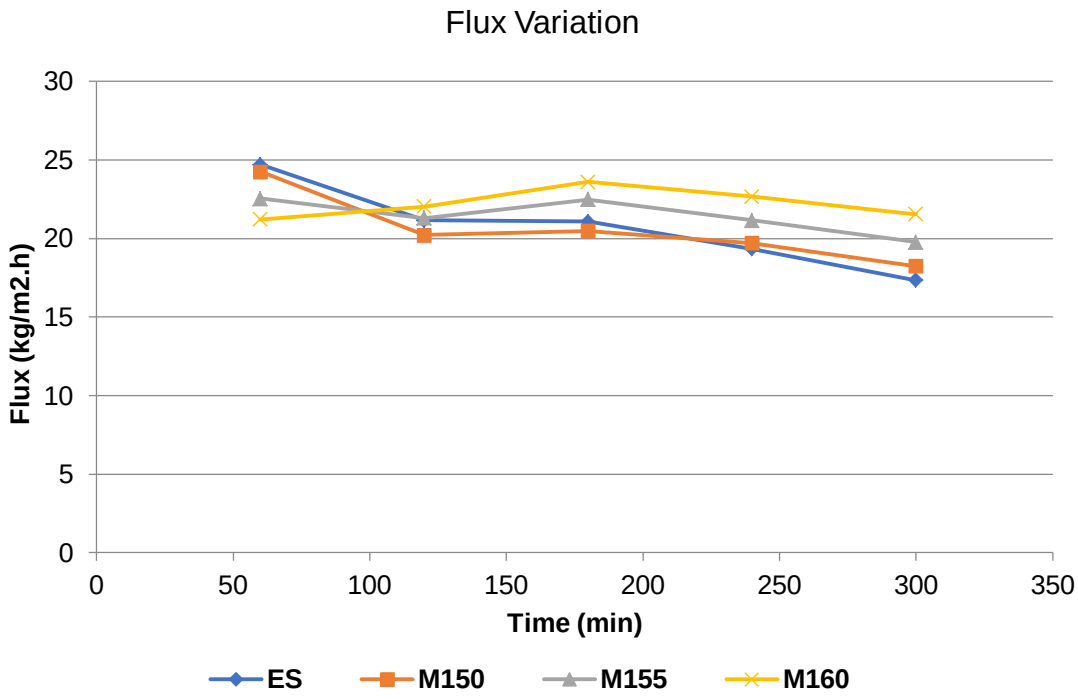

Figure 13-Flux Variation of the permeate given by the Heat pressed membranes

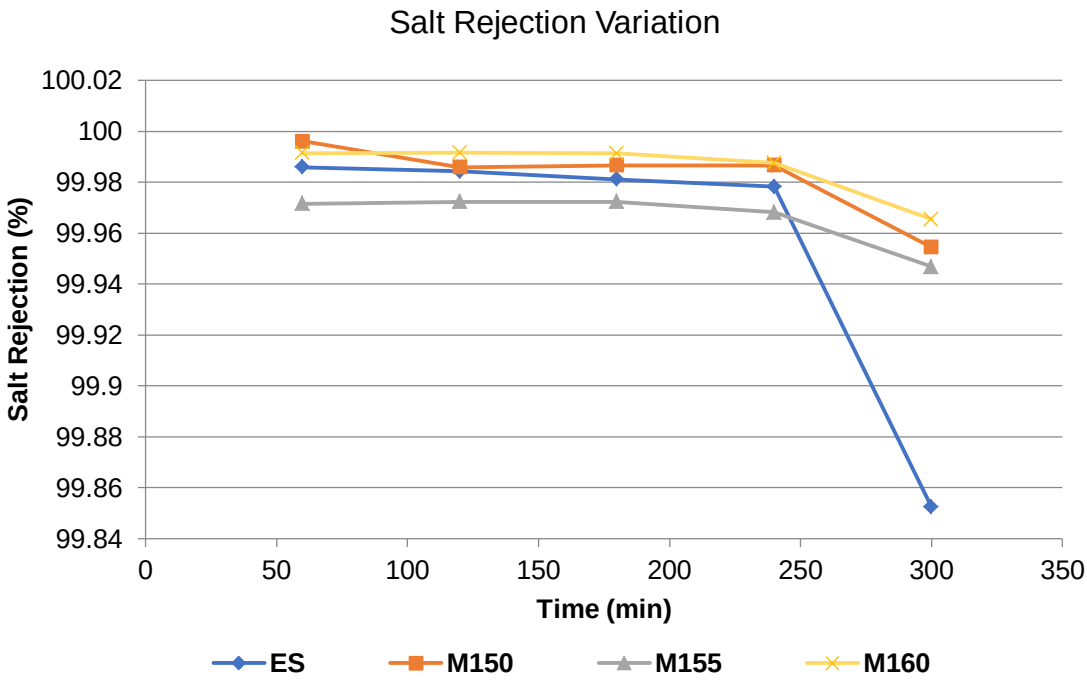

Figure 14-Salt Rejection Variation of Membranes after Heat pressing

The obtained results from DCMD test (Fig. 14) show that all modified membranes have witnessed pore wetting after 4.5 hours of starting the test and this was shown by the decrease in the salt rejection percentage with time. Still, the heat pressed membranes have shown a better salt rejection percentage than the unmodified electrospun membrane throughout the whole test period. In fact, among all membranes, the heat pressed membrane at 160 ˚C showed the best salt rejection results. Concerning the flux, although all the fluxes seem close to each other none of the flux variations appears unstable (Fig.13). Accordingly, we can say that heat pressing has remarkably improved the salt rejection percentage and pore wetting of the electrospun membranes but it seems not enough to be practically used in DCMD.

2. Ethanol Treatment

The modification involves heating the ethanol and the water bath shaker at 65 ˚C prior to immersing the membrane completely in the ethanol jar that was totally closed and returned to the water bath. After the membrane spent 24 h in the ethanol at 65 ˚C it was removed and left to dry overnight at room temperature.

To check whether the characteristics of the membrane improved by this treatment, all previous characterization tests were applied for the new membrane called **M160-et** and results are shown in the figures below.

a. <u>Change in properties</u>

Thickness, average pore diameter, contact angle, tensile strength, liquid entry pressure, fiber diameter, and pore size distribution are all shown below.

i. Contact Angle

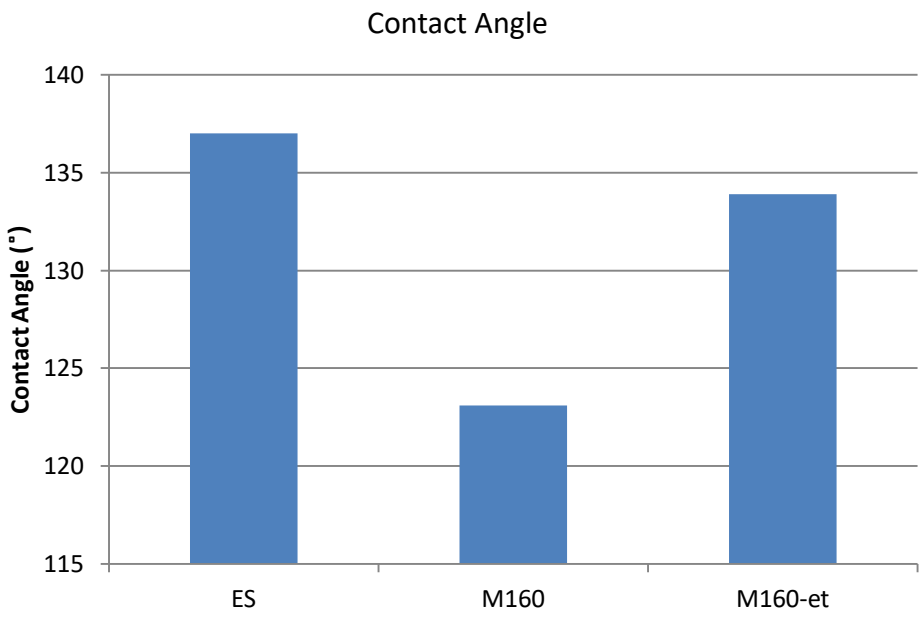

Figure 15-Contact angle after ethanol treatment

ii. Thickness

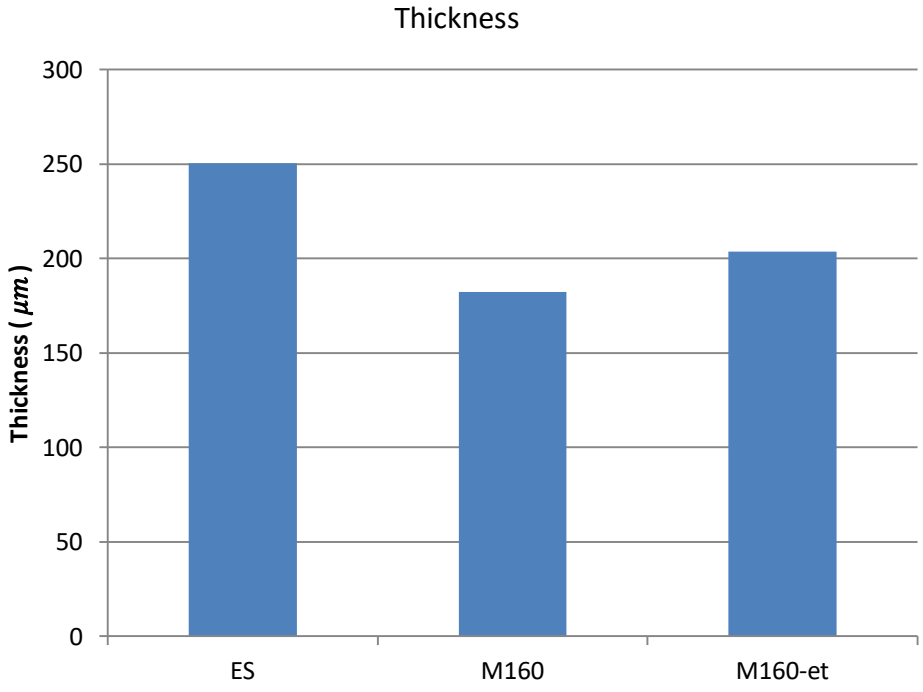

Figure 16-Thickness variation of after ethanol treatment

iii. Average pore size

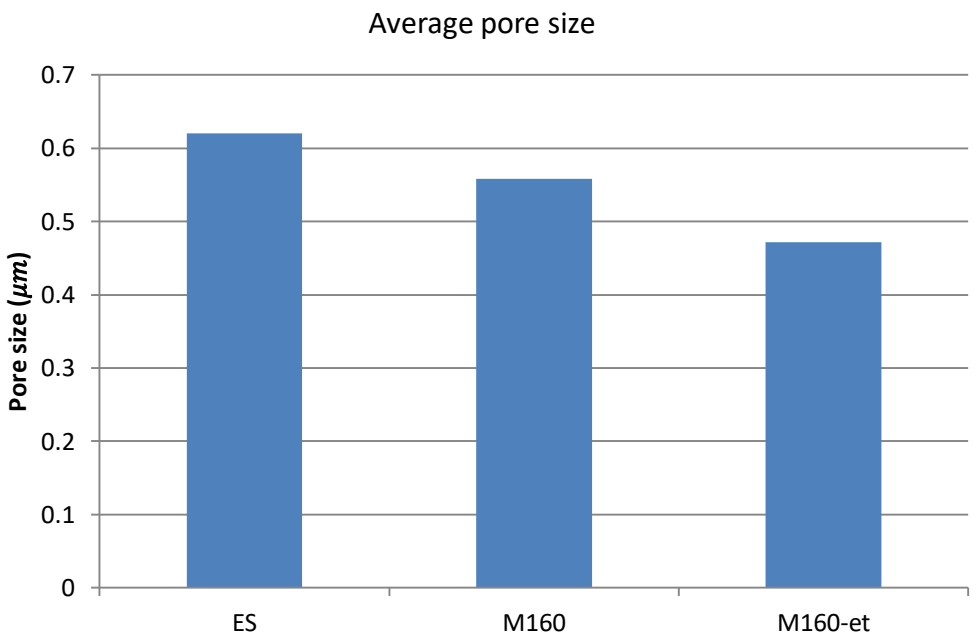

Figure 17-Average pore size variation after ethanol treatment

iv. Liquid entry pressure

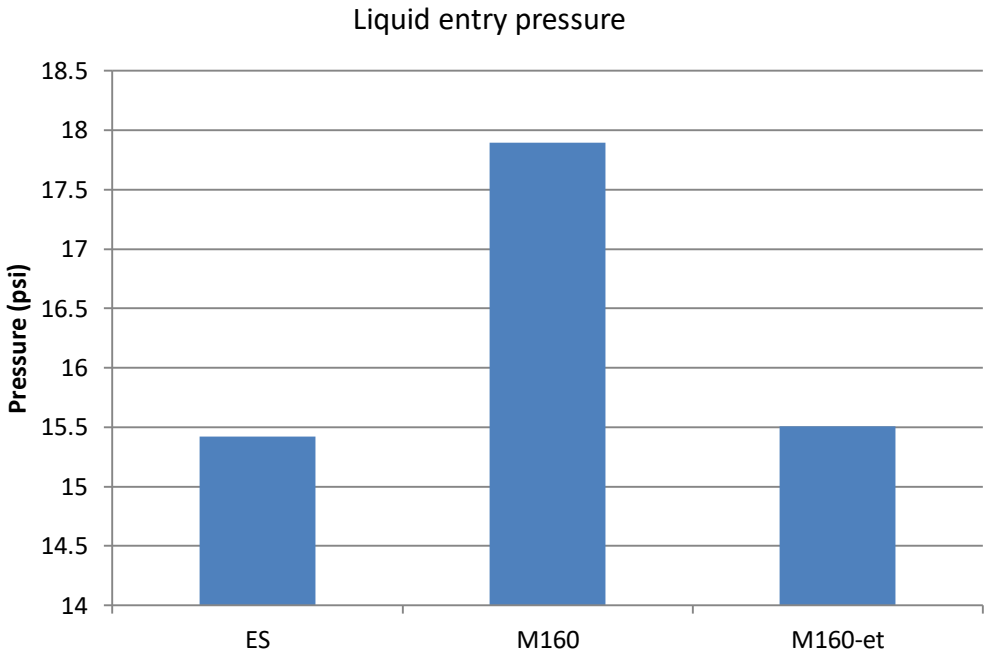

Figure 18-Liquid entry pressure variation after ethanol treatment

v. Fiber Diameter

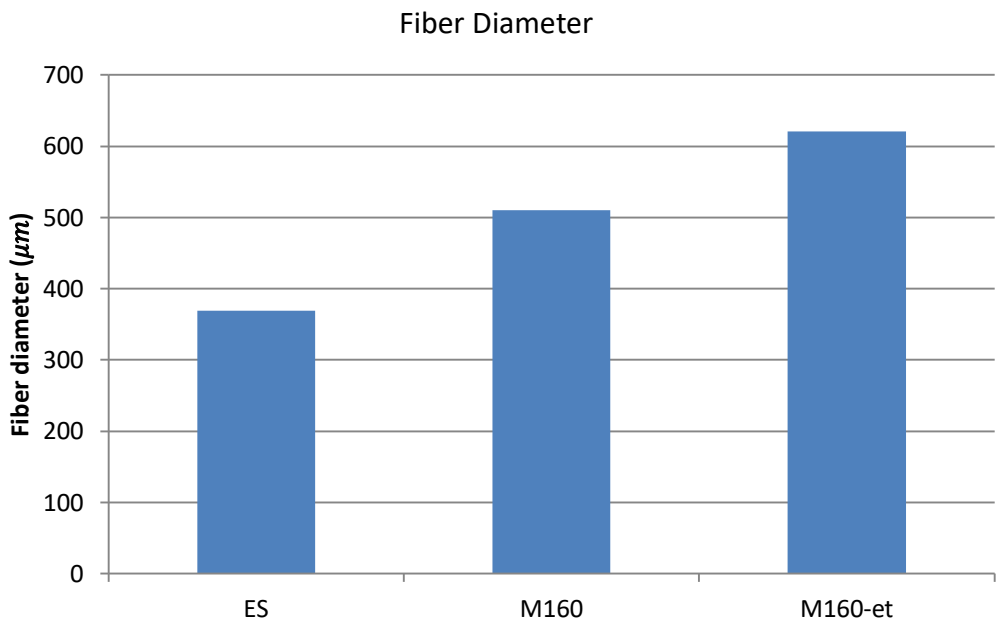

Figure 19-Fiber Diameter variation after ethanol treatment

vi. Tensile Strength

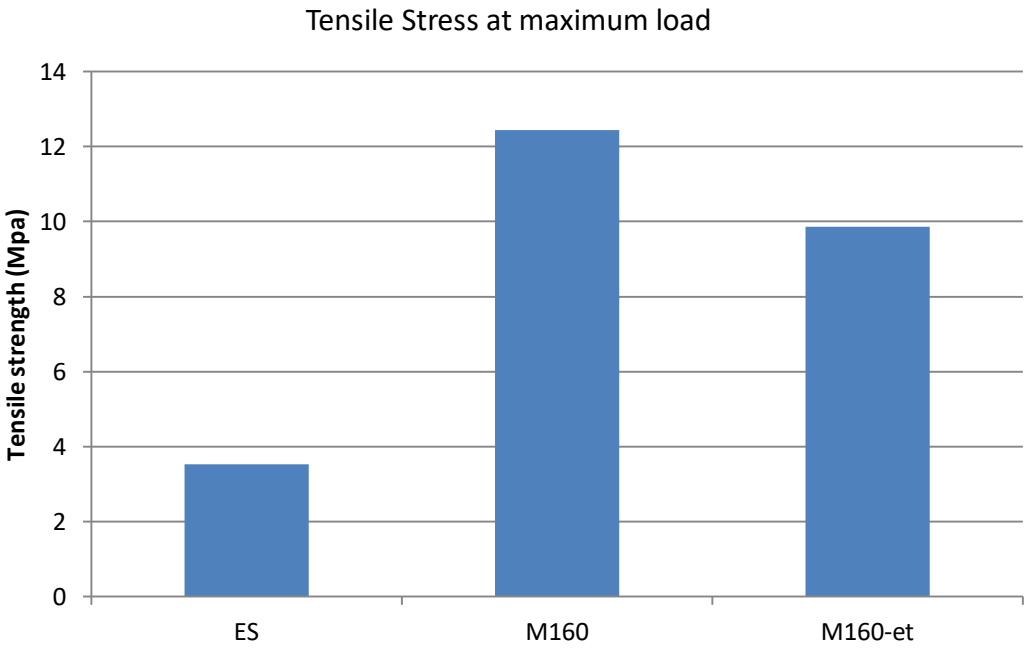

Figure 20-Tensile strength variation after ethanol treatment

vii. Pore size distribution

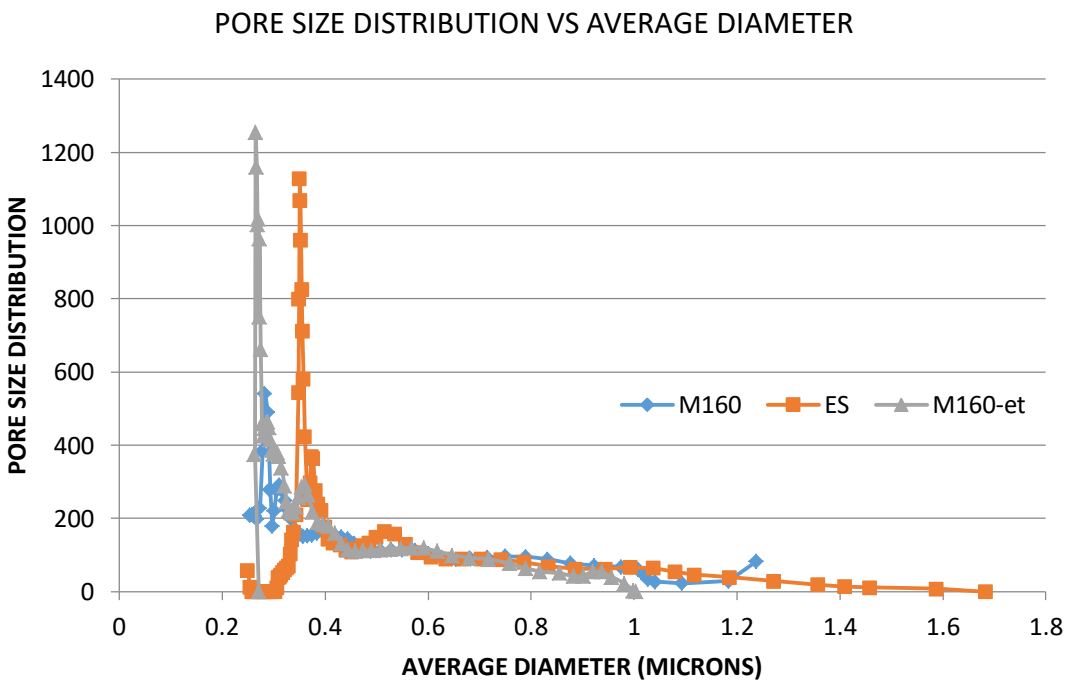

Figure 21-Pore size distribution after ethanol treatment

viii. SEM Pictures

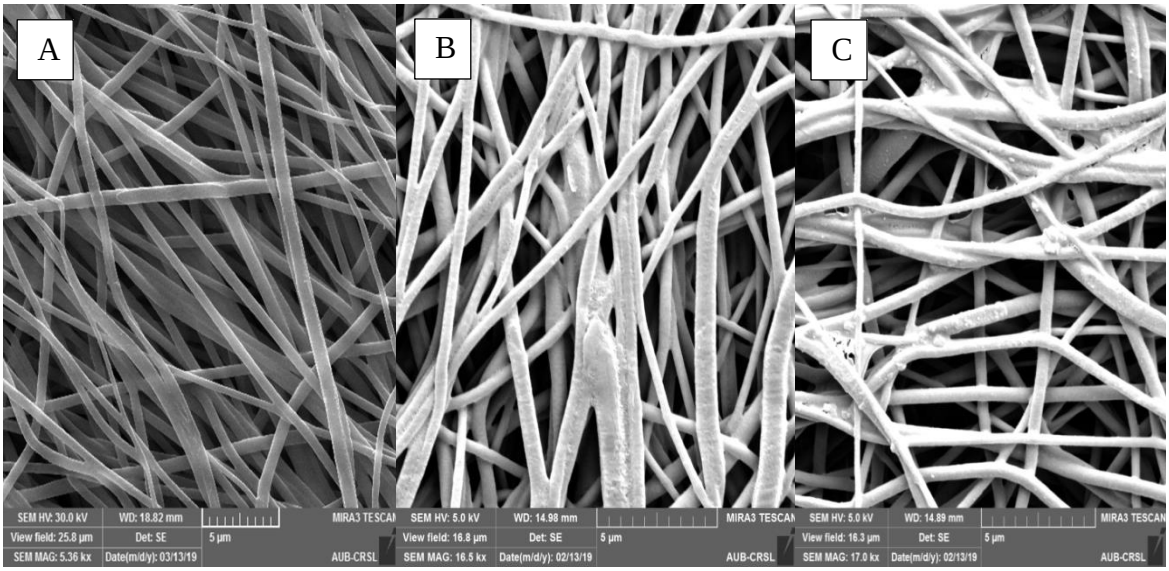

Figure 22-SEM pictures of PVDF-HFP electrospun membrane, A: Before any treatment. B: after heat pressing at 160 C. C: After ethanol treatment at 65 C.

As shown in (Fig.15) the contact angle of the electrospun membrane was regained after the ethanol treatment (134˚) after it decreased due to heat pressing. This shows that the hydrophobicity of the membrane is regenerated and this is due to the effect of ethanol on the fibers that are totally wet and swollen. In fact, the particular change in the morphology of the fibers has affected the thickness, the average pore diameter, and the average fiber diameter of the membrane. Where, the thickness of the membrane increased to 204 μm after it was 183 μm after heat pressing (Fig.16).

On the other hand, the fiber diameter has continued to increase just like it increased after the heat pressing (Fig.19). Where the fiber diameter was initially 369 nm, it increased to 620 nm after heat treatment then became 510 nm after the ethanol treatment. This happened as a result of the partial melting of the fibers by each step of thermal treatment causing fibers to fuse together closing some pores.

This specific effect of the ethanol treatment on pores has been shown by a decrease in the average pore diameter in addition to a decrease in the maximum pore size (Fig.17 and Fig. 21). The average pore diameter decreased slightly from 0.5 μm after heat pressing to 0.47 μm after ethanol treatment. Whereas, the maximum pore size was around 1.3 μm after heat pressing and decreased to nearly 1 μm after ethanol treatment.

In addition to that, we can see a decrease in the peak in the pore size distribution indicating a decrease in the number of pores that is a result of pore closing by fiber fusion. Although the effect of heat pressing on the liquid entry pressure (LEP) was positive, the liquid entry pressure decreased after ethanol treatment (Fig.18). The LEP of the electrospun membrane was around 15 psi it increased to 18 psi after heat pressing but it decreased again to around 15 psi after ethanol treatment.

Checking the tensile strength at maximum load of the membranes, we can see that the tensile strength of the membrane increased due the effect of the heat pressing but decreased again after the ethanol treatment (Fig.20). More specifically, the electrospun membrane had a low tensile strength (3.5 MPa) that increased sharply to around (12.4 MPa) after heat pressing due to the horizontal and vertical fusion of the fibers inside the membrane that caused it to be much stronger. In contrast, we can see a decrease in the tensile strength of the membrane after ethanol treatment (10 MPa) where the fibers absorbed the ethanol and this had decreased the vertical fusion of the fibers.

b. DCMD Performance

i. Flux

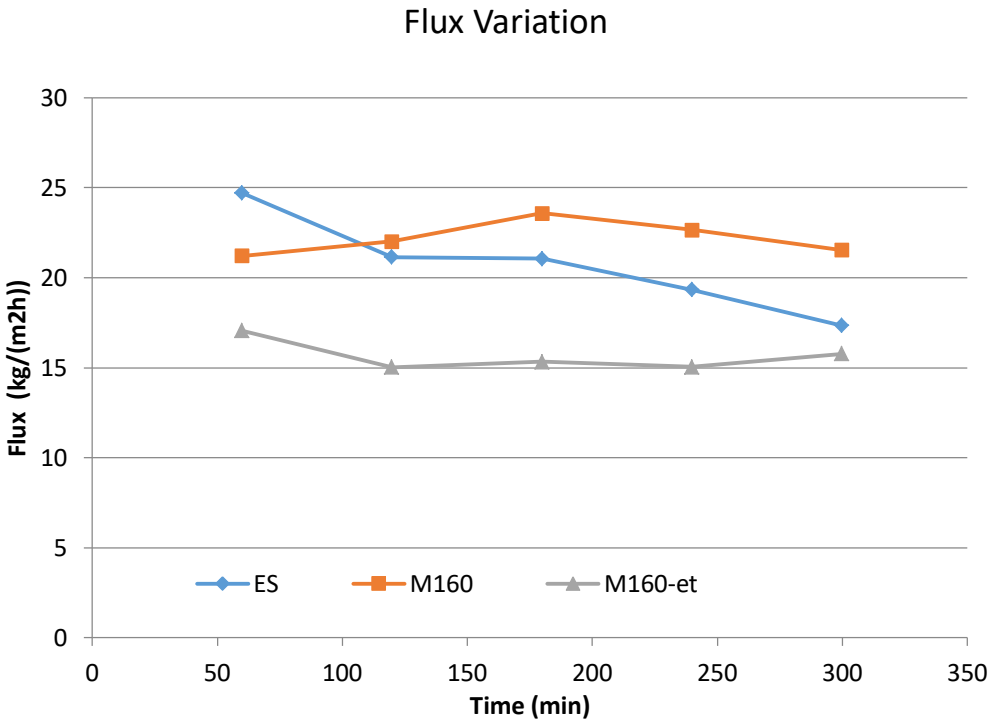

Figure 23-Flux variation after ethanol treatment

ii. Salt Rejection

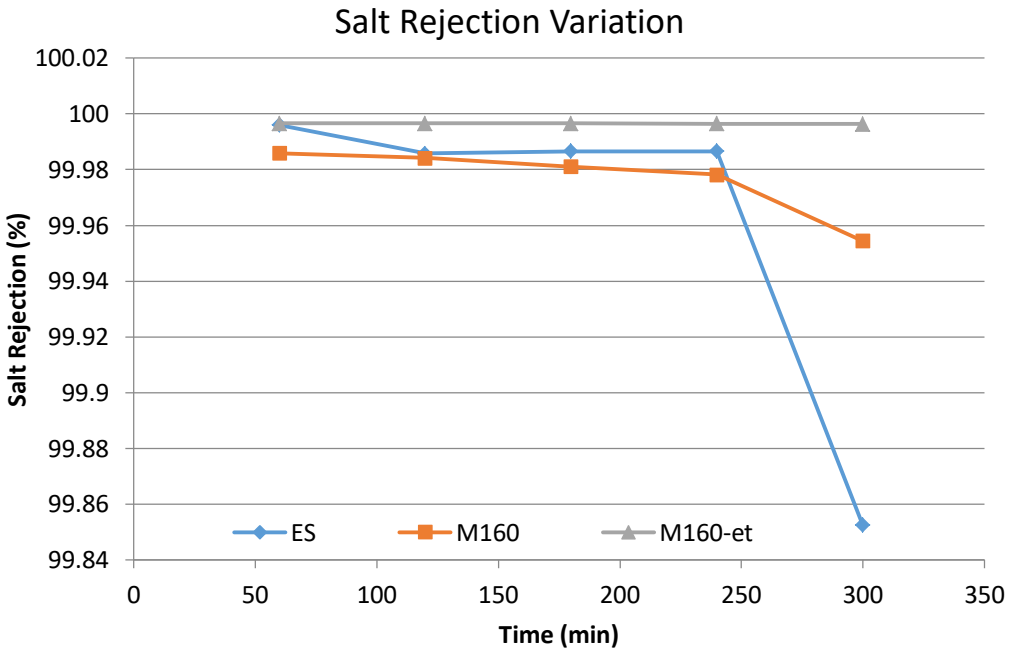

Figure 24-Salt Rejection of Commercial membrane

The membrane after ethanol treatment has shown promising properties that are adequate for DCMD application, so it was tested in our lab-scale DCMD. As shown in (Fig. 23) the flux of this membrane appears very stable compared to the electrospun membrane or the heat pressed membrane. This is a result of the non-wetting of the pores of this particular two-step treated membrane as shown in (Fig. 24). The salt rejection percentage of this membrane appears very high and stable indicating no significant pore wetting (remained >99.99%) and no break point was witnessed throughout the five-hour test unlike the two other membranes. This happened due to the absence of large pore diameters that were eliminated by ethanol thermal treatment as well as the improvement of the fiber morphology that has improved the surface properties of the membrane decreasing its vulnerability to wetting caused by loose surface fibers.

C. Benchmarking with commercial membranes

After the two-step modified electrospun membrane has shown successful results for a five-hour DCMD test, it was necessary to put it into comparison with a commercial membrane with a similar average pore diameter. The characteristics of the commercial Polytetrafluoroethylene (PTFE) membrane are shown in the table and figures below.

Table 5-Commercial membrane Characteristics

	Thickness (μm)	Average pore Diameter (μm)	Contact Angle (˚)	Support
PTFE	93	0.45	124	polypropylene
M160-et	203	0.47	134	unsupported

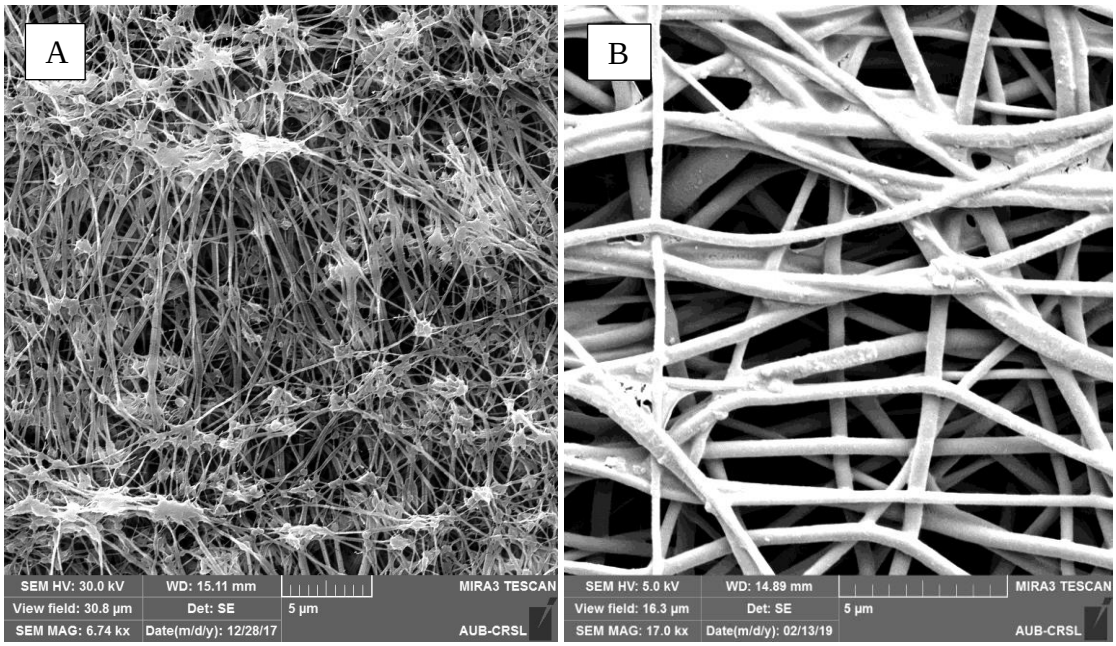

Figure 25-Membrane morphology of A: Commercial PTFE, B: Electrospun modified membrane

1. *DCMD Test*

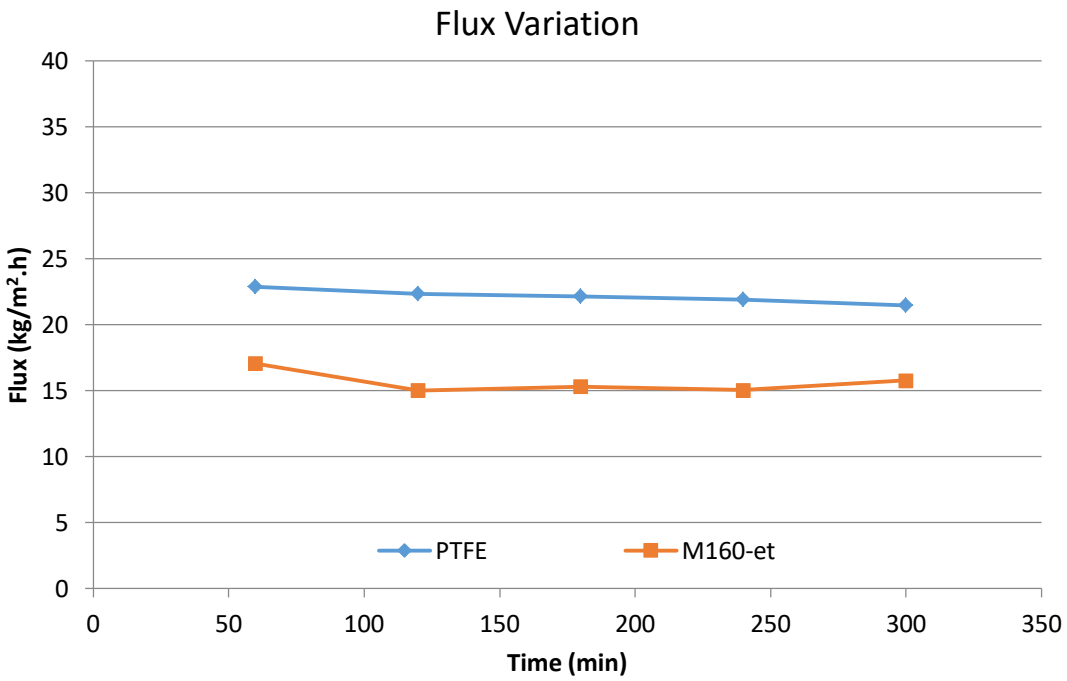

Figure 26-Benchmarked Flux Variation

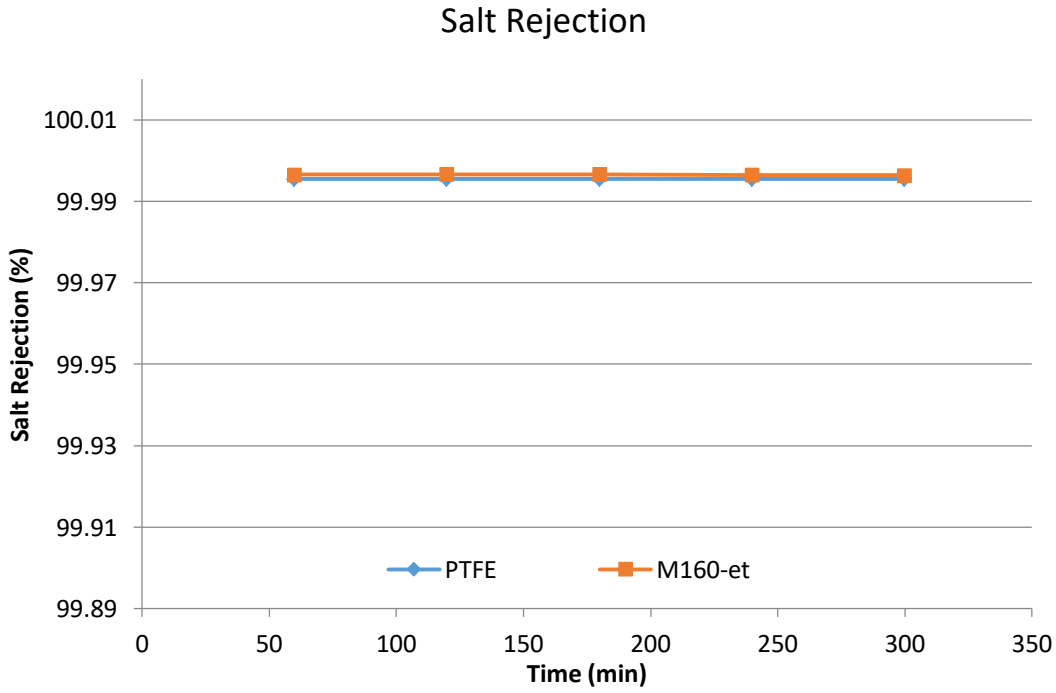

Figure 27-Benchmarked Salt Rejection

As shown in (Table 5) our membrane has a slightly higher average pore diameter, higher contact angle, and is thicker than the commercial membrane. Besides, the SEM pictures (Fig. 25) show that both membranes have different morphology and this is because the fabrication technology used for the commercial membrane is not electrospinning.

As shown in (Fig.26) the fluxes of both membranes are stable but the commercial membrane shows a higher flux (22 $kg/m^2.h$) than the electrospun membrane (15 $kg/m^2.h$). This is mainly due to the difference in the thickness of both membranes as well as the number of pores. Where, the higher the thickness of the membrane is the more mass transfer is present leading to a decrease in the obtained flux. On the other hand, the modified electrospun membrane has witnessed pore closing due to fiber fusing under the effect of thermal treatments; this leads to a lower number of evaporation spaces for the water vapor molecules to be transported from one side to another across the membrane causing also a lower amount of water to be purified.

Besides, both membranes have shown very similar salt rejection percentages throughout the DCMD tests as shown in (Fig.27) where they were around 99.99 %. This fact shows that our modified electrospun membrane is suitable for DCMD processes just like commercial membranes.

CHAPTER V

CONCLUSION

It was shown using experimental data that electrospun membranes can't be directly used in DCMD. This is because of the large pore diameters and loose surface fibers that increase the risk of pore wetting in the DCMD harsh conditions. Accordingly, these hydrophobic porous membranes need special modification to improve their properties and DCMD performance.

It was also proven that heat pressing, if used as a thermal physical modification; it improves the different properties of the membrane (thickness, average and maximum pore diameter, tensile strength, LEP…). Besides, this thermal modification has an adverse effect on the hydrophobicity of the membrane where it caused a decrease in the contact angle. Therefore, it was shown that the performance of the membrane in DCMD is greatly improved by heat pressing at the level of salt rejection while the obtained permeate flux was still unstable.

In addition to this, the ethanol treatment, done after the heat pressing, showed a great improvement in the membrane's most important properties. Whereby, the ethanol thermal modification was capable of improving the surface properties of the membrane by increasing the water contact angle and to closing all large pores. Moreover, the ethanol treatment decreased the average pore diameter as well as the LEP and tensile strength but increased the thickness. After testing this two-step modified membrane it showed excellent results including relatively stable flux in addition to stable and very high salt rejection.

When compared to commercially available expensive PTFE membrane with similar pore diameter that is believed to have very good performance in DCMD, the results show that the modified electrospun membrane had similar performance. Although a lower permeate flux was obtained by the electrospun membrane compared to the commercial membrane, this was explained by the difference in pore distribution, the number of pores, and the thickness of both membranes. On the other hand, our membrane had similar stable salt rejection percentages like the commercial membrane (>99.99%).

To sum up, the two-step PVDF-HFP modified electrospun membrane has an excellent performance in the DCMD process. The obtained result shows a permeate flux around (15 $kg/m^2.h$) and a salt rejection (>99.99 %). These results make our membrane suitable to be used on DCMD for general water purification and especially seawater desalination.

REFERENCES

1. Ahmad, H.M., A.E. Khalifa, and M.A. Antar, Water Desalination Using Direct Contact Membrane Distillation System. Proceedings of the Asme International Mechanical Engineering Congress and Exposition, 2015, Vol 6a, 2016.
2. bbc. [cited 2018; Available from: http://www.bbc.com/future/story/20170412-is-the-world-running-out-of-fresh-water.
3. United Nations. [cited 2018 Jan]; Available from: http://www.un.org/en/sections/issues-depth/water.
4. Hagedorn, A., et al., Methodical design and operation of membrane distillation plants for desalination. Chemical Engineering Research & Design, 2017. 125: p. 265-281.
5. Ke, H., et al., Electrospun polystyrene nanofibrous membranes for direct contact membrane distillation. Journal of Membrane Science, 2016. 515: p. 86-97.
6. Ragunath, S., S. Roy, and S. Mitra, Selective hydrophilization of the permeate surface to enhance flux in membrane distillation. Separation and Purification Technology, 2016. 170: p. 427-433.
7. Abass, O.K., et al., A novel MD-ZVI integrated approach for high arsenic groundwater decontamination and effluent immobilization. Process Safety and Environmental Protection, 2016. 102: p. 190-203.
8. Okiel, K., et al., Performance assessment of synthesized CNT/polypropylene composite membrane distillation for oil field produced water desalination. Desalination and Water Treatment, 2015. 57(24): p. 10995-11007.
9. Lu, K.-J., J. Zuo, and T.-S. Chung, Tri-bore PVDF hollow fibers with a super-hydrophobic coating for membrane distillation. Journal of Membrane Science, 2016. 514: p. 165-175.
10. Rastegarpanah, A. and H.R. Mortaheb, Surface treatment of polyethersulfone membranes for applying in desalination by direct contact membrane distillation. Desalination, 2016. 377: p. 99-107.
11. Mansour, S., A. Giwa, and S.W. Hasan, Novel graphene nanoplatelets-coated polyethylene membrane for the treatment of reject brine by pilot-scale direct contact membrane distillation: An optimization study. Desalination, 2018. 441: p. 9-20.
12. Rashid, K., Enhancement the Flux of PVDF-co-HFP Hollow Fiber Membranes for Direct Contact Membrane Distillation Applications. Vol. 10. 2016. 2189.
13. Lee, E.-J., et al., Electrospun nanofiber membranes incorporating fluorosilane-coated TiO2 nanocomposite for direct contact membrane distillation. Journal of Membrane Science, 2016. 520: p. 145-154.
14. Lee, J.G., et al., A novel multi-stage direct contact membrane distillation module: Design, experimental and theoretical approaches. Water Res, 2016. 107: p. 47-56.
15. Jung, J., et al., Hydrophobic surface modification of membrane distillation (MD) membranes using water-repelling polymer based on urethane rubber. Desalination and Water Treatment, 2015. 57(22): p. 10031-10041.

16. Efome, J.E., et al., Enhanced performance of PVDF nanocomposite membrane by nanofiber coating: A membrane for sustainable desalination through MD. Water Res, 2016. 89: p. 39-49.
17. Jiříček, T., et al., Flux Enhancement in Membrane Distillation Using Nanofiber Membranes. Journal of Nanomaterials, 2016. 2016: p. 1-7.
18. Lu, X., et al., Amphiphobic PVDF composite membranes for anti-fouling direct contact membrane distillation. Journal of Membrane Science, 2016. 505: p. 61-69.
19. Eykens, L., et al., Characterization and performance evaluation of commercially available hydrophobic membranes for direct contact membrane distillation. Desalination, 2016. 392: p. 63-73.
20. Nawi, N.I.M., M.R. Bilad, and N.A.H.M. Nordin, Effect of dope solution temperature on the membrane structure and membrane distillation performance. IOP Conference Series: Earth and Environmental Science, 2018. 140: p. 012032.
21. Tijing, L.D., et al., Superhydrophobic nanofiber membrane containing carbon nanotubes for high-performance direct contact membrane distillation. Journal of Membrane Science, 2016. 502: p. 158-170.
22. Makanjuola, O., I. Janajreh, and R. Hashaikeh, Novel technique for fabrication of electrospun membranes with high hydrophobicity retention. Desalination, 2018. 436: p. 98-106.
23. Ardeshiri, F., et al., PVDF membrane assisted by modified hydrophobic ZnO nanoparticle for membrane distillation. Asia-Pacific Journal of Chemical Engineering, 2018. 13(3): p. e2196.
24. Smruti Ragunath, S.R., Somenath Mitra, Carbon nanotube immobilized membrane with controlled nanotube incorporation via phase inversion polymerization for membrane distillation based desalination. Separation and Purification Technology, 2017.
25. Bhadra, M., S. Roy, and S. Mitra, Flux enhancement in direct contact membrane distillation by implementing carbon nanotube immobilized PTFE membrane. Separation and Purification Technology, 2016. 161: p. 136-143.
26. Lee, J., et al., Development of Omniphobic Desalination Membranes Using a Charged Electrospun Nanofiber Scaffold. ACS Appl Mater Interfaces, 2016. 8(17): p. 11154-61.
27. Bhadra, M., S. Roy, and S. Mitra, A Bilayered Structure Comprised of Functionalized Carbon Nanotubes for Desalination by Membrane Distillation. ACS Appl Mater Interfaces, 2016. 8(30): p. 19507-13.
28. Agbaje, T.A., et al., PVDF/magnetite blend membranes for enhanced flux and salt rejection in membrane distillation. Desalination, 2018. 436: p. 69-80.
29. Bhadra, M., S. Roy, and S. Mitra, Desalination across a graphene oxide membrane via direct contact membrane distillation. Desalination, 2016. 378: p. 37-43.
30. Wang, J.-W., et al., β-Sialon ceramic hollow fiber membranes with high strength and low thermal conductivity for membrane distillation. Journal of the European Ceramic Society, 2016. 36(1): p. 59-65.
31. Boo, C., J. Lee, and M. Elimelech, Omniphobic Polyvinylidene Fluoride (PVDF) Membrane for Desalination of Shale Gas Produced Water by Membrane Distillation. Environmental Science & Technology, 2016. 50(22): p. 12275-12282.

32. Zheng, R., et al., Preparation of omniphobic PVDF membrane with hierarchical structure for treating saline oily wastewater using direct contact membrane distillation. Journal of Membrane Science, 2018. 555: p. 197-205.
33. Liu, Y., et al., Fabrication of novel Janus membrane by nonsolvent thermally induced phase separation (NTIPS) for enhanced performance in membrane distillation. Journal of Membrane Science, 2018. 563: p. 298-308.
34. Wang, Z., D. Hou, and S. Lin, Composite Membrane with Underwater-Oleophobic Surface for Anti-Oil-Fouling Membrane Distillation. Environ Sci Technol, 2016. 50(7): p. 3866-74.
35. Yao, M., et al., Effect of heat-press conditions on electrospun membranes for desalination by direct contact membrane distillation. Desalination, 2016. 378: p. 80-91.
36. Aly M. Elzahaby , A.E.K., M.M. Bassuoni, Ayman Refat Abd Elbar Direct contact membrane water distillation assisted with solar energy.
37. Carnevale, M.C., et al., Direct Contact and Vacuum Membrane Distillation application for the olive mill wastewater treatment. Separation and Purification Technology, 2016. 169: p. 121-127.
38. Zoungrana, A., et al., Treatment of metal-plating waste water by modified direct contact membrane distillation. Chemical Papers, 2016. 70(9): p. 1185-1195.
39. Fadhil, S., et al., Novel PVDF-HFP flat sheet membranes prepared by triethyl phosphate (TEP) solvent for direct contact membrane distillation. Chemical Engineering and Processing: Process Intensification, 2016. 102: p. 16-26.
40. Kim, S., D.W. Lee, and J. Cho, Application of direct contact membrane distillation process to treat anaerobic digestate. Journal of Membrane Science, 2016. 511: p. 20-28.
41. Mokhtar, N.M., et al., The potential of direct contact membrane distillation for industrial textile wastewater treatment using PVDF-Cloisite 15A nanocomposite membrane. Chemical Engineering Research & Design, 2016. 111: p. 284-293.
42. Cho, D.W., et al., Treatment of Simulated Coalbed Methane Produced Water Using Direct Contact Membrane Distillation. Water, 2016. 8(5).
43. Guo, J.X., et al., Fouling behavior of negatively charged PVDF membrane in membrane distillation for removal of antibiotics from wastewater. Journal of Membrane Science, 2018. 551: p. 12-19.
44. Tun, L.L., et al., Dewatering of source-separated human urine for nitrogen recovery by membrane distillation. Journal of Membrane Science, 2016. 512: p. 13-20.
45. Wen, X., F.Z. Li, and X. Zhao, Removal of nuclides and boron from highly saline radioactive wastewater by direct contact membrane distillation. Desalination, 2016. 394: p. 101-107.
46. Feng, X., L.Y. Jiang, and Y. Song, Titanium white sulfuric acid concentration by direct contact membrane distillation. Chemical Engineering Journal, 2016. 285: p. 101-111.
47. Siyal, M.I., et al., Surface modification of glass fiber membranes by fluorographite coating for desalination of concentrated saline water with humic acid in direct-contact membrane distillation. Separation and Purification Technology, 2018. 205: p. 284-292.

48. H.Y. Wong, K.K.L., E. Drioli, O.B. Seng, Nanoparticle Separation Using Direct Contact Membrane Distillation and Its Fouling Study. Journal of Membrane Science and Research 2 (2016) 186-192, 2015.
49. Zhang, Y., et al., A hybrid process combining homogeneous catalytic ozonation and membrane distillation for wastewater treatment. Chemosphere, 2016. 160: p. 134-140.
50. Alicia Kyoungjin An, J.G., Sanghyun Jeong , Eui-Jong Lee , S. Assiyeh Alizadeh Tabatabai , TorOve Leiknes High flux and antifouling properties of negatively charged membrane for dyeing wastewater treatment by membrane distillation. 2016.
51. Fang Li, J.H., Qin Xia, Mengmeng Lou, Bo Yang, Qing Tian, Yanbiao Liua,, Direct contact membrane distillation for the treatment of industrial dyeing wastewater and characteristic pollutants. 2017.
52. Li, Y., et al., Separation and recovery of heavy metals from waste water using synergistic solvent extraction. 1st International Conference on New Material and Chemical Industry (Nmci2016), 2017. 167.
53. Sun, Q., et al., Separation and recovery of heavy metals from concentrated smelting wastewater by synergistic solvent extraction using a mixture of 2-hydroxy-5-nonylacetophenone oxime and bis(2,4,4-trimethylpentyl) -phosphinic acid. Solvent Extraction and Ion Exchange, 2018. 36(2): p. 175-190.