SUPERHYDROPHOBIC SURFACE MODIFICATION OF CARBON NANOTUBES FOR POLYMER MEMBRANE IN DIRECT CONTACT MEMBRANE DISTILLATION

A Thesis

by

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ABSTRACT

Direct contact membrane distillation (DCMD) is a promising method for water purification and membrane is the key component governing the performance of the membrane distillation (MD) process which need the high porosity, thin thickness, narrow pore distribution and enough pore size. However, the commercial PVDF membrane still have a very low MD efficiency which block the industrial application.

In this study, fluorosilanization and silanization modification methods were applied to modify the carbon nanotubes (CNTs) respectively and the combination of these methods were also employed. The polyvinylidene fluoride (PVDF) membranes with different surface modification of CNTs were prepared by electrospun method and employed in MD process. The effect of different methods of surface modification on membrane morphology, dispersion hydrophilicity, porosity and DCMD performance were investigated. These results should demonstrate that whether the modified CNTs is a promising material for PVDF membrane in DCMD application or not. Finally, the possible mechanism of functioned CNTs in PVDF membrane was explained.

DEDICATION

This thesis id dedicated to:

My mother and father who are two most important people for me in the world,

My advisor Dr. Ying Li who gave the confidence and environment to do the research and suggestion on research and learning,

My colleague Dr. Fuping Fan, Dr. Xianmei Xiang, Dr. Chao Li, Mr. Wei Deng, Mr. Xuhui Feng, all of them gave me suggestions on research and life. I learned a lot from them.

I dedicate this research.

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CONTRIBUTORS AND FOUDING SOURCES

Contributors

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NOMENCLATURE

MD	Membrane distillation
DCMD	Direct contact membrane distillation
CNTs	Carbon nanotubes
PVDF	Polyvinylidene fluoride
LMH	Liter per Square Meter per Hour
RO	Reverse osmosis
NF	Nanofiltration
MF	Microfiltration
FO	Forward osmosis
UF	Ultrafiltration
APTS	3-aminopropyltriethoxysliane
FTCS	1H,1H,2H,2H-perfluorododecyl trichlorosilane
OTS	Octadecyltrichlorosilane
DMF	N, N-dimethylformamide
WCA	Water contact angle
PTFE	Polytetrafluoroethylene
DI	Deionized
LEP	Liquid Entry Pressure
FT-IR	Fourier-transition infrared
FE-SEM	Field Emission Scanning Electron Microscopy
SR	Salt rejection

J	Water flux
AGMD	Air Gap Membrane Distillation
VMD	Vacuum Membrane Distillation
SGMD	Sweeping Gas Membrane Distillation
MWCNTs	Multi-walled carbon nanotubes

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CHAPTER I

INTRODUCTION AND BACKGROUND

1.1 Water scarcity issue

In the late 20s century, the water demand and supply have become one of the most important issues. Lacking fresh water affects all the continent and it is the largest global risk in the next decade. There is only 0.14% of water that can be used by human and animal on the earth. In the remaining water, more than 97% is the saline and 3% is hard to access. According to the data from the world economic forum, more than one third people is still under the serious water scarcity issue at least a month. Water shortage is normally caused by an excess of water demand over available supply and this problem was claimed because of a high rate of serve demand from all the water-using field which has many sectors compared to the available supply. For example, the agriculture is the largest sector for the water shortage. Some data showed that the 70% of global water was consumed by agriculture. The composition of fresh water is the surface water resource such as the lakes and rivers, the other resources of fresh water are from the ground and the glaciers [1,4]. But in many places, the groundwater was overdeveloped which caused ground subsidence. Moreover, with the increasing temperature of global climate, the rate at which the glacier melts are rising very quickly which also has a negative effect on water supply. Under both the growth of population and the development of economy, the food and industrial consumption will be increasing which make the issue more complex. The high level of water scarcity was showed in the regions that have a high population density, a large area of irrigated agriculture or there is not too much natural water availability.

It is found that even more than 40 billion people experience a water scarcity. Some people also had another opinion that the global climate change is the main reason for the reducing the available fresh water. The climate change speed up the melting of glacier which is the main resource of the river flow and stream. This phenomenon will reduce the water storage in the lakes and ponds causing a shrinkage of them [3]. Overall, water scarcity would be the largest issue in the 21's century.

1.2 Water treatment technology

With the serious water scarcity issue, people want to use water treatment to get the purified water for reuse in order to partly solve the problem. Many kinds of water treatment technology were created to convert the seawater into fresh water to make it acceptable for reuse [1]. Desalination is a commonly used method to get the fresh water for the coastal countries that suffer a water shortage issue. In the middle east of Asia, loads of fresh water plant were established based on the desalination technology. There are three main methods including thermal, membrane based and chemical desalination method. For the thermal method, the working principle is sample and it depends on the temperature difference between the boiling and freezing of water and salt [1]. The chemical method has ion exchange and liquid-liquid extraction. There are four kinds of membrane desalination technology including the reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and membrane distillation [2]. These membranes are classified by the pore size of the membrane with the RO membrane ranging from 0.1 nm to 1 nm, the NF from 1 nm to around 10 nm, the UF from 10 nm to 100 nm and the MF from 100 nm to 10 μm [3]. Another technology which is applied in desalination in the forward osmosis (FO). RO is the most popular method for desalination water plant because its high efficiency while the RO process must utilize a larger amount of electricity in order to generate high pressure to maintain the process which cost a lot

and have a negative effect on the atmosphere due to the carbon dioxide as the many electricity consumed [4]. FO is an osmosis process that is used to induce a net flow of water through the membrane into the draw solution [5]. The driving force of FO process is the osmotic pressure gradient while the driving force of RO process is the pressure gradient. Another issue for FO and RO is the waste brine pollution [1]. Figure 1 shows the membrane-based technology for desalination. Some new kind of technology is needed to be created in order to solve the problem caused by the common treatment method and have a low cost, low energy consumption and bio-friendly.

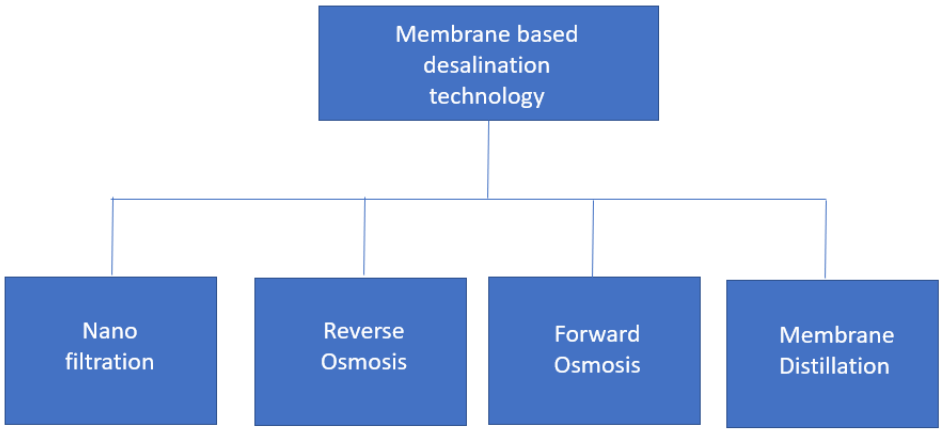

Figure 1.The membrane-based technology for desalination

Membrane distillation attracted a lot of attention and has been considered a promising technology for water treatment. Membrane distillation (MD) is thermal-driven technology that using the temperature difference between the feed side and the distilled side to generate vapor pressure to make the water vapor go through the membrane to get the clean water[6, 7]. It can utilize the waste heat or even the solar energy and some renewable energy to heat the feed side which is energy conservation, easily operated and economic-friendly. Membrane distillation has four

common configurations: air gap membrane distillation (AGMD), vacuum membrane distillation (VMD), direct contact membrane distillation (DCMD) and sweeping gas membrane distillation (SGMD) [1]. In this study, DCMD system were operated because of its convenience of setup, high water flux and high salt rejection.

1.3 Electrospun technology

The electrospun technology has attracted a lot of attention since late 20's century [8]. The whole setup is composed of four main parts including the syringe, the power supply, the pump and the rotating collector. The working principle is that the power supply will generate the high voltage to produce electric force to overcome the surface tension of polymer solution in the syringe. The nanofiber will be got in the rotating collector and the polymer solvent will be evaporated during the electrospun process. The figure 2 shows the schematic diagram of electrospun setup. There are many electrospun parameters that would affect the diameter of nanofiber such as the voltage, the needle diameter, the speed of rotating collector, the humidity, the concentration and the recipe of polymer solution and the flow rate. The electrospun nanofiber can be used in many filed like the biomedical and membrane fabrication.

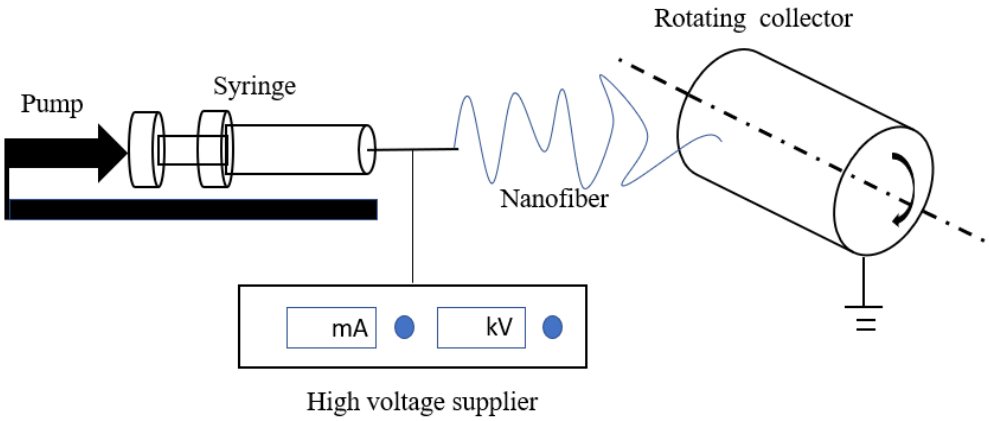

Figure 2. The schematic diagram of electrospun setup

1.4 Carbon nanotube and carbon nanotube membrane for water treatment

The carbon nanotube In recent decade years, carbon nanotubes (CNTs) was applied in water treatment filed because of its unique chemical and physical properties including the anti-fouling property and physico-chemical property[9-12]. Some work has been done to prove that doping covalent modification of CNTs into polymer membrane can improve the efficiency of water treatment significantly. 3-aminopropyltriethoxysliane (APTS) functioned CNTs in PVDF membrane achieved 92.48% bovine serum albumin (BSA) rejection but only 64.2% for the nascent PVDF membrane[13]. Fluorosilanized surface modification was widely applied in nanocomposites not only generate hierarchical structure to increase the surface roughness but also introduce fluorosilanization groups between the carboxyl groups on the surface of the particle to enhance the hydrophobicity[14, 15]. 1H,1H,2H,2H-perfluorododecyl trichlorosilane (FTCS) was employed to modify the virgin PVDF electrospun nanofiber membrane and this TiO_2-FTCS modified membrane showed a very high hydrophobicity and wetting resistance[16]. Fluorination and covalent modification of CNTs improved the dispersion in the PVDF-HFP solution and have a 60% higher water flux in DCMD performance compared with commercial PVDF membrane[14].

1.5 Membrane preparation for membrane distillation to achieve a higher water flux

The membrane distillation has not been used for water treatment in the water industry because of the weak membrane performance. After long time operation of MD process, there would be some fouling and wetting issue for the available commercial membrane [17-19]. Currently, the membrane for MD are mainly the polymeric membrane such as the polyvinylidene fluoride (PVDF) and Polytetrafluoroethylene (PTFE) [1, 20]. These membranes are actual designed for microfiltration. PVDF is a commonly used material in electrical device, pipe fabrication and

membrane preparation because of its special chemical resistance, low density and low cost. In order to have a higher DCMD performance, the membrane should have a higher porosity, a high hydrophobicity and narrow pore size distribution without any reduction of mechanical strength.

1.6 Surface modification of CNTs

Surface modification has been widely used in many fields such as the biomedical, nanoparticle synthesis and corrosion protection [6]. CNTs was applied in water treatment filed because of its unique chemical and physical properties including the anti-fouling property and physic-chemical property. Some researchers pay attention to surface modification of CNTs in order to further improve the performance of CNTs. Some work has been done to prove that doping covalent modification of CNTs into polymer membrane can improve the efficiency of water treatment significantly. 3-aminopropyltriethoxysliane (APTS) functioned CNTs in PVDF membrane achieved 92.48% bovine serum albumin (BSA) rejection but only 64.2% for the nascent PVDF membrane [7]. The Fluorination and covalent modification of CNTs improved the dispersion in the PVDF-HFP solution and have a 60% higher water flux in DCMD performance compared with commercial PVDF membrane [8]. The Multi-walled carbon nanotubes (MWCNTs) was modified by the oxidizing inorganic acids to get the oxidized carbon nanotube. Then the surface modification of the resulting products (o-MWCNTs) was made by applying the refluxing the tubes with multi-functional amines **[21]**. The modified carbon nanotube was added into epoxy to get the composites. The results showed that the surface modification can strongly improve the interaction between the bulk material and nanotubes There are two points of novelty in this thesis. Firstly, two different silanes with different length of chains were applied together to modify the surface of carbon nanotube and the sequence of combination of different modification method to CNTs was also investigated. Finally, the functioned CNTs electrospun membrane and the comparison of

pristine electrospun membrane with commercial membrane were examined and the mechanism of surface modification was explored as well.

1.7 Research objective and scopes

The main purpose of this study is to improve the water flux of DCMD and a long-time operation by applying the surface modified CNTs to modify the electrospun PVDF membrane. Therefore, the commercial membrane, the pristine electrospun membrane, the CNTs-PVDF membrane which is the pristine carbon nanotube functioned PVDF membrane, and the modified CNTs-PVDF membrane which is the functioned CNTs-PVDF membrane were studied and summarized in terms of the DCMD performance, salt rejection ratio and hydrophobicity. CNTs has been previously used to modify the electrospun membrane; however, but the performance is still not satisfied. In addition, these reported works only focused on the fluorosilanization modification of CNTs but ignored the silanization modification which can introduce the silane groups on the CNTs surface and the combination of silanization and fluorosilanization modification can provide different lengths of functioned groups on the surface of CNTs which benefits for both the surface morphology and membrane hydrophobicity or even improve DCMD performance. There was no one investigates that the silanization modification and the effect of combination of these two modifications for CNTs in water treatment yet.

The fluorosalinization modification, silanization modification method and combination of these two modification methods together were developed in order to improve the performance of membrane. One main purpose of this study is to investigate the sequence of surface modification to CNTs to membrane characteristics, hydrophobicity and DCMD performance. Moreover, the commercial PVDF membrane, the pristine PVDF membrane and CNTs-PVDF membrane were

compared in order to prove the function of CNTs and the unique nanofiber structure of electrospun membrane.

1.8 Outline of thesis

In this study, the author is focusing on membrane fabrication to achieve the unique surface morphology, high hydrophobicity, and high water flux in DCMD test. The introduction part in the chapter 1 describes the background of water scarcity. In order to solve the issue, the water treatment technology has been created. The membrane requirement for membrane distillation and the surface modification of CNTs for membrane are introduced to yield a high DCMD performance. Also, the scope and objective and outline of this thesis are stated. Chapter 1 is the summary of some literature that focused on the history, mechanism, configuration, the membrane required and the affective parameters. Moreover, the membrane preparation method such as the phase inversion method and electrospun method are explained. The role of CNTs in water treatment and modification of CNTs are covered. Chapter 2 shows the experimental materials and methods, including the surface modification of CNTs and the membrane preparation processes. The equipment, characterization methods and the membrane performance are indicated. In chapter 3, the results are discussed. The hydrophobicity, surface morphology, thickness, porosity, mean pore size and DCMD performance were claimed. The possible mechanism of surface modification of CNTs was explained. Chapter 4 is the conclusion of the thesis, which highlights that the surface modification CNTs-PVDF is a promising way for high-performance membrane distillation.

CHAPTER II

MATERIALS AND METHODS

2.1 Materials

Polyvinylidene fluoride (PVDF) powder with 64.03 $gmol^{-1}$ was purchased from VWR. N, N-dimethylformamide (DMF), acetone was bought from VWR as solvent. Lithium Chloride was used as the additives for improving the conductivity of polymer solution. Nitric acid, ethanol was ordered from VWR. Carbon nanotubes (average diameter: 6-9 nm, length: 5μm, >99%) was obtained from Sigma-Aldrich. F-127, 1H,1H,2H, 2H-perfluorododecyl trichlorosilane (FTCS), Octadecyltrichlorosilane (OTS) and toluene were used for surface modification of CNTs and commercial PVDF membranes was bought from EMD, Millipore Corporation, USA for comparison with other membranes in DCMD test. All these chemicals were used without further purify.

2.2 Methods

2.2.1 Pretreatment of CNTs

0.5g CNTs was mixed with 80mL concentrated nitric acid in sonication for 4 h and then heated at 80°C for 24 h. This produce was aimed to get the carboxyl function groups on the surface of CNTs for further modification. After acid treatment, the CNTs was centrifuged at 12000 rpm for 10 min and washed by 1L DI water to remove the acid residual. Then CNTs was put into the vacuum chamber at 60 °C for 24 h.

2.2.2 Silanization modification of CNTs

The OTS solution was prepared by mixing the 0.5 wt% OTS and toluene together and stirring at 200 rpm for 1 h. The pretreated CNTs and 50 mL toluene were also mixed. The mixture was at sonication for 2 h and then the OTS solution was added into the mixture. The reaction was

proceeded at 110°C for 24 h. The resultant OTS-CNTs nanocomposites was centrifuged and washed by both toluene and ethanol for three times and dried at 80 °C in the vacuum chamber for 6 h.

2.2.3 Fluorosilanization modification of CNTs

0.5 wt% of FTCS solution was first stirred at 200 rpm in toluene for 1 h under 3 °C. The toluene was pursed by Ar gas to remove the oxygen and cool down at 3°C in advance. Then the pretreated CNTs and 50 mL toluene were mixed together at sonication for 2 h. After CNTs was dispersed well, the FTCS solution was added into the mixture. The process took for 24 h to get the FTCS-CNTs nanocomposites. The final nanocomposites were centrifuged and toluene was applied to remove the extra un-reacted reagent. Finally, the nanocomposites were dried in vacuum chamber at 70°C for 6 h.

2.2.4 Combination of silanization and fluorosilanization modification of CNTs

First, 0.5wt% OTS solution was added to pretreated CNTs and toluene mixture for 12 h at 110°C. Following the drying at 70°C for 6 h, the OTS-CNTs was treated with 0.5wt% FTCS solution for another 12 h at the same condition mentioned above. The functioned CNTs was called F-CNTs-1 and washed by toluene for three times and dried at 70°C for 6 h again for further use. Another Functioned CNTs which is called F-CNTs-2 was prepared by changing the sequence of OTS and FTCS. The pretreated CNTs was first reacted with FCTS and then OTS at the same condition mentioned above. The principle of modification methods of CNTs was shown in supporting information. The preparation procedures of CNTs surface modification were shown in table 1.

Table **1** The preparation procedures of CNTs surface modification

Sample	First step			Second step		
	Reaction chemical	Reaction time(h)	Drying time (h) at 70 °C	Reaction chemical	Reaction time (h)	Drying time (h) at 70 °C
OTS-CNTs	OTS	24	6	No	0	0
FTCS-CNTs	FTCS	24	6	No	0	0
F-CNTs-1	OTS	12	6	FTCS	12	6
F-CNTs-2	FTCS	12	6	OTS	12	6

2.2.5 Electrospun nanocomposites membrane preparation

30 wt% of PVDF powder was dissolved and stirred in the mixture of DMF and acetone at 50°C for 12 h to get a homogeneous solution. Then 20wt% of different kinds of modified CNTs/DMF suspension were mixed with 30 wt.% PVDF solution to make sure that the final concentration of PVDF is 17wt% in DMF and acetone mixed solvent (3:2 by weight ratio). 0.004wt% lithium chloride was added in order to improve the conductivity of polymer solution.

15 mL doping polymer solution was placed in a 20 mL syringe with a metal needle which has an inner diameter of 0.377 mm and the syringe was put on a syringe pump which kept a feed rate at 0.9mL/h. A metal rotating collector was covered by the aluminum foil and had a rotation speed of 500 rpm/min to collect the electrospun membrane. The voltage was adjusted to 20 kV. The distance between the collector and needle is 15 cm. The environment humidity and temperature were about 53%±3% and 75F±2F respectively. Moreover, the pristine PVDF electrospun membrane was also fabricated under the same parameter. The table 2 was the details of different electrospun membrane where EM represents the pristine electrospun membrane.

Table 2 The parameters of different electrospun membranes

Membrane	PVDF (wt%)	Ratio of DMF: Acetone (wt%)	LiCl (wt%)	CNTs or Functioned CNTs (wt%)	Flow rate (ml/h)	Voltage (kV)	Distance (cm)	Humidity (%)
EM	17	3:2	0.004	0	0.9	20	15	53
3% CNTs	17	3:2	0.004	3	0.9	20	15	51
3% OTS-CNTs	17	3:2	0.004	3	0.9	20	15	55
3% FTCS	17	3:2	0.004	3	0.9	20	15	53
3% F-CNTs-1	17	3:2	0.004	3	0.9	20	15	53
3% F-CNTs-2	17	3:2	0.004	3	0.9	20	15	54

2.2.6 Characterization of modified CNTs

The Fourier-transition infrared (FT-IR, Thermo Scientific, iS50 FT-IR) spectra was applied to record the characteristic peaks of OTS-CNTs, FTCS-CNTs, F-CNTs-1 and F-CNTs-2.

2.2.7 Characterization of electrospun nanocomposites membrane

2.2.7.1 The surface morphology of electrospun membrane

The Field emission scan electron microscopy (FE-SEM, JEOL JSM-7500F) was used to observe the surface morphology of membranes. The samples were coated gold by the sputter coater before test.

2.2.7.2. Porosity, pore size, nanofiber diameter, thickness and liquid entry pressure of water (LEP)

The porosity was measured by the gravimetric method [16]. The 2 cm × 2 cm sample was cut from the membrane and whole the membrane was immersed into the absolute ethanol for 1 h to make

sure that the membrane was fully wetted. The weight of membrane before and after wetted was measured. The membrane porosity ε was calculated by Eq (1):

$$\varepsilon = \frac{(m_2 - m_1)/\rho_1}{(\rho_2 - \rho_1)m_1 + \rho_1 m_2} \quad (1)$$

where ρ_1 is the density of PVDF, ρ_2 is the density of ethanol, m_2 is the weight of wetted membrane and m_1 is the weight of dry membrane.

The mean pore size, maximum pore size, nanofiber diameter, nanofiber diameter distribution were measured by analysis at least 10 SEM images for each membrane sample by ImageJ software.

The thickness of membrane was measured by a micrometer caliper which has an accuracy of 1μm and 5 different positions were measured for each membrane to get the average value [9].

The membrane wetting resistance was measured by liquid entry pressure (LEP) which is the minimum pressure that make the water droplets permeate the pore of the membrane. A homemade setup was applied to measure the liquid entry pressure. The schematic diagram was shown in Figure 2. The membrane was placed in the membrane module. One side of the liquid feed was connected to the N_2 gas cylinder and another side was connected to the membrane module. During the LEP test, the pressure in the setup was increased by 0.1 bar manually. The measure pipette was filled with some water and record the initial level of the liquid. When the increasing level of liquid in the measure pipette was observed, the pressure at that time was record as the liquid entry pressure [22].

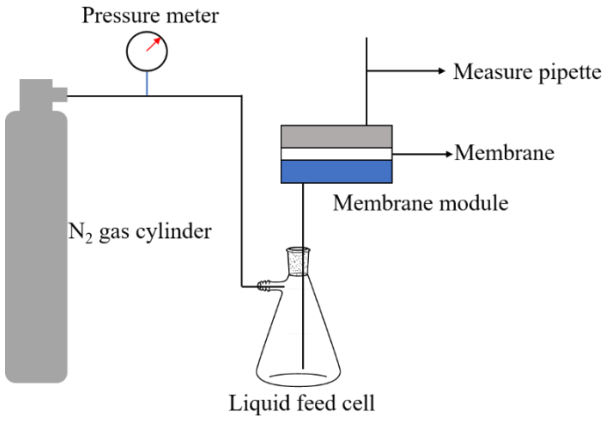

Figure 3. The schematic diagram of homemade LEP measurement

2.2.7.3. Water contact angle (WCA)

The hydrophobicity of membrane was evaluated by water contact angle. The water contact angle was measured by the optical digital camera (Digital viewer) equipped with a stage and photo analysis software. A 5 µL of DI water droplet was dropped on the membrane surface carefully and the camera took photos to analysis the contact angle. The water contact angle was measured 5 times for each sample and then calculated to get the average value [23].

2.2.7.4 DCMD performance and salt rejection performance

The DCMD performance was tested by a laboratory scale setup with a 42 cm^2 membrane surface area (CF042, Sterlitech, USA) illustrated in Figure 3. All the tubes in the setup were insulated by the insulation tape to reduce the heat loss. 3.5% NaCl solution was applied in the feed side and DI water was used in the distillated side. The solution was set at 60°C maintained by a heat plate in the feed side and 20°C cooled by a chiller in the distillated side and they were circled in opposite direction. The distillated tank was filled with 300 mL DI water on a digital balance. The data was

recorded half an hour. A conductivity meter was placed in the distillated side to measure the conductivity and temperature[24]. Water flux J (LMH) was calculated by Eq (2).

$$J = \frac{\Delta m}{\rho A \Delta t} \tag{2}$$

where the Δm was the weight gain at the distillated side (g), ρ was the density of distillated solution and (g/cm^3), A is the direct contact area of membrane (cm^2) and Δt is the operation time of DCMD (h).

The salt rejection efficiency (SR%) was calculated by the ratio of conductivity gain of solution at distillated side and the initial conductivity of solution at feed side. The salt rejection was obtained by Eq (3).

$$SR(\%) = \left(1 - \frac{\Delta C_d}{C_f}\right) \times 100\% \tag{3}$$

where ΔC_d was the conductivity gain of distillated solution (μs/cm), C_f was the initial conductivity of feed solution (μs/cm). The data was recorded half an hour[16, 25].

Seven kinds of membranes were tested in this section.

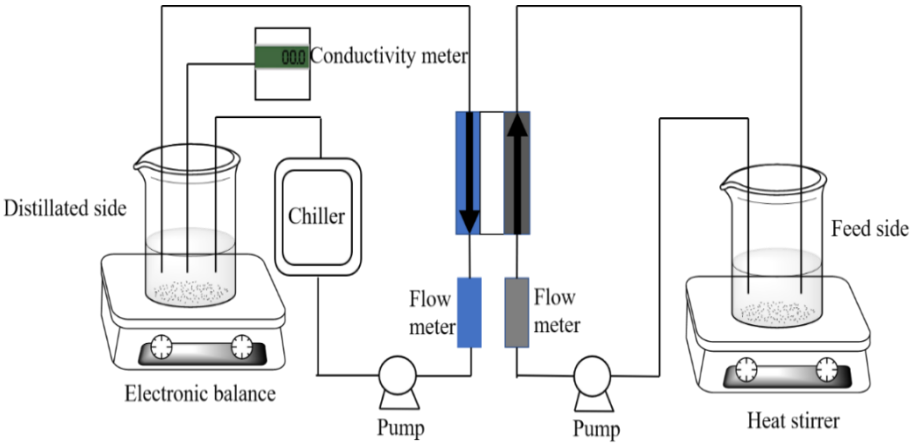

Figure 4. The schematic diagram of laboratory scale DCMD setup

CHARPET III

RESULTS AND DISCUSSION

3.1. Characterization of Functioned CNTs

3.1.1. FTIR analysis of Functioned CNTs

The FTIR spectra of pristine CNTs, OTS-CNTs, FTCS-CNTs, F-CNTs-1 and F-CNTs-2 were shown in Figure 4. The peak at around 1080 cm^{-1} was the Si-O-Si bond stretching which illustrated that the surface modification agent (FTCS and OTS) has grafted on the surfaces of OTS-CNTs, FTCS-CNTs, F-CNTs-1 and F-CNTs-2. There was no peak at the same location in the spectra of pristine CNTs. The peak at 1273 cm^{-1} was the C-F_2 bond stretching which confirmed that FTCS was introduced into FTCS-CNTs, F-CNTs-1 and F-CNTs-2 successfully while there was no peak at 1273 cm^{-1} in the spectra of OTS-CNTs and pristine CNTs.

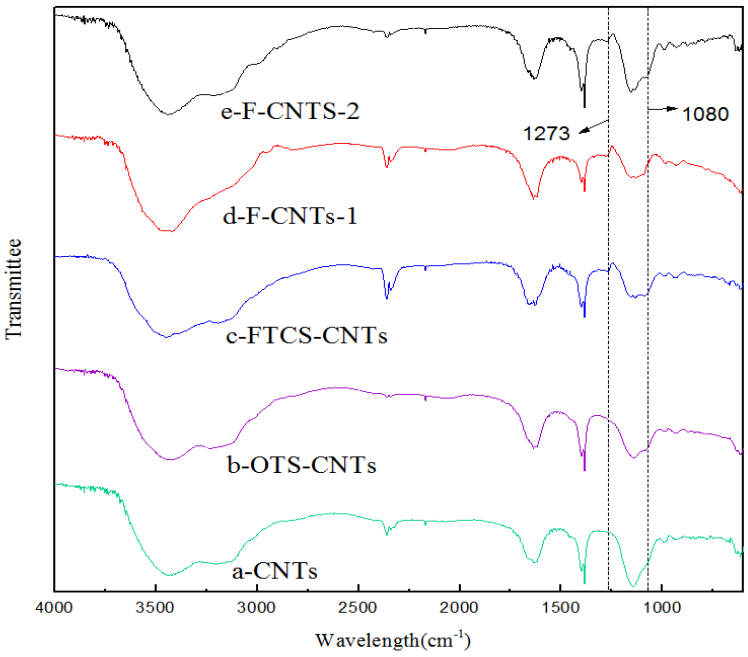

Figure 5. The FTIR image of Functioned CNTs

3.1.2. The dispersion of CNTs in solvent

Figure 5 showed the dispersion images of pristine CNTs, OTS-CNTs, FTCS-CNTs, F-CNTs-1 and F-CNTs-2 in the mixed solution (DMF: acetone=3:2 wt%). These CNTs solutions were first treated in sonication for 30 min and then shaken for 5 min in order to disperse well. The pristine CNTs and OTS-CNTs were immediately settled down and CNTs were precipitated in the bottom after 1 h which indicated that the silanization modification to CNTs cannot improve the dispersion in the mixed solution. But FTCS-CNTs, F-CNTs-1 and F-CNTs-2 remained suspended after 24 h which demonstrated that fluorosilanization modification to CNTs can improve the suspension stability of CNTs in the mixed solvent and combined fluorosilanization and silanization modification of CNTs also showed a very good dispersion in the solvent which is good for further electrospun process.

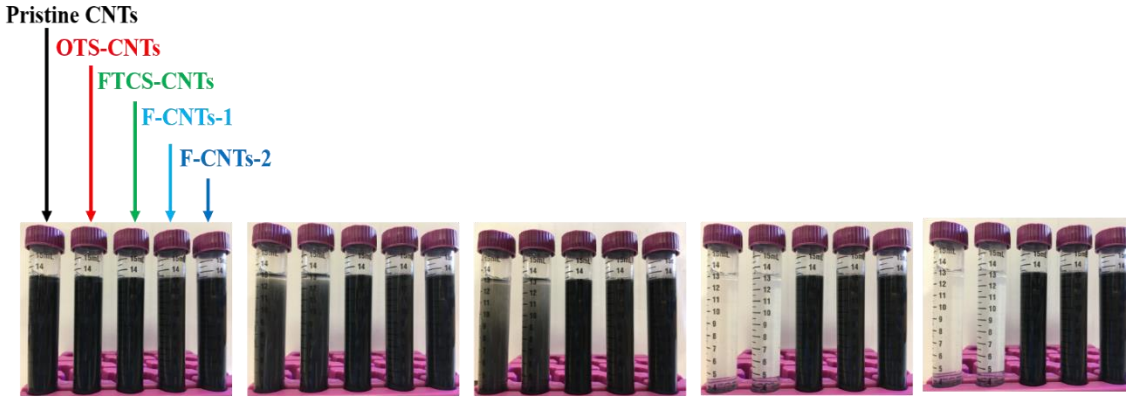

Figure 6. The dispersion images of pristine CNTs, OTS-CNTs, FTCS-CNTs, F-CNTs-1 and F-CNTs-2

3.2. Characterization of electrospun membrane

3.2.1. Surface morphology of electrospun membrane

Nanocomposites which were applied to modify membrane has attracted much attention from many researchers such as TiO2, SiO2, ZnO and other species[16, 26, 27]. CNTs has been widely used to improve the hydrophobicity and surface properties of membrane[28-30]. By combining the functioned CNTs and the electrospun technology, the functioned CNTs-PVDF membrane was fabricated. The SEM images of pristine PVDF membrane (a), 3% CNTs-PVDF membrane (b), 3% OTS-CNTs-PVDF membrane (c), 3% FTCS-CNTs-PVDF membrane (d), 3% F-CNTs-1-PVDF membrane (e) and 3% F-CNTs-1-PVDF membrane (f). From the SEM image a, b and c, CNTs-PVDF membrane had more polymer crystalline phase than the pristine PVDF membrane which was the same to other researchers' results that reported [14]. There was no obvious difference between the pristine CNTs-PVDF membrane and functioned CNTs-PVDF membrane which showed that the fluorosilanization and silanization modification of CNTs has no effect on the PVDF nanofiber morphology. CNTs cannot be observed in the SEM images because most of the CNTs was filled interior of the nanofiber. After the acid treatment, the structure of pristine CNTs was destroyed from high ratio of length to diameter to more uniform structure which decrease the π-π interaction between CNTs[14]. Surface modification of CNTs would significantly decrease the number of hydrophilic groups on the CNTs during the hydrolysis and condensation process of FTCS and OTS which also increase the roughness and hydrophobicity. Surface modification can also decrease the surface energy of CNTs which lead a good dispersion in polymer matrix.

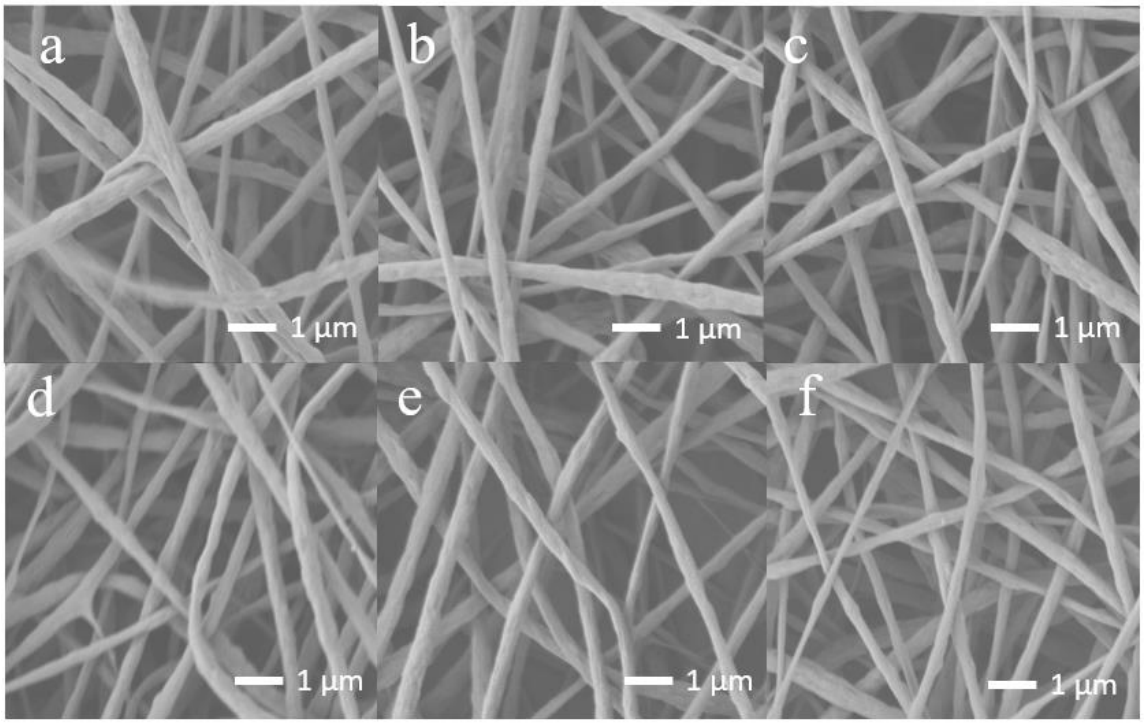

Figure 7. The SEM images of pristine PVDF membrane (a), 3% CNTs-PVDF membrane (b), 3% OTS-CNTs-PVDF membrane (c), 3% FTCS-CNTs-PVDF membrane (d), 3% F-CNTs-1-PVDF membrane (e) and 3% F-CNTs-2-PVDF membrane (f).

3.2.2. Nanofiber diameter, diameter distribution, thickness and liquid entry pressure (LEP)

Table 3 showed the parameters of electrospun membranes and commercial membrane.

The table 3. The parameters of electrospun membranes and commercial membrane

Membrane	Thickness (um)	Porosity (%)	Mean pore size(um)	Max pore size(um)	Fiber diameter (um)	LEP (kPa)
Commercial membrane	125±2	75.45±1.3	0.22	0.403	N/A	120.78± 2.3
Electrospun membrane-1	73±3	87.32±0.7	0.634	0.803	0.452±0.03	65.34±1.6
Electrospun membrane -2	134±3	85.66±1.1	0.702	0.932	0.472±0.02	94.32±4.5
3%CNTs-PVDF membrane	79±5	85.34±1.0	0.877	1. 287	0.367±0.07	63.23±5.5
3%OTS-CNTs-PVDF membrane	76±2	84.23±1.2	0.965	1.279	0.354±0.05	56.23±7.2
3%FTCS-CNTs-PVDF membrane	83±5	83.98±1.0	0.932	1.643	0.344±0.04	60.19±5.1
3%FTCS-CNTs-1-PVDF membrane	86±2	85.45±0.9	0.892	1.542	0.335±0.05	58.73±2.3
3%FTCS-CNTs-2-PVDF membrane	77±3	83.67±1.1	0.974	1.543	0.341±0.04	68.23±2.3

The thickness of electrospun membranes were much thinner than the commercial membrane which was benefit for the DCMD performance because the water vapor will travel less distance through the membrane. The porosity of electrospun membrane (about 85%) is a little higher than the commercial one (about 75%) which was attributed to the unique structure of nanofiber. The mean pore size of commercial membrane we bought was 0.22 μm that is much smaller than electrospun membrane (0.634 μm). But the functioned CNTs-PVDF membrane had a higher mean pore size which is around 0.9 μm and maximum pore size even up to 1.643 μm. The diameter of electrospun membrane was the thickest with the mean diameter of 0.452 μm. Compared to the pristine PVDF electrospun membrane, the CNTs-PVDF electrospun membrane had a smaller nanofiber diameter and functioned CNTs-PVDF membranes had the similar mean diameters. The change of diameter between the PVDF and CNTs-PVDF, functioned CNTs-PVDF electrospun membrane may be

because adding the CNTs would increase the conductivity of polymer solution but also increase the viscosity of polymer solution further to improve the surface tension of solution[6, 14]. The electrospun process was that the electric force overcomes the surface tension of polymer solution and polymer solution would be ejected from the needle by the electric force generated by high voltage supply[31]. In this case, the raise of electric force caused by increasing of conductivity was higher than the raise of surface tension from the increasing of viscosity duo to the adding the CNTs into polymer solution. The nanofiber diameter of functioned CNTs-PVDF membranes was a little smaller than the pristine CNTs-PVDF membrane which illustrated that the surface modification for CNTs will improve the dispersion of CNTs in polymer solution. The functioned CNTs would have less tendency to form agglomeration inside of polymer solution because the fluorosilanization and silanization can significantly decrease the surface energy of CNTs.

Liquid entry of water (LEP) is a key parameter to evaluate the wetting resistance of membrane which is the pressure that make the water droplets penetrate the membrane. The higher LEP means that the membrane would be hard to be wetted. According to the Cantor-Laplace equation (LEP $= \frac{-2\beta_y \cos\theta}{r_{max}}$), where β is the geometry factor, y is the surface tension of water, θ is the water contact angle, r_{max} is the maximum diameter of pore size in membrane[14, 16]. From Cantor-Laplace equation, the LEP is proportional to the water contact angle and proportional to maximum pore size inversely. In order to improve the LEP of membrane, the hydrophobicity or small pore size of membrane with narrow size distribution of membrane would be got[32]. The commercial membrane had a LEP about 120 KPa which is almost twice higher than the electrospun membrane. This phenomenon was attributed to the maximum pore size of electrospun membrane was much larger than commercial membrane. The largest LEP for electrospun membrane was 68.23 KPa

which is strong enough for DCMD operation in experiments. In order to achieve a higher efficiency of DCMD performance, the membrane should have a small pore size and narrow pore size distribution and high porosity[33]. The large pore size of electrospun membrane would have a bad influence on the anti-fouling property of membrane because larger pore size would make easier to blocked by foulant which may affect the long-term operation of DCMD.

3.2.3. Membrane hydrophobicity

There are many factors that affect hydrophobicity of membrane such as the surface roughness and the chemical composition of materials. The water contact angle of membrane is showed in figure 10. The water contact angle of commercial membrane and electrospun PVDF membrane is 122° and 132° respectively. 3% CNTs-PVDF membrane has the same contact angle that both are 142° which indicated that the silanization modification of CNTs had no help to the hydrophobicity of CNTs. But the FTCS-PVDF membrane has a contact angle around 150°. The reason was that the fluorosalinization modification of CNTs introduced many fluoride groups on the surface of CNTs and benefited from that, the hydrophobicity of CNTs improve a little bit comparing to the pristine CNTs and OTS-CNTs. The F-CNTs-1-PVDF membrane has the largest water contact angle at 153° but the contact angle of F-CNTs-2-PVDF was 148°. The difference between these two membranes is that the sequence of fluorosalinization and silanization modification for the CNTs. The F-CNTs-1 membrane was firstly modified by OTS and then by FTCS which F-CNTs-2 oppositely. Because the length of OTS and FTCS was different, after surface modification of CNTs, it would form a rougher surface than the pristine CNTs which generate a rougher surface membrane than the pristine CNTs-PVDF membrane. For F-CNTs-2 membrane, Some of the OTS may cover the surface that occupied by the FTCS previously and some of the fluoride group may block by the CH_2 and in this condition, the effect of the hydrophobic group was higher than the

effect of surface roughness of nanocomposites. This may be the reason that the FTCS-CNTs membrane had a larger water contact angle than that of F-CNTs-2 membrane and F-CNTs-1 membrane had the same results.

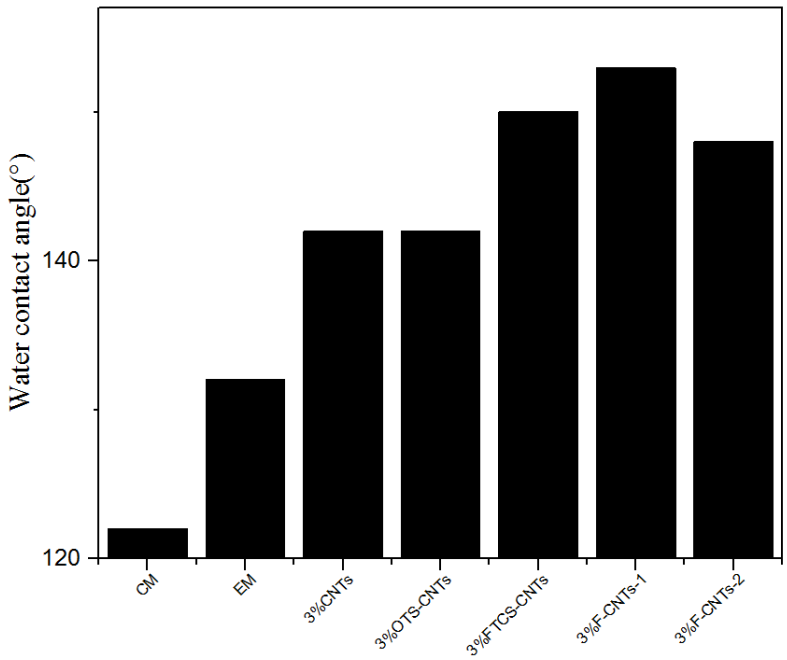

Figure 8. The water contact angle of membranes

3.2.4. DCMD performance

Figure 11. showed the DCMD performance of membranes. 3.5% NaCl solution was applied and seven kinds of membranes including the commercial membrane, the pristine electrospun membrane which is shown as electrospun-1, the electrospun membrane with the same thickness as the commercial membrane which is shown as electrospun-2, CNTs-PVDF membrane and four kinds of functioned CNTs-PVDF membrane were tested in the DCMD test. The membrane that applied in DCMD should have an appropriate pore size, narrow pore size distribution and high porosity[1, 34]. The DCMD performance of membranes were showed in the Figure 11. For the commercial PVDF membrane, the water flux was around 12 LMH and remained stable during the

6 h test while electrospun-2 membrane had a water flux around 22 LMH, which is 90% higher than the commercial one. This result is duo to electrospun membrane had a higher pore size and high porosity since both of them had the similar thickness. The electrospun-1 membrane had a water flux around 30 LMH which is about 250% higher than the efficiency of commercial membrane and also 36% improvement than the electrospun-1 membrane . There were three main reasons to explain this phenomenon. First, the thickness of electrospun-1 membrane was approximately 80 μm but the commercial PVDF membrane even had a thickness of 125 μm which is much thicker than the electrospun-1 membrane and reduce the water vapor diffusion distance and resistance between the feed side and distillated side. Second, the porosity of electrospun membrane was 87% but only 75% for the commercial one and the larger pore size which makes more water vapor pass through the membrane. Third, the electrospun membrane had the nanofiber and interconnected pore structure. This unique structure of electrospun membrane has the larger surface roughness than the commercial one. All these three reasons attributed the higher efficiency. Also, the final conductivity of distillated side was increased slightly from the initial value of 7 μs/cm to 10 μs/cm as shown in Figure 11.b. For the electrospun membrane, the conductivity was still remained at a very low level but still a little increase from 7.62 μs/cm to 10.89 μs/cm. The variety of conductivity of electrospun membrane was 3.27 μs/cm which is a little larger than that of commercial one which is 2.23 μs/cm. This may due to the larger pore size for the electrospun membrane made water molecular easier to go through the membrane.

The water flux of CNTs-PVDF and OTS-CNTs-PVDF membrane were similar which both at about 36 LHM. The value was 20% higher than the data of pristine PVDF membrane. This was because that adding the CNTs into the polymer nanofiber would introduce a multi-layer of CNTs inside of the nanofiber and this kind of layers will block the water molecular permeate through the pore step

by step and achieve the superhydrophobicity of membrane[14]. Some CNTs would form the protrusion on the nanofiber surface which can further improve the surface roughness. Moreover, the surface of CNTs had many activated sites for adsorption and desorption of vapor molecular which allow a fast diffusion process for the vapor molecular[14, 35]. OTS-CNTs membrane showed the same efficiency that indicated that the silanization modification for CNTs has no positive effects on the hydrophobicity and efficiency of DCMD. The reason was possibly that silanization modification method cannot change of surface roughness of CNTs significantly. Some researcher also claimed that CNTs in will generate a promoted vapor permeability to prevent the pore.

FTCS-CNTs electrospun membrane had a water flux about 41 LMH and there was a 13.8% improvement compared to the CNTs-PVDF membrane and a 36% improvement to the pristine electrospun membrane. The highest DCMD performance was achieved by the F-CNTs-1 membrane which is approximately 45 LMH but the F-CNTs-2 membrane only had a water flux about 42 LMH. From the experiment data, it was clearly seen that fluorosalinization modification could improve the hydrophobicity of membrane by grafting the hydrophobic groups on the surface of CNTs. Both of F-CNTs-1 and F-CNTs-2 membrane combined the fluorosilanization and silanization modification of CNTs and these two modifications could improve the surface roughness of CNTs by grafting different length of chains on the CNTs surface. Resulting from combined modification, the surface roughness become rougher than the single modification membrane. Due to different sequence of modification, there may be more hydrophobic group on the surface of F-CNTs-1 membrane than that on the surface of F-CNTs-2, which makes the F-CNTs-1 membrane has a higher water contact angle and DCMD performance. All the conductivity of CNTs-PVDF membrane on the distillated side remained at a low level.

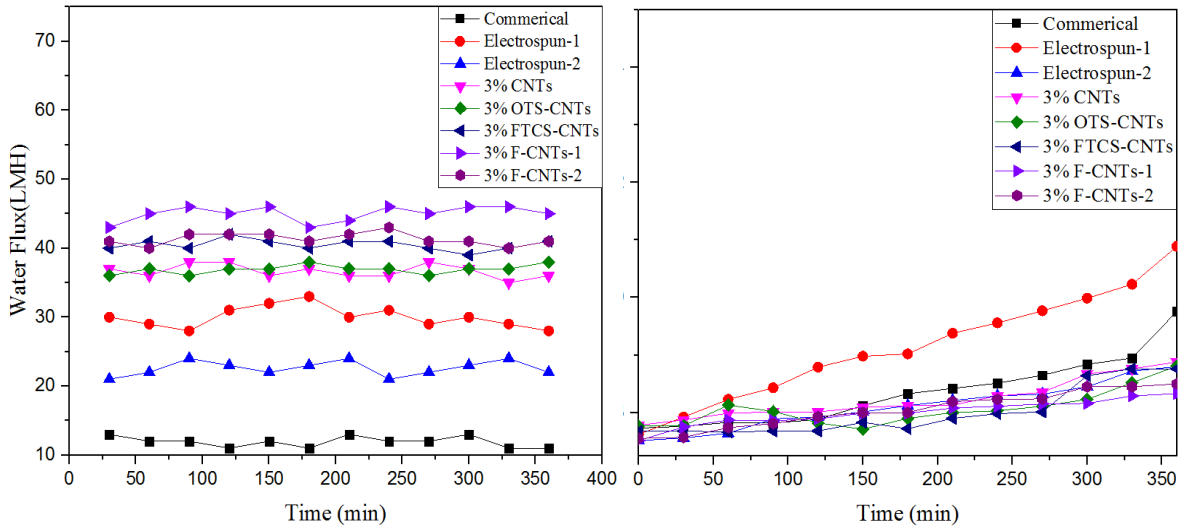

Figure 9. The DCMD performance of membranes (a) and the conductivity of water in the distillated side (b)

3.2.5. Salt rejection performance

Figure 12 showed the salt rejection performance of membranes. All the membranes showed a high salt performance (above 99.9%). The lowest salt rejection was the pristine electrospun membrane. The reason was mainly that the electrospun membrane has a much larger mean pore size than the commercial one. And the functioned CNTs membrane had a quite high salt rejection. This suggested that the functioned CNTs-PVDF membrane could be applied in the sea water desalination.

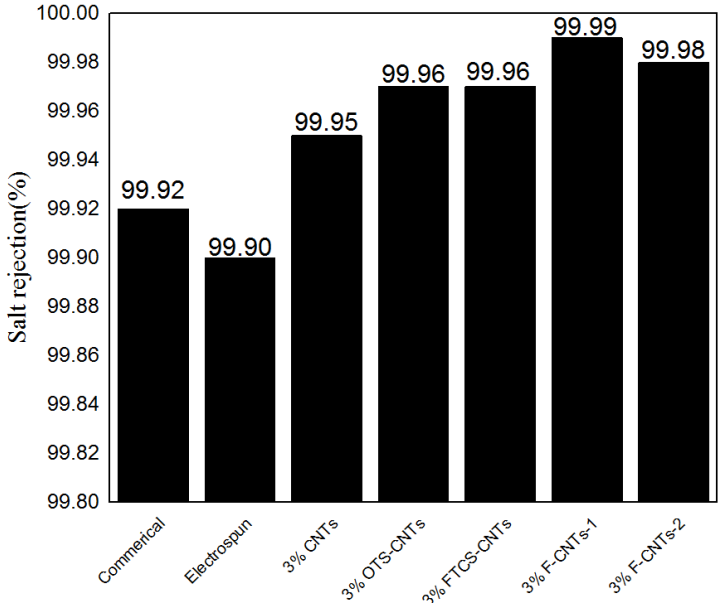

Figure 10. The salt rejection performance of membranes

3.2.6. The possible mechanism for CNTs and functioned CNTs in membrane

The schematic diagram of possible mechanism showed in Figure 13. The role of CNTs in the membrane was that CNTs itself have a strong hydrophobicity[36]. These CNTs may form several layers inside of the nanofiber. This kind of layers can prevent the water molecular go through the pore step by step in order to improve the wetting resistance and some CNTs could form the protrusion by the end of the CNTs on the surface of nanofiber[14]. That hierarchical structure could increase the surface roughness of nanofiber. Moreover, Immobilizing the CNTs in the pores altered the water-membrane interactions which decrease the tendency of a pore to become wet with liquid and achieve a high mass flux[10]. Also, the CNTs have a very high rapid sorption and desorption capacity and the process that vapor molecular go through the membrane is followed the molecular diffusion process[14, 35]. Benefited from these, the vapor transportation would increase. The inner pore and CNTs would form the 3D electrospun membrane containing the

superhydrophobic pore walls[14]. The superhydrophobic pore walls repelled water vapor molecules thereby mitigating negative effects such as friction or adsorption from occurring between the pore wall and the water vapor molecule. The vapor transportation would also be enhanced by the agglomeration of CNTs inside of nanofiber, which leads to form the wrinkles on the surface, due to their strong Van der Waals attraction[32].

After fluorosilanization surface modification, some fluoride functioned groups would be introduced on the surface and inner of nanofiber to further increase the hydrophobicity of CNTs and nanofiber to achieve a superhydrophobicity. By combining the silanization surface modification, another chain was introduced on the surface of CNTs. Because these two surfactants have different length of chains, it would form a structure shown on the Figure 13 as the functioned CNTs. Two kinds of chemicals with different length of chain can further increase the surface roughness of CNTs and nanofiber to improve the hydrophobicity. Another thing is that the surface modification can reduce the surface energy and the Van der Waals attraction between the CNTs, this would be helpful for improving the dispersion of CNTs in the polymer solution [14, 32].

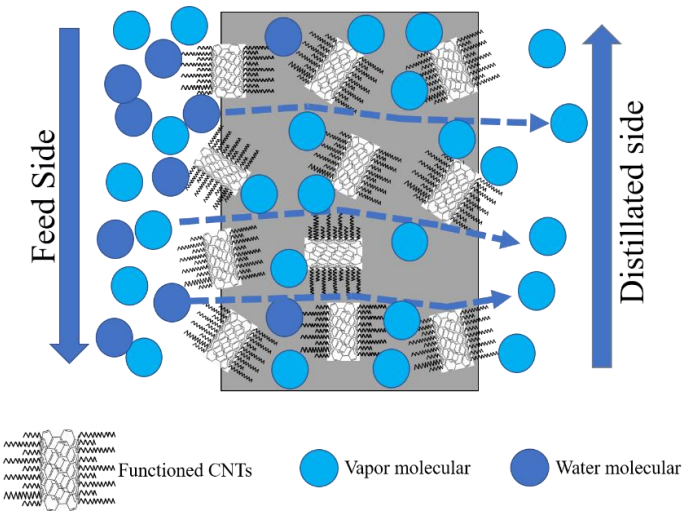

Figure 11. The schematic diagram of possible mechanism of surface modification of CNTs.

CHAPTER IV

CONCLUSIONS

In this study, the fluorosilanization and silanization modification method were applied on CNTs surface modification together. The superhydrophobic membrane was achieved by combining functioned CNTs prepared by combining of fluorosilanization and silanization surface modification. The F-CNTs-1 nanocomposites was prepared by the process that the acid treated CNTs is first treated with OTS and then have a reaction with FTCS. The water contact angle of F-CNTs-1 PVDF membrane was 153° which is 25.4% higher than the commercial membrane. Compared to the commercial one, the LEP of all electrospun membrane were smaller due to the larger mean pore size. The porosity, mean pore size and maximum pore size were also larger than commercial one while the diameter of nanofiber was decreased because of CNTs can improve the conductivity of polymer solution. For the DCMD performance, all the electrospun membrane had a significantly improvement up to approximate 4 times to the commercial membrane. The highest water flux was achieved by the F-CNTs-1 PVDF eletrospun membrane with the value of 45 LMH. In addition, the functioned CNTs-PVDF membrane had a very high salt rejection (above 99.9%) and the conductivity of solution in the distillated side remained at a very low level. All these results suggested that the functioned CNTs-PVDF was a potential membrane for DCMD operation.

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