Recent progress of membrane distillation using electrospun nanofibrous membrane

Leonard D. Tijing a, June-Seok Choib, Sangho Leec, Seung-Hyun Kim d, Ho Kyong Shona, b

Abstract

Rapid population growth has resulted in imbalance in the supply and demand of fresh water for human consumption. As the sources of fresh water from surface water and fresh groundwater have been consistently depleting at an alarming rate, alternative sources such as seawater and brackish water are sought out. Desalination of water is considered as one of the most sustainable and best water resource alternatives. Membrane distillation (MD) is an emerging and promising technology for water desalination and purification. It presents many advantages over the common desalination technologies such as reverse osmosis. The two major factors hindering the application of MD are suitable membrane design and structure, and energy efficiency of the MD process. In recent years, membrane design has seen increasing research and interest. Advances in science and technology have led to new materials and techniques that could find potential application for membranes in MD. In the past few years, electrospinning of nanofibers has gained much interest and attention in their application for MD membranes, and so far has promising results. This review focuses on the recent progress in the application of nanofibrous membrane fabricated by electrospinning for MD application.

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Acknowledgments

References

1. Introduction

Fresh water shortage for human consumption and irrigation is one of the major problems faced globally today. Nowadays, more than 1 billion people lack access to drinking water [1]. Seawater comprises majority of the world’s water resources and only 2.5% is fresh water, but only a portion of this fresh water is available for human consumption. Finding alternative ways to provide fresh water is of utmost importance. Since seawater is widely available, many research studies have been focused on converting seawater into drinking water [2,3] or for irrigation [4]. Other alternative ways are to treat brackish or wastewater into potable water [5,6].

Membrane technology plays an important role in desalination, and in water and wastewater treatment. Several membrane-based technologies such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) are currently being used [7]. In desalination, multi-stage flash distillation (MSF) and RO are the most widely used methods globally with a salt rejection higher than 98% [8]. Extensive research about RO has been conducted by several groups [9–13] and many review papers [9,14–16] are widely available in literature. RO presents an efficient way of desalination, however, it is an energy-intensive process, so there is a need for an alternative cost-effective process to turn seawater into drinking water. In recent years, several groups have focused on studying alternative methods for RO such as NF, electrodialysis, capacitive deionization, forward osmosis (FO), and membrane distillation (MD). Among the current water desalination and purification technologies, MD process presents many attractive features compared to other technologies. Increasing array of research is being conducted to optimize the performance of MD in desalination focusing both on theoretical and experimental studies [17–21]. Several experimental parameters are investigated on their effect on MD flux performance such as the feed and permeate temperature, salt concentration, and membrane properties (morphology, hydrophobicity, porosity, pore size and pore size distribution, etc.). There has been a surge of MD studies in the past 10 years (see Fig. 1). In 2013 alone, as of the writing of this paper, the number of MD publications as searched through the Web of Science with the topic ‘membrane distillation’ is already more than 200 publications, and it still continues to rise. Recently, an increasing number of studies is geared on modifying or entirely changing the MD membrane. Khayet [22] reviewed the fabrication and MD performance evaluation including experimental and theoretical studies of several commercial and laboratory-made MD membranes. Alkhudhiri et al. [23] recently reported a comprehensive review on MD performance addressing membrane characteristics, fouling, heat and mass transfer concepts, and effects of operating conditions.

In the past few years, nanotechnology has been gaining momentum in its application for water and wastewater treatment, and desalination. Many studies are now utilizing nanoparticles and nanofibers to impart additional properties and functionalities to the membrane, and also for membrane preparation, fabrication and modification. A few review articles in literature in the past few years have been dedicated to the application of nanotechnology to water and wastewater treatment [24–26]. Subramanian and Seeram [27] reported the recent developments on the use of electrospun nanofibers for desalination application by NF and MD. Feng et al. [28] reviewed the preparation and characterization of electrospun nanofiber membranes for water treatment and other membrane separation processes. Camacho et al. [29] have

Fig. 1. Annual publication on the subject of membrane distillation for the past 10 years (2004–October 2013) as searched through Web of Science.

Fig. 2. Schematic layout of the MD process and a list of ideal membrane characteristics for highly efficient MD.
recently published a comprehensive review of the advances in MD for water desalination and purification. Though these reviews included developments in MD, no review has yet been dedicated purely to the application of nanofibers for desalination by MD only. Especially in the past 2 years, significant increase in research studies has been undertaken utilizing the excellent properties of electrospun nanofibers for the fabrication or modification of MD membranes for desalination. Thus, there is a need to update the recent advances in MD utilizing nanofibers. In this paper, we focused our review on the recent progress of the use of electrospun nanofibrous membrane for MD application. We also compared the performance of nanofibrous membranes for MD to other types of MD membranes.

2. Membrane distillation

MD is a thermally driven (non-isothermal) separation process, driven by vapor pressure difference existing between the porous hydrophobic membrane surfaces (see Fig. 2). A membrane, which should be hydrophobic, is positioned in between a hot feed and a cold permeate, only allowing vapor molecules to pass through the membrane. The hot feed side is normally operated at lower temperatures (50–90 °C) than the boiling point of water. The hydraulic pressure in MD is much lower compared to pressure-driven separation processes such as RO. In general, MD is not limited to concentration polarization phenomena and thus the hydrodynamics do not significantly influence the permeate flux. Accordingly, it is possible to use low feed velocities thereby reducing the energy cost.

The history of MD dates back to 1963, when the first MD patent [30] was filed, and in 1967, when the first journal article [31] was published. One is referred to the publication of Khayet and Matsuura [32] for a more detailed history of MD. MD has been applied for desalination [33–35], treatment of water and wastewater [36], and even treatment of radioactive waste [37–39]. Solar energy has been utilized to power MD processes [18,34,40]. Khayet [41,41] reviewed the water production costs and energy consumption of solar desalination by MD.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Schematic</th>
<th>Details</th>
<th>Performance/remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct contact membrane distillation (DCMD)</td>
<td><img src="image" alt="DCMD Schematic" /></td>
<td>- Membrane is in direct contact with liquid phase on both sides</td>
<td>- Simplest configuration (does not need external condenser) - High permeate flux - Low energy efficiency - Most popular MD configuration for laboratory research - Highest conduction loss compared to other configurations</td>
</tr>
<tr>
<td>Air gap membrane distillation (AGMD)</td>
<td><img src="image" alt="AGMD Schematic" /></td>
<td>- A stagnant air gap in the permeate side is interposed between the membrane and a condensation surface - Air gap is around 2–10 mm</td>
<td>- Highest energy efficiency - Permeate flux is generally low - Suitable for desalination [48] and removal of volatile compounds from aqueous solution [49] - More popular in commercial application [50]</td>
</tr>
<tr>
<td>Vacuum membrane distillation (VMD)</td>
<td><img src="image" alt="VMD Schematic" /></td>
<td>- Permeate side is vapor or air under vacuum - Permeate is condensed outside the module</td>
<td>- Useful for removal of volatile materials from aqueous solution [51]</td>
</tr>
<tr>
<td>Sweep gas membrane distillation (SGMD)</td>
<td><img src="image" alt="SGMD Schematic" /></td>
<td>- Stripping cold inert gas is used as carrier for the produced vapor in the permeate side - Condensation happens outside the module</td>
<td>- Useful for removal of volatile materials from aqueous solution</td>
</tr>
</tbody>
</table>
The salient features of MD process to produce fresh water include the following:

a) theoretically 100% salt rejection;
b) simple membrane construction;
c) lower operating temperatures than conventional distillation processes (≈50–90 °C) [42];
d) relatively low operating pressure (a few hundred kPa) [43];
e) low energy consumption with waste heat;
f) potential to utilize low grade heat (i.e., solar thermal energy or waste heat);
g) less membrane mechanical integrity requirement; and
h) no extensive pre-treatment.

Additionally, MD can be integrated with other separation processes such as NF and RO [44,45]. But even though the MD membrane is simpler in construction compared to membranes of other desalination processes, the current MD membrane and process still suffer from several limitations such as (i) low permeate flux rate, (ii) wetting of the pores during MD operation, and (iii) gradual deterioration of the membrane performance due to temperature polarization after operation for long periods. Most of the present commercialized MD membranes are based on MF membranes that were fabricated by conventional thermal or dry/wet phase inversion technique. These membranes usually have large pores and low porosity, consequently suffering from low permeate flux. Thus, the first limitation of MD is the low permeate flux due to material selection, membrane structure such as porosity and thickness, and polymer surface properties. It is known that the increase in pore size, porosity and hydrophobicity of the membrane as well as the decrease in membrane thickness increase the permeate flux. However, lower thickness would also lead to weaker membrane and higher heat transfer flux by conduction, which poses a disadvantage to the MD process. Thus, the second limitation is the balance between mechanical integrity of the membrane and low heat transfer flux while trying to make the membrane support layer thinner to improve its flux performance.

2.1. MD configurations

The MD process is divided into four configurations depending on the way the permeate side is processed: (1) direct contact membrane distillation (DCMD); (2) sweeping gas membrane distillation (SGMD); (3) vacuum membrane distillation (VMD); and (4) air gap membrane distillation (AGMD). Several articles have extensively explained and reviewed the different MD configurations [46,47]. Table 1 summarizes the differences between the four MD configurations.

Each configuration has its own merits and demerits, however, from among the four types, DCMD is the most studied MD configuration, which comprises more than half of all studies about MD due to its simplicity in design and operation [47,52]. But DCMD also presents the lowest energy efficiency from all the configurations, primarily due to high heat loss from conduction through a thin membrane [53].

AGMD is considered to have the highest energy efficiency and is more popular for commercial application. The air gap width is usually in the range of 2–10 mm [54–56], which is way larger than the membrane thickness that is usually less than 300 nm. The air gap width is considered to be the main controlling factor due to its high thermal and mass transfer resistances.

In VMD, a pump is used to create vacuum in the permeate side, thus forming a vapor pressure difference across the membrane. The vapor is condensed by an external condenser. This set-up has low conduction heat loss, making it advantageous for MD [57]. Generally, smaller pore sizes (<0.45 μm) are used in VMD due to high possibilities of pore wetting [32]. VMD is usually used to remove volatile materials from aqueous solution.

SGMD is somewhat similar to AGMD, however, in SGMD, the gas is moving or sweeping and the vapor is condensed in an external condenser. SGMD has higher mass transfer rates compared to AGMD and lower conduction heat loss than DCMD.

2.2. Theoretical analysis of MD

Most of the previous research on MD has been on theoretical and experimental studies. Theoretical studies comprise 44% of the total published reports and about 15% are on the design and preparation of MD membranes [22]. In the past decade, an increasing number of studies has been focused on the design, fabrication and modification of new membranes for MD. To optimize results in research, theoretical modeling coupled with experimental investigation is the ideal way. In the past, several theoretical models have been developed by many research groups to predict MD permeate flux. The studies were basically based on the kinetic theory of gases. Khayet [22] recently reviewed the theoretical modeling studies for MD. It was observed that most of the theoretical models are based on at least one adjustment parameter, to predict the MD permeate flux [22]. The theoretical models usually assume a uniform size of pores in the whole membrane [43,58], however, the membrane is normally made up of pores with different sizes, thus a better modeling should take into account the pore size distribution (PSD) [59]. It was reported that the width of the PSD strongly affects the vapor flux [59], where narrow PSD produces better performance. Khayet et al. [60] concluded that laboratory-made membranes may have larger errors if there is a broad PSD.

Three basic mechanisms govern the vapor mass transfer through the membrane, namely: Knudsen diffusion, Poiseuille or viscous flow and molecular diffusion, or their combination known as transition mechanism. The Knudsen number, Kn, which is the ratio of the mean free path of molecules and the mean pore size of the membrane determines the dominant mass transfer mechanism. Recent modeling studies using Monte Carlo simulation models have found excellent agreement between the experimental and simulated results when considering pore space interconnectivity [61]. Recently, Essalhi and Khayet [62] considered pore interconnectivity in their theoretical studies. The viscous type of flow was neglected because the feed and permeate hydrostatic pressures were both maintained at atmospheric pressure.

In their work [62], the contribution of each mass transport mechanism was determined, which is in contrast with what is done in other theoretical studies using the Bosanquet equation [63], and the effective diffusion coefficient ($D_e$) is calculated by the following equation [62]:

$$D_e = \left( \frac{1}{\left( \frac{3\pi \sigma}{2e d_i} \right)^{1/2}} \right) \left( \frac{\pi R T}{8 M_w \epsilon} \right)^{-1} + \left( 1 - \frac{\sigma p_a}{M_w \epsilon P_{D_{w/a}}} \right)^{-1} \left( \frac{\alpha}{D_K} + \frac{1 - \alpha}{D_M} \right)^{-1}$$

where $D_K$ is the Knudsen diffusion coefficient, $D_M$ is the molecular diffusion coefficient, $\alpha$ is the contribution of Knudsen diffusion to mass transfer, $M_w$ is the molecular weight of water, $R$ is the gas constant, $\delta$ is the thickness of the nanofibrous membrane, $d_i$ is the mean size of the inter-fiber space, $\epsilon$ is the void volume fraction, $\tau$ is the tortuosity, $p_a$ is the pressure inside the nanofibrous membrane, $P$ is the total pressure (atmospheric), and $P_{D_{w/a}}$ is the ordinary diffusion of water vapor in air. The tortuosity refers to the straightness of the pores and is related to the interconnectivity of the pores.
The water production rate \( J_w \) was calculated using the following equation [22]:

\[
J_w = \frac{D_c \Delta p_{w,m}}{D_c (P_{w,f} - P_{w,p})} = \frac{D_c (P_{w,f}^0 a_{w,f} - P_{w,p}^0)}{D_c (P_{w,f}^0 a_{w,f} - P_{w,p}^0)} = \frac{D_c (P_{w,f}^0 a_{w,f} - P_{w,p}^0)}{D_c (P_{w,f}^0 a_{w,f} - P_{w,p}^0)}
\]

(2)

where \( \Delta p_{w,m} \) is the water vapor pressure difference between the feed and permeate ENM/liquid interfaces, \( a_{w,f} \), \( T_{w,f} \), \( x_{w,f} \) and \( P_{w,f}^0 \) are the activity, activity coefficient, mole fraction and vapor pressure of water at the feed/membrane surface, respectively, and \( P_{w,p}^0 \) is the vapor pressure of water at the permeate.

Temperature polarization coefficient is generally used as a benchmark for energy efficiency, i.e., the higher the value, the better the energy efficiency. The following equation was used to determine the temperature polarization coefficient in DCMD [22]:

\[
\theta = \frac{T_{m,f} - T_{m,p}}{T_{f,b} - T_{p,b}} \times 100
\]

(3)

where \( T_{m,f} \) is the temperature at the feed liquid/vapor interface, \( T_{m,p} \) is the temperature at the permeate liquid/vapor interface, \( T_{f,b} \) is the temperature at the bulk feed liquid, and \( T_{p,b} \) is the temperature at the bulk permeate liquid.

2.3. MD membrane characteristics

The role of the membrane design and structure is deemed the most important for high efficiency MD process. However, most of the research studies in the past decades have been on the exploration of the effect of operating conditions and parameters and theoretical models. Only in the recent years have there been great efforts on the design and structure of the membrane itself focusing on the fabrication of new membranes that possess high hydrophobicity, high porosity, low tortuosity, and high thermal, mechanical and chemical stability. Fig. 2 lists the characteristics of an ideal MD membrane. Developing an ideal membrane is a big challenge because there is always a trade-off between the rejection and permeate flux and between thickness and mechanical strength and heat transfer flux.

The two most common MD membrane designs used commercially and in laboratory experiments are flat-sheet and hollow fiber membranes (see Fig. 3). Hollow fibers have more surface area per unit volume but are reported to have lower fluxes than flat-sheet membranes [29]. But recent progress in materials preparation and synthesis has resulted in comparable permeate fluxes of hollow fiber membranes with those of flat-sheet membranes [64]. However, it was also reported that hollow fibers are more susceptible to mechanical failures compared to flat-sheet membranes [29]. Feng et al. [65] recently investigated the progress in hollow fiber membrane development in the past 12 years focusing on membrane characterization by AFM, new membrane design for gas separation, introduction of new polymers and techniques for high performance hollow fibers, and new developments in PVDF-based membranes.

MD requires less demanding membranes compared to pressure-driven processes such as RO and NF. Even so, the MD membranes must take into account several ‘good’ membrane characteristics for enhancing MD performance considering both heat and mass transfer effects. The transport of vapor across the membrane can be generally defined by the following equation [29]:

\[
f = K(T) \left( \frac{r e}{b} \right)^{\alpha}
\]

(4)

where \( f \) is the permeance of the membrane, \( K(T) \) is a function of temperature and molecular weight of the gas, \( r \) is the average pore radius, \( b \) is the membrane thickness, \( e \) is the membrane porosity, \( r \) is the membrane porosity, and \( i \) is the membrane tortuosity, \( \alpha \) depends on the permeation type of the vapour when it passes through the membrane.

2.3.1. Thickness

The thickness of a membrane has a great effect on the permeate flux. It has an important role in determining the mass transfer resistance [47]. Generally, thicker membrane results in lower permeate flux due to increased mass transfer resistance. At thinner membrane, higher permeate fluxes can be achieved primarily due to lower mass transfer resistance and shorter overall vapor
transport path (Eq. (4)), however, it also reduces the thermal resistance, which consequently results in lower interface temperature difference. Thus, there must be a suitable thickness to compromise between permeate flux and thermal resistance. The selection of optimum membrane thickness depends on whether the membrane is supported or unsupported type, and the type of feed solutions [68]. Several membrane designs are now being utilized for MD including single, double, and even triple-layer membranes. Single layer membranes are the common types wherein the whole of the membrane is made of the same hydrophobic material and structure with or without a support layer. The support layers of commercial membranes are reported to be 80% of the total thickness of the membrane [68]. The multi-layered membranes (double- and triple-layer) utilize a hydrophobic active layer and less-hydrophobic to hydrophilic support layers. The important aspect of the different designs is the thickness of the active layer, i.e., the surface that faces the feed side. One must be cautious in using too thin active layer thickness as this would result in liquid penetration through the pores of the membrane. Furthermore, the thickness of the membrane is also related to its mechanical integrity. Though MD membrane requires less mechanical integrity compared to other separation processes, it still should possess adequate strength and chemical resistance. Based on simulation experiments and on the thermal conductivity of commercial membranes, it was reported that the optimum thickness is between 30 and 60 μm [69]. It was observed that there was not much effect of thickness on the energy efficiency of non-supported membranes, wherein energy efficiency only increased until 20 μm thickness and did not further increase beyond that [70].

2.3.2. Pore size and pore size distribution (PSD)

The mean pore size and PSD are crucial parameters for the performance of MD. An optimum pore size is needed to have a balance in high permeate flux and good pore wetting resistance. Higher permeate flux can be obtained at bigger pore sizes, however, smaller pore sizes are also needed to avoid pore wetting. It was suggested that pore sizes should be below 0.5 μm to avoid pore wetting [71]. Several studies have shown increasing MD flux for commercial and laboratory-made flat-sheet and hollow fiber membranes at increasing pore sizes [68,72–75]. Pore sizes for MD membrane usually range from 100 nm to 1 μm [47]. A previous study has observed an increase in pore size by up to 25% in the first 72 h of test using polypropylene membranes [76], which affects the permeate flux performance. MD membranes have pores with varying sizes, thus they exhibit a pore size distribution (PSD) rather than a uniform pore size. PSD is suggested to play a dominant role in the MD process, however, only very few studies have considered PSD for MD research [59]. Different pore sizes can exhibit different flow mechanisms. The pore size distribution should be as narrow as possible, i.e., not too much variation in pore sizes. Large PSD will lead to pore penetration, thereby allowing solutes from feed to pass through the membrane. PSD is reported to be more important in VCMD than in DCMD [59]. PSD can be described to have a normal distribution or a log-normal distribution. Most of the previous studies have reported PSD to fit a log-normal distribution rather than a normal distribution [59,77,78].

2.3.3. Surface hydrophobicity

A hydrophobic surface is a requisite for MD process. Highly hydrophobic material can prevent water from wetting the inside of the membrane, thus only allowing vapor to pass through. Material composition and surface geometrical structure determine the wettability of the surface. The current MD membrane design is mostly based on commercial MF membranes that are fabricated by conventional thermal or dry/wet phase inversion technique. Most of the studies used hydrophobic porous membranes made of polypropylene (PP) [79,80], polytetrafluoroethylene (PTFE) [68], and polyvinylidene fluoride (PVDF) [81,82]. All three polymers have good thermal and chemical resistance and are all hydrophobic, which is a requisite for an MD membrane. PTFE has the lowest surface energy (i.e., most hydrophobic) among the three but PVDF is the most widely used because of its easy processability. The surface could be made hydrophobic by using materials with low surface energy or by modifying the surface into rougher surfaces with hierarchical nanostructure surface morphology [42,83]. However, the surface roughness is usually more critical than the low surface energy. This is because when two surfaces with different hydrophobicity are roughened, both can possess superhydrophobic property. Several surface modification techniques are utilized to enhance the hydrophobicity of the membrane. Among such include plasma treatment, layer-by-layer assembly, incorporation of surface modifying molecules or functional groups, and loading of hydrophobic nanoparticles in the polymeric matrix. The main aim is to obtain a superhydrophobic surface, i.e., with a contact angle greater than 150° and a low sliding angle (< 10°) [84]. In a recent study [85], PVDF membranes were coated with TiO2 and different templating agents and tested for DCMD. The TiO2-coated membranes showed porous, multi-level structures and superhydrophobic surfaces, which lead to improvement in salt rejection and substantial reduction in pore wetting.

2.3.4. Porosity

Porosity is also referred to as the void volume fraction of the membrane. Both the surface and volumetric porosities affect the MD flux performance. High porosity membrane presents more evaporation surface area or more pore channels for diffusion, thus it can lead to higher permeate flux. Additionally, the presence of more voids increases the thermal resistance of the membrane because air which is present in the pore spaces has much lower conductivity than the membrane material. So that both heat efficiency and permeability of the membrane are increased at increased porosity. However, one should take note that increasing the porosity could also result in decreased mechanical integrity, which could lead to loss of membrane performance. MD membrane porosity is reported to be from 35% to as high as 93% [47,86]. Previous studies reported that porosity has the most influence on the performance of DCMD compared to other membrane characteristics [61,87].

2.3.5. Tortuosity

Tortuosity is the deviation of the pore structure from the straight cylindrical pore structure normal to the membrane surface (or in simple term, it refers to the straightness of the pores). It is inversely proportional to the permeate flux, i.e., higher tortuosity results in lower permeability (Eq. (4)). A value of 2 is usually used as membrane tortuosity factor to predict permeate flux in MD studies [22] but a value as high as 3.9 was also reported [88]. The tortuosity factor can be predicted through fractal theories of random walks for loosely packed membrane structure and is quantified by the following equation [89,90]:

\[
\tau = \frac{1}{\varepsilon}
\]

(5)

where \(\tau\) is the tortuosity factor and \(\varepsilon\) is the porosity.

2.3.6. Liquid entry pressure (LEP)

LEP is the minimum transmembrane pressure or the point where liquid will enter or penetrate the pores of the membrane. To avoid MD pore wetting, the hydrostatic pressure must be lower
than the LEP. But even though the operating pressure is lower than the LEP, pore wetting can still occur via partial pore wetting. This happens especially when fouling particularly scales occurs at the membrane surface, thereby changing the membrane properties [91]. Furthermore, accelerated pore wetting could happen if salt crystals are formed inside the pores, leading to lower LEP [91,92]. In MD process, the LEP should be as high as possible. The LEP value is mainly affected by the hydrophobic behavior of the material and its pore size and shape. Thus, a material with low surface energy (i.e., hydrophobic) is appropriate and the maximum pore size should be as small as possible. However, making the pore size small also affects negatively the permeation ability of the membrane. Thus, an appropriate pore size, porosity and pore size distribution should be used. The LEP can be calculated by the following Laplace (Cantor) equation [29]:

\[ LEP = \frac{-2B\gamma_l}{r_{max}} \cos \theta < P_{\text{process}} - P_{\text{pore}} \]  

where \( B \) is the geometric factor, \( \gamma_l \) is the surface tension of the solution, \( \theta \) is the contact angle between the solution and the membrane surface (i.e., depending on the hydrophobic property of the membrane), \( r_{max} \) is the largest pore size, \( P_{\text{process}} \) is the liquid pressure on either side of the membrane, and \( P_{\text{pore}} \) is the air pressure in the membrane.

### 2.3.7. Thermal conductivity

The membrane material should have low thermal conductivity to have good thermal resistance. The usual commercial hydrophobic materials used in MD have low thermal conductivities in the range 0.04–0.06 W/mK [22]. Membrane with high porosity helps in reducing heat transfer conduction across the membrane because of the presence of air in the pores, which has very low thermal conductivities. Another way is to use a multi-layered membrane composed of hydrophobic and hydrophilic materials, wherein the hydrophobic layer is kept thin, while the hydrophilic layer is thicker to enhance the resistance to conductive heat transfer, but should be cautious not to be too thick so as not to increase the mass transfer resistance considerably.

### 2.4. MD membrane fouling

Fouling in general is the accumulation of unwanted deposits on the surface of the membrane or inside the pores of the membrane that degrades its permeation flux performance [79,93]. This is one of the major problems in membrane-based processes. The foulants found in membrane technology including MD can be divided into organic, inorganic, and biological fouling mechanisms. Organic fouling refers to the adsorption/deposition of organic substances on the membrane surface such as humic and fulvic acid, protein and polysaccharides, carboxylic acid, extracellular polymeric substances (EPS) and many others. The deposited organic foulants are hard to clean by physical methods and usually need chemical treatment [94]. Inorganic fouling is usually termed as scaling, being the deposition of precipitated minerals from the feed solution. Scaling is one of the major challenges that hinder the full-scale operation of MD for desalination [95]. The three most common scales in MD are calcium carbonate (CaCO₃), calcium sulfate (CaSO₄), and silicate. Several factors affect the rate of scaling such as the degree of supersaturation, flow conditions, membrane surface and solution temperature, water properties, the surface properties such as roughness and morphology, the kind of substrate material, and any nucleation site available such as particulates or impurities in water [96]. Biological fouling or biofouling is the accumulation and growth of biological species. Microorganisms are the main culprit of biofouling. However, it is less likely to occur in MD processes due to the high salinity of feed, which limits microorganism growth, and higher operating temperature than the growth temperature of most bacteria [97]. Even so, there are bacterial species that can survive and grow at extreme surroundings, thus biofouling could still occur in MD.

A mixed fouling mechanism is most likely to occur in real MD process. The kind of fouling mechanism depends on several factors such as the feed water properties (e.g., hardness, pH, ionic strength, etc.), membrane surface properties, geometry, and morphology, and the physico-chemical properties of the foulants [94]. The accumulated materials can cause severe pore wetting and can lead to pore flooding, wherein the liquid penetrates or floods the inside of the pores of the membrane. Additionally, minerals from

<table>
<thead>
<tr>
<th>Fouulant</th>
<th>Set-up</th>
<th>Membrane type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humic acid</td>
<td>DCMD</td>
<td>Flat-sheet (PVDF)</td>
<td>[102]</td>
</tr>
<tr>
<td>Humic acid</td>
<td>AGMD</td>
<td>Flat-sheet (PVDF)</td>
<td>[103]</td>
</tr>
<tr>
<td>Fungi, bacteria</td>
<td>DCMD</td>
<td>Capillary (PP)</td>
<td>[97]</td>
</tr>
<tr>
<td>Bacteria</td>
<td>DCM</td>
<td>Hollow fiber (PP)</td>
<td>[104]</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>DCMD</td>
<td>Flat-sheet (PVDF)</td>
<td>[98]</td>
</tr>
<tr>
<td>Alkaline (mainly CaCO₃)</td>
<td>DCMD</td>
<td>Capillary (Polypropylene)</td>
<td>[105]</td>
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<tr>
<td>CaCO₃, CaSO₄, silicate</td>
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<td>[108]</td>
</tr>
<tr>
<td>CaCO₃, CaSO₄, silica</td>
<td>DCMD</td>
<td>Flat-sheet (PP)</td>
<td>[109]</td>
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</table>

Fig. 4. Typical electrospinning set-up consisting of nozzle, high voltage power supply and grounded collector.
the feed can also intrude inside the pores and could possibly pollute the distillate; or the scales can form inside the pores, thus clogging them, drastically lowering the mass transfer rate. It has also been reported that fouling deposits can lower the hydrophobicity of the surface [98]. Fouling and cleaning of membranes also been reported that fouling deposits can lower the hydro-

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Effect of solution, process and other parameters on the morphology of electrospun fibers.</th>
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<td>Parameter</td>
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</tr>
<tr>
<td>Solution parameters</td>
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<tr>
<td>Concentration</td>
<td>Increasing concentration results in bigger fibers [127]</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>Very low concentration can form beads on fibers</td>
</tr>
<tr>
<td>Viscosity</td>
<td>More bead formation at low molecular weight</td>
</tr>
<tr>
<td>Conductivity/surface charge density</td>
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</tr>
<tr>
<td>Surface tension</td>
<td>Thinner fibers are formed with the increase of viscosity</td>
</tr>
<tr>
<td>Process parameters</td>
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</tr>
<tr>
<td>Applied voltage</td>
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<tr>
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</tr>
<tr>
<td>Collector</td>
<td>Typically feed rate is below 1 mL/h</td>
</tr>
<tr>
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</tr>
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<td>Increased temperature results in decreased fiber diameter</td>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>Drying temperature</td>
<td>Drying temperature should be below the boiling temperature of the solvent to avoid bubble and eventually pore formation in the fiber</td>
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3. Electrospinning

Electrospinning is a versatile process of producing fibers in the non-woven mat form with diameters ranging from few microns to nanometer scale by applying high electric fields [110,111]. The electrospun non-woven mats provide very large specific surface area, high strength-to-weight ratio, and high porosity (~80%) and degree of interconnection, which make them attractive for different applications such as in filtration, textile, fuel cells, biomedical application, and recently, in desalination, and water and waste water treatment [111–113]. Moreover, the properties of nanofibers can be tailored according to the need in terms of layer thickness, fiber diameter, porosity, and added functionalities by manipulating the electrospinning parameters, material selection, and post-processing treatments [112,114]. Depending on the desired properties, electrospinning can be done via solution or melt electrospinning. In solution electrospinning, polymers are dissolved in a solvent or a solvent mixture. This is the commonly-used type because of its easy preparation and set-up. On the other hand, melt electrospinning makes use of a especially designed nozzle, wherein polymer pellets are directly melted in the nozzle with the application of high temperature [115]. In this set-up, no solvent is needed. Some of the polymers from over 200 polymers [116] that have been electrospun include nylon-6, cellulose acetate (CA), poly(vinyl alcohol) (PVA), polyacrylonitrile (PAN), polyethylene terephthalate (PET), polystyrene (PS), polyethersulfone (PES), polyurethane (PU), and polyvinylidene fluoride (PVDF) [117,118].

Basically, there are three main components in electrospinning: (i) a high voltage power supply, (ii) a syringe containing polymer solution (or melt) with metallic spinneret, and (iii) a grounded collector (see Fig. 4). The polymer solution or melt is placed inside the syringe and a pressure is applied usually by a syringe pump. The polymer solution is fed to the spinneret wherein a high voltage is applied (usually around 5–40 kV depending on the solution properties), the drop at the tip of the spinneret experiences electrostatic repulsion and Coulombic force. Once the electric field overcomes the surface tension of the polymer solution, a jet is ejected from the Taylor cone (conical shape distortion of the droplet), experiencing stretching and whipping instability going to the negative electrode (i.e., grounded collector). As the jet travels through the space, the solvent is evaporated and solidified nanofibers are collected on the grounded collector in the form of non-woven mat. The collected nanofibrous mat is usually subjected to further drying at room temperature or at
other desired temperature in a conventional oven, a vacuum oven, or in open air.

Owing to the very small dimension of nanofibers, they present as excellent substrate for nanoparticles so as to provide additional functionalities to the composite nanofiber. Several nanoparticles (NPs) such as carbon nanotubes (CNTs), graphene, silver (Ag) NPs, titanium dioxide (TiO₂) NPs, iron oxide NPs, etc. [110,113,119,120] have been incorporated or decorated on/in nanofibers via direct dispersion of NPs in polymer solution prior to electrospinning, or via in situ reduction of NPs. A number of studies [121–124] and review articles [112–114,125] have been published about electrospinning of pristine and composite nanofibers, which include the preparation of polymer solutions and the effect of different process parameters on the nanofibrous membrane. The electrospinning configurations can also be varied to enable fabrication of different types of composite mats or nanofiber orientation [126]. Among the configurations include multi-nozzle set-up and co-axial electrospinning. In multi-nozzle electrospinning, two or more nozzles, which contain the same or different polymeric solutions, are configured to electrospin onto one collector, thus resulting in a mono- or multi-component nanofibrous mat. In co-axial electrospinning, concentric nanofibers made of sheath (outside) and core (inside) layers are fabricated [83,124]. This set-up is particularly useful for polymers that are not easily dissolved in solvents, so that these polymers can be spun as a sheath layer of a spinnable polymer solution.

3.1. Electrospinning parameters

The desired morphology and properties of electrospun membrane can be tailored by controlling the solution and process parameters. The solution parameters include the concentration, molecular weight, viscosity, conductivity, and surface tension. The process parameters on the other hand include voltage, applied electric field, feed rate, tip-to-collector distance (TCD), and collector shape, while other parameters that should also be considered include ambient temperature and humidity during electrospinning, and post-spinning drying. The major challenge in electrospinning is the optimization of these parameters to obtain nanofibers with the desired morphologies and properties. Table 3 summarizes the effect of solution, process and other parameters on the fiber formation during electrospinning.

A suitable concentration is needed for electrospinning to achieve good fiber formation. Very low concentration in solution results in sputtering and spray forming beads instead of fibers. Furthermore, a low concentration tends to form many drops at the spinneret tip. On the other hand, increasing the concentration tends to form bigger diameter fibers [127]. At an appropriate concentration, uniform and cylindrical fibers could be formed, thus optimization of the concentration along with other parameters is necessary to obtain smooth nanofiber formation.

Polymer molecular weight reflects the entanglement of polymer chains in a solution. It affects the rheological and electrical properties of the solution such as viscosity, conductivity, surface tension and dielectric strength. Low molecular weight tends to produce more beads, while increasing the molecular weight produces bigger and smoother fibers.

Viscosity is closely related to polymer concentration and molecular weight. It plays an important role in determining the fiber morphology. At low viscosity or a more dilute solution, non-continuous fibers can be formed with high possibility of bead formation, while at high viscosity usually in the range 1–200 poise [128], bigger and smoother fibers are formed. Too high viscosity is difficult to spin and could clog up the spinneret during electrospinning. Various polymers have different optimum viscosities for optimal formation of smooth fibers.

In general, higher conductivity of the solution produces thinner fibers. The increased conductivity gives increased charge carrying ability, thus elongating more as it is subjected in electric field. Many studies have added salts to increase the conductivity of the solution. At low conductivities, insufficient elongation under electric field is experienced by the fibers, thus leading to some bead formation.

The surface tension of a solution normally depends on the solvents used. Generally, low surface tension could generate smooth and uniform fibers at low electric fields. Increasing the surface tension tends to produce droplets and beads. One can tailor the surface tension of the solution by using different solvents or mixture of solvents at different ratios.

Attaining a threshold applied voltage of the polymer solution is necessary to commence electrospinning. Electrospinning has been carried out at applied voltages between 5 and 40 kV. The effect of applied voltage on the fiber formation has conflicting reports in literature. A study by Reneker and Chun [129] reported that electric field did not considerably affect the fiber diameter using polyethylene oxide as a model polymer. Other studies suggest the formation of bigger fiber diameters at higher voltage [130] due to increased amount of polymer solution ejected. Several groups have reported that increasing the applied voltage would decrease the fiber diameter due to the increased electrostatic repulsive force on the charged jet. Rather than focusing on the effect of voltage, a better parameter would be to use the strength of the electric field [111].

The polymer solution is usually fed using a syringe pump, where the feed rate can be accurately controlled. The effect of feed rate on the fiber formation depends on the type of polymer used and the properties of the polymer solution. A low feed rate usually below 1 mL/h is desirable to allow more evaporation time and obtain smooth and uniform fibers. However, too slow feed rate would also not be able to continuously produce fibers, and at higher feed rates, drops would be rampant at the spinneret side, and bead formation would be highly possible due to lack of time to evaporate and dry prior to deposition in the collector.

A collector is a conductive substrate placed in front of the spinneret at a certain distance that collects the solidified fibers. The collector must be grounded so as to provide electric field in the system. Two most common collector designs are the flat plate and the rotating drum. For a larger fiber fabrication and more uniform thickness, a rotating drum is usually utilized. Aluminum foil could be used as collector directly. Or another way is to cover the conductive collector with aluminum foil or Teflon sheet or a baking paper for ease of peeling the nanofibrous membrane after electrospinning. Many collector designs are now available, which can help tailor to the desired fiber morphology and structure. Sahay et al. [131] reviewed the design modifications of an electrospinning set-up for advanced applications. A rotating wheel connector could be used to produce aligned fibers.

The tip-to-collector distance (TCD) affects the strength of electric field along with the applied voltage. Sufficient distance from the spinneret tip should be used to allow the fibers enough time to elongate and dry before reaching the collector. When fibers are ejected from the tip, the solvent from the polymer solution needs to evaporate so that only solidified fibers with a little residual solvent will deposit on the collectors. Thus, at short TCD, fibers are not usually formed; instead a wetted foil could be used as collector directly. Or another way is to cover the conductive collector with aluminum foil or Teflon sheet or a baking paper for ease of peeling the nanofibrous membrane after electrospinning. Many collector designs are now available, which can help tailor to the desired fiber morphology and structure. Sahay et al. [131] reviewed the design modifications of an electrospinning set-up for advanced applications. A rotating wheel connector could be used to produce aligned fibers.

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The temperature and humidity of the surroundings during electrospinning could affect the resulting fiber morphology and structure. Generally, high temperature could result in thinner fiber. On the other hand, high humidity results in more porous fiber structure. This is because the presence of moisture in air could be entrapped in the formed fiber and thereby make pores. At low humidity, faster evaporation rate compared to the removal of solvent from the spinneret tip could be achieved, which could present a clogging problem in the spinneret. Thus, humidity must be taken into account during the electrospinning process.

The drying temperature and humidity after electrospinning will also affect the formed fibers. One should take note that drying temperature should be below the boiling point of the solvent used. Drying the fibers at higher temperature could result in the production of pores inside or on the surface of the fiber due to bubble formation from the residual solvent. Similarly, low humidity environment should be used for drying to avoid moisture to accumulate in or on the fiber being dried, and prevent pore formation.

4. Electrospun nanofibrous membrane for MD and other applications

Progress in science and technology has led to the development of new materials and techniques that drastically improve the performance of existing or conventional materials. With the advent of nanotechnology, things are becoming smaller but more powerful. One good example is the production of nanofibers via an electrospinning process. In the past two decades, electrospinning has experienced a sudden surge in research due to its wide array of potential applications particularly in biomedical and energy sectors. The past few years have seen nanofibers being employed as promising membrane materials for filtration, water and wastewater treatment, and water purification applications. Several groups have had successes in the use of electrospun nanofibrous membrane as main or support material for pressure-driven membrane processes such as MF, UF, NF and RO. For example, Yoon et al. [133] investigated the UF/NF filtration efficiency of electrospun PAN nanofibers with an active layer made of chitosan. The PAN membrane had a porosity of 70% and obtained much higher flux rate compared to commercial NF membranes after 24 h of operation, while maintaining >99.9% rejection efficiency when used for oily wastewater filtration. You et al. [134] developed a low pressure, high flux nanofibrous membrane for UF application. PAN membrane was fabricated by electrospinning and a thin film of PVA layer was deposited via a solution treatment method. The thin film nanofibrous membrane was evaluated by an oil/water emulsion separation system and the results showed very high flux, with high rejection rate but at low feed pressure.

Recently, but still in its infancy, nanofibers are also being used for osmotic membrane separation process such as FO and PRO. Hoover et al. [118] used electrospun PET nanofibers as support layer for FO or PRO thin film membrane. The middle layer was made of cast Psf, while the active layer was made of polyamide fabricated by interfacial polymerization. The fabricated membranes showed good water permeability and salt rejection, and the nanofibers enhanced the delamination resistance at high cross-flow velocities. With the trend of using nanofibers in desalination and water purification processes, electrospinning has also found its way to MD application. However, only very few research groups have yet used electrospun nanofibers for membrane distillation. A number of studies have been conducted in the past 5 years utilizing the excellent properties of nanofibers for MD, and we have summarized the progress here in this review.
4.2. Effect of nanoﬁbrous membrane thickness on DCMD

The thickness of an MD membrane is an important parameter in the overall performance of MD. Studies have shown that the decrease in membrane thickness increases the permeate ﬂux, while the increase of pore size and porosity increases it [135,136]. For pressure-driven processes, the selection of membrane thickness should take into consideration the mechanical integrity of the membrane as it will be subjected to high pressures. However, in the case of MD, there is less requirement for mechanical integrity, thus thinner membrane can be considered, however, it should also take into account the effect on heat transfer.

In a recent work, Essalhi and Khayet [86] investigated the effect of different thicknesses of electrospun PVDF nanoﬁbres by varying the electrospinning times in desalination by DCMD. They used 25 wt% PVDF dissolved in acetone/DMAc solvent mixture and electrospun using 24 kV voltage, 1.23 mL/h polymer solution feed rate, and 27.7 cm TCD. The temperature and humidity of the electrospinning chamber were maintained at 23 °C and 36%, respectively. Table 4 summarizes the resulting thickness, mean ﬁber diameter and water contact angle of the fabricated membranes. By varying the electrospinning times (from 1 h to 4 h, with 30 min interval), the nanoﬁbrous membranes resulted in increasing the thicknesses from 145 to 1530 μm. Several characterization techniques were utilized and the DCMD performance was evaluated at different feed temperatures (40, 50, 60, 70, 80 °C) and different concentrations (0, 12, 30, 60 g/L) of sodium chloride solutions. The fabricated membranes showed void fraction and water contact angle of 0.85–0.93 and 137.4–141.1°, respectively, depending on the electrospinning time. Thicker thickness and higher liquid entry pressure (LEP) of water were observed with the increase in electrospinning time, however, the LEP was found to be not uniform throughout the thickness of the fabricated membrane. Varying the electrospinning time showed no signiﬁcant effect on the diameter of the nanoﬁbres. When the nanoﬁbrous membranes were subjected to mechanical testing, it was found that increasing the electrospinning time, which resulted in thicker membranes, also increased the tensile properties of the samples as shown in the typical stress–strain curves in Fig. 7. However, no trend was observed in their elongation. When compared with a commercial membrane HVHP with similar thickness, the as-spun PVDF ﬁbres showed slightly lower tensile strength but were an order of magnitude higher in its elongation performance. This phenomenon could be attributed to the highly porous (less dense) and web structure of PVDF nanoﬁbres (85–93% porosity) compared to HVHP (75% porosity).

In DCMD test, higher permeate ﬂuxes were observed at thinner membrane, higher feed temperature and at lower salt concentration (see Fig. 8). As the membrane gets thicker, the permeate ﬂux gets lower. The variation of permeate ﬂux at different feed temperatures was reported to be more pronounced at thinner thickness, i.e., < 400 μm, which was in agreement with other MD studies using different membranes [43,70]. Overall, the results showed better
DCMD performance reaching a permeate flux of $15.2 \times 10^{-3}$ kg/m$^2$ s (feed temperature=80 °C, permeate temperature=20 °C) and NaCl rejection factor $> 99.39\%$ compared to other studies using flat-sheet membranes [137] and electrospun PVDF nanofibers [138]. Furthermore, no wetting was observed in the PVDF electrospun nanofibrous membrane after 25 h DCMD operation.

From the many theoretical studies of MD which are mostly based on flat-sheet membranes and hollow fiber membranes, most ignore the pore interconnectivity on its effect to vapor flux. With the emergence of nanotechnology specifically the use of nanofibers as membranes for MD, Essalhi and Khayet [62] for the first time developed a theoretical model considering the gas transport mechanism using electrospun PVDF nanofibers as self-supporting membrane for DCMD under different feed temperatures and feed salt concentrations. In their model, they considered the structural characteristics of the nanofibrous membrane, the nature of mass transport across the membrane and the heat transfer mechanisms. The predicted permeate fluxes were compared to the experimental results. The nanofibrous membranes were fabricated and characterized according to their previous study [86] using 25 wt% PVDF in acetone/DMAC solvent system. Several nanofibrous membranes were fabricated at different electrospinning times producing different thicknesses of membranes. The DCMD test was carried out at different feed temperatures (40–80 °C) and feed salt concentrations (12–60 g/L).

The results indicated good agreement between the theoretical and experimental values over a wide range of feed temperatures and feed concentrations. The results showed that increasing the ratio between the mean fiber diameter and the inter-fiber spaces

Fig. 9. Schematic representation of the heat-press treatment of the PVDF nanofibers.

Fig. 10. Top (A1–D1) and cross-sectional (A2–D2) SEM images of the fabricated dope-9 PVDF membranes at low sprayer speed and low molecular weight, and their corresponding contact angle measurements (A3–D3): (A) before heat pressing; after heat-pressing at (B) 160 °C, (C) 170 °C, and (D) 180 °C. Adapted from [139].
also increased the Knudsen contribution. The Knudsen diffusion was 17.9–37.4 times higher than the molecular diffusion. It was found that temperature polarization has more dominant effect compared to vapor pressure polarization and concentration polarization. Increasing the thickness of the nanofibrous membrane showed an increase in temperature and vapor pressure polarization coefficients, but a decrease in concentration polarization coefficient. The highest temperature polarization coefficient was 90%, which was obtained for the nanofibrous membrane that was spun for 4 h, i.e., possessing the thickest thickness.

The thermal efficiency was found to be more than 78.8% and showed increasing efficiency at higher feed temperatures. The temperature polarization coefficient and thermal efficiency reported in this study are higher than those reported in literature. The model presented can be applied for nanofibrous membranes using different polymers and electrospinning conditions to predict the permeate flux of DCMD.

4.3. Effect of post heat-treatment of nanofibrous membrane on DCMD

Liao et al. [139] fabricated a PVDF membrane by electrospinning and tested its performance in a DCMD set-up. Several electrospinning parameters were varied to optimize the membrane pore sizes such as polymer solution composition, chamber humidity and moving speed of the spinning needle. The effect of heat-press treatment of the PVDF nanofibrous membranes on its DCMD performance was also investigated. The PVDF solutions (5–15 wt%) made from low and high molecular weight PVDF were prepared using either DMAC or DMF/acetone as solvents, and with or without adding 0.004 wt% LiCl inorganic additive. The electrospinning parameters used include 25 kV or 28 kV applied voltage, TCD=12 cm or 15 cm, and chamber humidity of 50% and 70%. The solution feed rate was not given. The as-spun fibers were then dried overnight in a vacuum chamber at 60°C to ensure the evaporation of residual solvents. The dried PVDF membrane was subjected to heat-press treatment by pressing the membrane between two flat glass panes placed in a dry oven at 170°C for 1 h as schematically presented in Fig. 9.

Fig. 10 shows SEM images and contact angle measurements of the fabricated membranes before and after hot-pressing. The resulting as-spun PVDF nanofibers showed rough, hydrophobic surfaces with contact angle of 136–142°. The heat pressing of nanofibers made the membrane thinner and a slight decrease in hydrophobicity, from 141° to 138°. By heat pressing from 160–180°C, it was observed that the optimum hot press temperature was 170°C, higher than this would severely melt the nanofiber. The heat pressing also decreased the pore size and porosity from 71.4% to 53.7% of the electrospun nanofiber membrane due to compaction, but at the same time, increased its LEP from 24 to 35 kPa. Furthermore, the permeation flux increased after heat press treatment.

Fig. 11 shows the effect of heat-press treatment on the permeate flux over a 15-h period. The as-spun membrane showed a permeation flux of 17 kg/m² h but decreased to 11 kg/m² h after only 1 h of operation. The heat-pressed membrane obtained increased permeate flux of 21 kg/m² h, which is competitive with other commercial PVDF membrane having flux at 15 kg/m² h [52].

![Fig. 11. Effect of heat-press post-treatment on permeation flux and long term performance of PVDF membranes for DCMD application (feed temperature=323 K, permeate temperature=293 K, feed flow rate=0.6 L/min, permeate flow rate=0.6 L/min). Adapted from [139].](image-url)

![Fig. 12. Schematic representation and photographic images of water droplet entrapment in a nanofibrous membrane. Adapted from [139].](image-url)
The heat-pressed membrane also showed stable MD performance for a 15-h period. It is important to note that as-spun PVDF membrane, i.e., before treatment had higher porosity than heat-pressed PVDF membrane, however, the latter still showed better permeation flux. To help explain the result, the nanofibrous membrane structure was analyzed after DCMD test. Fig. 12 shows a schematic representation of the possible reason of decreased permeability of as-spun membrane. One could think of electrospun nanofibrous membrane as a series of overlapping layers of nanofibers, having gaps in between (Fig. 12A). For the as-spun membrane, the nanofiber layers are loosely overlapping thus giving a chance for feed water to enter and stay in between gaps during the MD process (Fig. 12B). The presence of stagnant drops in the inside layers of the as-spun membrane could lower the temperature difference between the feed and permeate sides, thus affecting the permeability. On the other hand, the heat-pressed
membranes were held compact to each other, so that even though the porosity and contact angle were decreased due to heat-pressing, it avoided the stagnation of drops in between the nanofiber layers (Fig. 12C). The photos of MD membranes after test in Fig. 12 confirmed the presence of water in as-spun PVDF membrane. Here, heat-press treatment is a necessary step to improve the membrane integrity, water permeation flux, and non-wetting property of the membrane. The heat-pressed PVDF nanofibrous membrane showed a permeation flux of 20.6 kg/m² h, which was 2–4 times higher than those obtained from commercial PVDF membranes and PVDF-clay nanofibrous membrane [138] reported in the literature for DCMD application.

In a separate study, Lalia et al. [140] investigated the DCMD performance of a polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) nanofibrous membrane fabricated by electrospinning. It is reported that co-polymers of PVDF have higher hydrophobicity and free volume than PVDF [141,142]. The study determined the effect of fiber diameter on the pore size distribution of the membrane. It was reported in literature that decreasing the fiber diameter leads to decreased pore size of the membrane [143]. Different concentrations (10–15 wt%) of PVDF-HFP in acetone/DMAc solvent system were used. Hot press treatment was employed to the nanofiber membrane prior to DCMD process to improve its structural integrity and mechanical properties. They compared their synthesized membrane to a commercial PVDF membrane. Fig. 13 shows the SEM images of the as-spun and hot-pressed membranes. The 15 wt% PVDF-HFP concentration showed fiber diameters ranging from 200 nm to 1.3 μm, while reducing the concentration to 10 wt% showed decreased nanofiber diameter in the range 100–500 nm. Decreasing the concentration (i.e., decreasing the viscosity) led to some bead formation in the nanofiber mat. The PSD was found to be narrower at lower PVDF-HFP concentration. Simple hot-pressing of the membranes further narrowed the PSD for each PVDF-HFP concentration. The as-spun PVDF-HFP nanofiber membranes showed a thickness ranging from 135 to 150 μm, and after hot-pressing became 65–112 μm in thickness. When two layers of PVDF-HFP were hot-pressed together, it resulted in more thickness and narrower PSD, and smaller mean pore size. When compared with a commercial PVDF membrane, the PSD of 10 wt% PVDF-HFP was similar with a slightly bigger mean pore size. Here, the hot-pressing of electrospun nanofiber membrane has resulted in effective reduction of the mean pore size as well as narrowing of the PSD, which could translate to increased resistance to pore wetting. The porosity of as-spun PVDF-HFP membrane was observed to be 90%, but was reduced to 60–70% after hot-pressing. Moreover, when two as-spun PVDF-HFP membranes were hot-pressed together, the porosity further reduced to 55–60%. This is due to thickness reduction, which ultimately decreases the pore volume after hot pressing. The prepared PVDF-HFP nanofiber membranes showed contact angle > 132° but was found to decrease by about 10% after hot-pressing treatment. This is due to the fact that smoother surface was obtained after hot-pressing compared to rougher and more sponge-like structure in the as-spun condition.

The mechanical properties of the fabricated and treated membranes were investigated. Generally, electrospun nanofibers are non-woven and randomly oriented in structure, and there is no interconnection at the nodes [144]. Hot-pressing of nanofiber membrane layers above the glass transition temperature of the polymer and below the melting could help fuse the nodes and improve the mechanical and structural integrity of the nanofiber membrane [145,146]. The burst pressure test to check the mechanical integrity of the membranes (see Fig. 14) showed increased burst pressure at increasing polymer concentration. This is attributed to the increased fiber diameter at higher polymer concentration. Hot-pressing the PDVF-HFP membrane resulted in interlocking of nanofibers and fusing together the fiber nodes, thus it resulted in better mechanical properties compared to as-spun PVDF-HFP nanofibers. The highest burst pressure was obtained for 2 layers of hot-pressed PVDF-HFP nanofibrous membranes.

For DCMD test, 10 wt% and 15 wt% PVDF-HFP hot-pressed 2-layers were used and compared to a commercial PVDF membrane with 0.2 μm pore size. The 2 layers hot pressed membranes were chosen based on their high mechanical properties. The maximum permeate flux for 10 wt% and 15 wt% PVDF-HFP were 20–22 kg/m² h and 8–9 kg/m² h, respectively. A 60% higher permeate flux at temperature difference greater than 15 ºC for 10 wt% PVDF-HFP when compared to that of commercial PVDF membrane (see Fig. 15) was observed. There was 48% higher mass transfer coefficient value of 2 layer-hot pressed membrane compared to that of commercial membrane. The hot-pressing and double-layering of PVDF-HFP nanofiber membranes could improve the characteristics of the membrane in attaining the features of a near-ideal MD membrane, which consequently results in improved DCMD performance.

A similar study using PVDF-HFP was also conducted by Su et al. [147] where they fabricated PVDF-co-HFP nanofiber membrane for water desalination by DCMD. The PVDF–HFP nanofiber showed slightly better hydrophobic property (128°) compared to PVDF nanofiber (125°). Using PVDF-HFP, a salt rejection of 99.9901% and a permeate flux of 4.28 kg/m² h were obtained.

Table 5

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
<th>Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young equation [84]</td>
<td>( \cos \theta_o = \left( \gamma_{sa} - \gamma_{sl} \right) / \gamma_{sl} )</td>
<td>Flat</td>
</tr>
<tr>
<td>Wenzel equation [150]</td>
<td>( \cos \theta_o = R \cos \theta_l )</td>
<td>Rough surface with homogeneous interface</td>
</tr>
<tr>
<td>Cassie–Baxter equation [151]</td>
<td>( \cos \theta_o = f_s \left( R \cos \theta + 1 \right) - 1 )</td>
<td>Composite interface (solid–liquid fraction and liquid–air fraction)</td>
</tr>
</tbody>
</table>

\( \theta_o \) = Static contact angle; \( \gamma_{sa} \) = surface energy of solid against air; \( \gamma_{sl} \) = surface energy of solid against liquid; \( \theta_l \) = contact angle on a rough solid surface; \( R \) = surface factor (non-dimensional); \( f_s \) = fraction of water droplet in direct contact with the surface.
4.4. Recent evolution of nanofibrous membranes

4.4.1. Effect of nanofiber surface modification

Pore wetting is a major limitation of an MD membrane. Basically, there are two ways to overcome the wetting problem: (a) increasing membrane hydrophobocity, or by decreasing pore size diameter [81]. However, reduced pore size would likely result in decreased permeability. Improving the hydrophobicity of the surface would have better effect on the anti-wetting behavior. Contact angle (CA) is a quantitative measure of the wettability of a surface. Three interfacial forces, namely, liquid–vapor surface tension, solid–vapor interfacial tension, and solid–liquid interfacial tension are in thermodynamic balance when a droplet of water is placed on a solid surface [148,149]. These forces determine whether the droplet becomes a thin film or forms into a cylindrical shape. Table 5 shows the different equations used to obtain the CAs of different surfaces. Generally, electrospun nanofibers show higher hydrophobicity than phase inversion or dense films even with the same experimental and material conditions. The main difference is the increased surface roughness of the nanofibers forming hills and valleys. However, neat polymer nanofibers usually do not possess superhydrophobic property. Particularly, the micro- and nanostructure of neat polymer nanofiber surfaces have high adhesive force to water, the so-called petal effect. For the purpose of MD application, the roll-off angle of water on the membrane surface should be as low as possible, and attain a superhydrophobic behavior, or the so-called lotus effect. The lotus effect promotes anti-fouling behavior of the surface, and increases the resistance to pore wetting. Surface modification is one of the ways to improve the roughness and modify the chemistry of the surface to obtain a superhydrophobic material.

In a study by Liao et al. [152], superhydrophobic PVDF nanofibers were fabricated for DCMD application. The hydrophobic behavior of the PVDF nanofibers was improved by employing surface modification techniques, which include dopamine surface modification, Ag nanoparticle deposition, and hydrophobic

Table 6: Characteristic properties of the fabricated and modified nanofibrous membranes and a commercial PVDF membrane.

<table>
<thead>
<tr>
<th>Sample code/characteristics</th>
<th>PVDF</th>
<th>I-PVDF</th>
<th>S-PVDF</th>
<th>Commercial PVDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle (deg)</td>
<td>138 ± 1</td>
<td>153 ± 1</td>
<td>158 ± 1</td>
<td>135 ± 1</td>
</tr>
<tr>
<td>Mean pore size (µm)</td>
<td>0.31 ± 0.02</td>
<td>0.34 ± 0.01</td>
<td>0.18 ± 0.01</td>
<td>0.28 ± 0.01</td>
</tr>
<tr>
<td>Max. pore size (µm)</td>
<td>0.59 ± 0.01</td>
<td>0.55 ± 0.01</td>
<td>0.41 ± 0.03</td>
<td>0.46 ± 0.01</td>
</tr>
<tr>
<td>Thickness (µm)</td>
<td>48.5</td>
<td>47 ± 4</td>
<td>52 ± 1</td>
<td>111 ± 1</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>79 ± 2</td>
<td>77 ± 1</td>
<td>68 ± 8</td>
<td>62 ± 1</td>
</tr>
<tr>
<td>LEF (bar)</td>
<td>0.41 ± 0.07</td>
<td>1.46 ± 0.12</td>
<td>0.86 ± 0.22</td>
<td>1.19 ± 0.48</td>
</tr>
<tr>
<td>Tensile modulus (MPa)</td>
<td>6.9 ± 3.0</td>
<td>17.0 ± 1.3</td>
<td>10.8 ± 2.5</td>
<td>10.2 ± 2.6</td>
</tr>
<tr>
<td>Tensile at break (MPa)</td>
<td>11.3 ± 2.8</td>
<td>10.6 ± 3.2</td>
<td>8.9 ± 1.5</td>
<td>4.7 ± 1.8</td>
</tr>
<tr>
<td>Strain at break (%)</td>
<td>47 ± 17</td>
<td>41 ± 11</td>
<td>34 ± 11</td>
<td>19 ± 11</td>
</tr>
</tbody>
</table>

Fig. 17. Low and high magnification FESEM images of pristine PVDF (a1, a2), I-PVDF (b1, b2) and S-PVDF (c1, c2). Adapted from [152].

Fig. 18. Permeate flux versus time graph of the DCMD test using the different fabricated and modified nanofibers and compared with a commercial PVDF membrane. Adapted from [152].
treatment. Electrospinning of PVDF solution and hot pressing post-treatment were carried out based on a previous study [139]. The fabricated nanofibers were divided into two: integrally modified (I-PVDF) and surface-modified (S-PVDF) nanofibers. Fig. 16 shows a schematic layout of the modification process of the PVDF membranes. The main difference between the two is the pre-wetting process, wherein I-PVDF was pre-wetted with IPA/water solution, while no wetting was done to S-PVDF. The subsequent steps for both I-PVDF and S-PVDF include dipping the nanofibers in dopamine solution (2 mg dopamine/mL of 10 mM tris, pH = 8.5) for 1 h. Then it was subsequently washed with deionized water. Ag was loaded to the dopamine-coated PVDF nanofibers in an electroless silver-plating bath containing 1 wt% AgNO3, 1 wt% D-glucose and 0.02 wt% ethanol. Subsequent washing and rinsing with deionized water followed. After which, the nanofibers were immersed in an ethanol solution (10 mM 1-dodecanethiol) to improve the hydrophobicity of the surface. It was followed with rinsing with absolute ethanol and then dried at 100 °C for 1 h.

The fabricated membranes resulted in changes in surface properties and geometrical structure as shown in Fig. 17. The I-PVDF and S-PVDF showed rougher surfaces compared to pristine PVDF nanofibers due to the presence of Ag NPs. The pristine PVDF nanofiber membrane had a contact angle of 138°, which is way higher than that of PVDF flat membrane, usually having a contact angle of about 90° [52]. However, both I-PVDF and S-PVDF showed much higher contact angles, reaching superhydrophobic state of 153° and 158°, respectively. The surface modification has turned the pristine PVDF (Fig. 17a1–a3) from having a ‘petal effect’ (i.e., water droplet tends to adhere more to the surface even at sliding angles [153], to a ‘lotus effect’ (i.e., fast sliding of water droplet on the surface) [154] (Fig. 17b and c). The improved hydrophobicity and rougher surface are attributed to the presence of hierarchical structures of Ag NPs and hydrophobic monolayers. Further checking of the nanofibers showed that Ag NPs were observed in the inner layers of the I-PVDF nanofibers (Fig. 17b3–b4), indicating fully treated nanofibers, while only the top surface was modified in S-PVDF (Fig. 17c3–c4) because no Ag NPs were observed in the inner layers. The porosity of I-PVDF (77%) was observed to be similar with pristine PVDF (79%), but S-PVDF was lower at 68% yet still higher than that of commercial PVDF (62%).

The surface modification also resulted in improved mechanical properties compared to neat PVDF and commercial PVDF (see Table 6). The neat PVDF nanofiber showed a tensile modulus of 6.9 MPa, while I-PVDF and S-PVDF had 17 MPa and 10.8 MPa, respectively. This is about 1.5–2.5 times increase from the neat PVDF. Furthermore, the modified PVDF nanofibers showed higher tensile modulus than the commercial PVDF (~10.2 MPa). The overall surface property enhancement and improvement in mechanical properties make the I-PVDF and S-PVDF suitable for MD application. Using 3.5 wt% NaCl as feed solution, the DCMD performance of the surface-treated nanofibrous membrane was compared with commercial PVDF membranes. Fig. 18 shows the flux versus time graph of the MD test. The I-PVDF membrane obtained a water permeate flux of 31.6 kg/m² h at feed and permeate temperatures of 60 °C and 20 °C, respectively. This was a little lower flux compared to that of pristine PVDF, but the pristine PVDF started to be wetted in less than 1 h, while I-PVDF showed still stable flux even after 8 h. The S-PVDF did not fare well at a flux of 5.4 kg/m² h compared to I-PVDF, which could be due to the dense layer formed on the top surface of S-PVDF, leading to high mass transfer resistance. The high flux of I-PVDF is mainly

<table>
<thead>
<tr>
<th>Sample (wt% clay in PVDF)</th>
<th>Fiber diameter (nm)</th>
<th>Pore size (µm)</th>
<th>Porosity (%)</th>
<th>LEP (kPa)</th>
<th>Contact angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt% (S1)</td>
<td>417 ± 120</td>
<td>0.58 ± 0.23</td>
<td>82 ± 3</td>
<td>90 ± 2</td>
<td>128 ± 1.5</td>
</tr>
<tr>
<td>2 wt% (S2)</td>
<td>500 ± 150</td>
<td>0.6 ± 0.17</td>
<td>82 ± 3</td>
<td>130 ± 3</td>
<td>134.4 ± 2.1</td>
</tr>
<tr>
<td>4 wt% (S3)</td>
<td>550 ± 128</td>
<td>0.63 ± 0.15</td>
<td>81.5 ± 3</td>
<td>170 ± 5</td>
<td>142.4 ± 1.9</td>
</tr>
<tr>
<td>8 wt% (S4)</td>
<td>625 ± 136</td>
<td>0.64 ± 0.22</td>
<td>81 ± 3</td>
<td>200 ± 6</td>
<td>154.2 ± 3.0</td>
</tr>
</tbody>
</table>

Fig. 19. (A) DCMD permeate flux and (B) salt rejection rate of the prepared neat and composite nanofibrous membranes. Adapted from [138].

Fig. 20. DCMD flux rate (a) and salt rejection (b) of the fabricated membranes with respect to time. Adapted from [138].

Table 7
Physical and morphological characteristics of the fabricated pristine and composite nanofibrous membranes. Adapted from [138].
attributed to the surface modification producing hierarchical structures and superhydrophobic surface, thus enhancing its anti-wetting property, while maintaining high porosity structure (similar to the pristine PVDF). When compared to other studies, L-PVDF was found to be more superior than those obtained with commercial PVDF membranes [155,156] and reported PVDF-clay nanofiber membrane [138] used for DCMD operation with water permeate fluxes ranging from 5.7 to 10.6 kg/m² h. Though other parameters are similar for the fabricated membranes and the compared commercial PVDF membrane, one important difference is the thickness, wherein the commercial PVDF membrane has double the thickness of the fabricated and modified nanofibrous membrane. This could be the main difference in terms of permeation flux efficiency. Here, if stable permeate fluxes could be maintained for long periods of operation, the integrally modified PVDF could be a potential alternative for DCMD application.

4.4.2. Effect of the incorporation of nanoparticle in/on nanofibers

In recent years, electrospun nanofibers, which possess a very high surface area, have been studied with increasing interest as a substrate for nanoparticles [119]. The addition of nanoparticles to impart functionalities in composite materials has been documented extensively [157–162]. For example, Zhang et al. [163] fabricated a superhydrophobic PVDF flat-sheet membrane by spraying a mixture of polydimethylsiloxane and hydrophobic SiO₂ NPs on the PVDF surface. Razmjou et al. [42] prepared a superhydrophobic PVDF membrane with CA of 163° by deposition of TiO₂ NPs via a low temperature hydrothermal treatment. It is known that if nanoparticles are properly and uniformly loaded in a substrate such as nanofiber, it could dramatically improve the overall properties and performance of the composite material. The incorporation of nanoparticles could affect the mechanical, thermal, and surface properties of the material, including increasing or decreasing the wettability of the surface. As a way of improving the hydrophobic behavior of PVDF nanofiber for MD application, Prince et al. [138] loaded Cloisite clay nanofibers in/on electrospun PVDF nanofibers. Different contents of clay (0, 2, 4, and 8 wt %) were blended with 12 wt% PVDF dissolved in DMAc/acetone solvent. Electrospinning was carried out at 16 kV voltage, a 1 mL/h feed rate, and 10 mL of total electrospun volume. The TCD was not mentioned.

The electrospun nanofiber membrane had a thickness of 300 µm. The morphological characterization showed increasing fiber diameter with the increase in clay content from 417 to 625 nm, which is attributed to the increased viscosity of the spinning solution at higher clay content as also observed by other studies (see Table 7) [164–166]. Furthermore, the contact angle increased with the increase in clay content, reaching as much as 154.2° at the highest clay content of 8 wt%, compared to 128° of pristine PVDF nanofiber. The better hydrophobicity of clay/PVDF nanofiber resulted in better LEP from 90 to 200 kPa. The incorporation of clay in/on PVDF nanofiber was also observed to improve the thermal stability of the composite membrane.

Due to the improved properties of the composite membranes, they were applied to DCMD. Fig. 19 shows the permeate flux and rejection rate of the prepared composite nanofibrous membranes with respect to the temperature difference. The feed temperature was varied from 50 to 80 °C, while the permeate temperature was maintained at 17 °C. The temperature difference was in the range 35–65 °C. A 3.5 wt% NaCl aqueous solution was used for all tests. Higher permeate flux was obtained with the increase in temperature difference of the hot and cold sides (see Fig. 19A). The permeate flux also increased with the increase in clay content compared to neat PVDF. The highest permeate flux was obtained at ΔT=65 °C using 8 wt% clay/PVDF (~5.6 kg/m² h) compared to neat PVDF (~4.8 kg/m² h). This permeate flux is much lower compared to other studies using electrospun nanofibers [86,139,140,152], which could be due to the higher membrane thickness used (~300 µm) compared with 70–150 µm of other studies. The salt rejection increased from 98.27% to >99.5% with increasing clay content (Fig. 19B). After conducting an 8-h DCMD test, it was observed that from 0 to 2 wt% clay content, the permeate flux and salt rejection factor started to decline steadily from 3 h of operation (see Fig. 20). This decline is attributed to pore wetting in the inter-fiber space of the tested membranes. However, at 6 wt% clay/PVDF, only a slight decrease was observed, while the 8 wt% clay/PVDF showed very stable permeate flux and salt rejection factor over the 8-h test. This excellent performance is not only attributed to the much improved hydrophobicity (anti-wetting) of the PVDF nanofiber membrane containing higher amount of clay NPs, but also to their larger pore sizes (i.e., 0.64 µm at 8 wt% compared to 0.58 µm for 0 wt%; porosity of all nanofibers is similar ~81–82%).

4.4.3. New MD membrane material – hydrophobic polyazole nanofibrous membranes

One of the most important requirements for an MD membrane is its hydrophobicity. The materials used for MD application are dominated by polypropylene, polytetrafluoroethylene, modified polyethersulfone, polyetherimide, and PVDF [22]. PVDF has high mechanical and thermal integrity and good chemical resistance, thus it is the most commonly used material for MD fabrication in a laboratory set-up. Since PVDF is also easily dissolved in common solvents, it is so far the only polymer used in electrospinning for MD application. However, taking into account the requirements of an ideal MD membrane, synthesizing and fabricating new materials from novel polymers that possess the necessary MD membrane requirements is always a welcome progress. This was

Fig. 21. FESEM images of fluorinated (a), polyoxadiazole, (b) polytriazole, and (c) polyoxadiazole copolymer nanofibrous membranes prepared by electrospinning. Adapted from [167].
They synthesized a new class of material, namely, aromatic fluorinated polyoxadiazoles (F-POD), polyoxadiazole copolymer (Co-POD), and polytriazoles (F-PT) for desalination by MD. These materials were originally intended for other membrane separation processes, but because of their high thermal stability and high hydrophobicity, they present good potential in MD application and tested them in DCMD set-up. For the detailed synthesis of the new polymers, one is referred to their previous studies [168,169]. The synthesized polymers were fabricated into porous membranes by electrospinning and phase inversion. For electrospinning, 18 wt% of each polymer was dissolved in DMF solvent. The polymer solutions were then electrospun at a voltage of 30 kV, a feed rate of 0.3 mL/h and a TCD of 20 cm. For polyoxadiazole copolymer, the solution needs to be heated at 70°C before electrospinning. The spun fibers were collected on an aluminum foil or on a non-woven polyester support. DCMD test was carried out using Red Sea water as feed and the effective membrane area used was 0.0025 m².

Fig. 21 shows the FESEM images of the electrospun nanofibrous membranes. All membranes showed bead-free nanofibers. F-POD showed fiber diameters of 160–300 nm (Fig. 21a), 100 nm for F-PT (Fig. 21b), and 70–420 nm for Co-POD (Fig. 21c) with a mean diameter of 140 nm. The pore sizes of the electrospun membranes were bigger compared to those made by phase inversion. The mean pore sizes of the membranes showed the following trend: Co-POD (1.3 μm) < F-POD (1.7 μm) < F-PT (2.7 μm). The Co-POD showed the narrowest pore size distribution from among all the nanofibrous membrane samples, followed by F-POD and F-PT. The phase inversion membranes also showed very narrow PSD.

LEP is the minimum hydrostatic pressure when pore wetting begins. It is affected by both pore size and hydrophobicity. As far as membrane selectivity is concerned, LEP is the most important parameter for MD process. Higher LEP results in better MD performance. Generally, at bigger pore sizes, LEP is lower. The LEP results showed Co-POD obtaining the lowest LEP of 0.62 bar, followed by F-PT at 0.76 bar and F-POD at 0.90 bar.

Fig. 22 shows the contact angle measurements of the fabricated membranes including dense films, phase-inversion membrane and electrospun nanofibrous membrane of the synthesized polymers and also PVDF. Contact angle varies according to the surface energy and the solid surface roughness [170]. It could be seen that comparing all the dense samples, F-POD has the highest contact angle. However, when compared together with phase-inversion and electrospun membranes, the most hydrophobic sample was the F-PT electrospun nanofibrous membrane with a contact angle of 162°. In general, the electrospun nanofibers from synthesized polymers showed consistently higher hydrophobicity compared to other samples. Even though the materials are the same, the nanofibers provided rougher surface compared to phase inversion and dense films, thus enhancing the hydrophobicity of the surface. The increase in surface roughness results in less contact area for solid and water, due to the presence of more air bubbles trapped at the interface, which leads to increased water contact angles [170,171].

DCMD test was carried out using the fabricated membranes by phase inversion and electrospinning. Real seawater was used and the feed temperature was varied from 40 to 80°C. Fig. 23 shows the effect of feed temperature on the flux rate of the prepared membranes. It could be observed that generally, the permeate flux increases with the increase in feed water temperature for all membranes. For all tests, regardless of the material, the electrospun nanofibrous membranes showed the highest permeate flux. The permeate flux for electrospun F-POD ranged from 15 to 78 kg/m² h and for electrospun F-PT from 14 to 85 kg/m² h. The electrospun F-PT membrane showed the highest permeate flux so far (at 85 kg/m² h) in literature using electrospun nanofibers. The salt rejection was more than 99.95% for all cases. However, in this study, the thickness of the membranes was not given for proper comparison with other membranes.

Fig. 22. Contact angle of dense polymer films and porous membranes prepared by phase inversion and electrospinning from PVDF, polyoxadiazole copolymer, fluorinated polyoxadiazole and fluorinated polytriazole. Adapted from [167].

Fig. 23. DCMD flux performance of (a) F-POD and (b) F-PT membranes made by phase inversion and electrospinning. The permeate temperature was 22°C. Adapted from [167].
In another study, electrospun nano-fibrous Matrimid membranes were fabricated for DCMD application [172]. Matrimid (18 wt%) was dissolved in N-methyl pyrrolidone (NMP) and electrospun to an applied voltage of 30 kV, feed rate of 15 mL/min and a TCD of 17 cm. This sample was electrospun directly onto a collector plate. Another sample was prepared by directly electrospinning onto a polyester support (termed here as composite sample). A porous Matrimid film by phase inversion was also prepared. The prepared samples were subjected to DCMD tests using feed temperature ranging from 40°C to 80°C. The resulting fibers showed an average diameter of 290 nm and a pore size of 2.15 μm. This pore size is much bigger compared to other MD tests using nano-fibrous membranes [138,140]. No porosity measurement was given. Matrimid nano-fibers showed narrower PSD compared to the phase inversion Matrimid film, however, the nano-fibrous membranes had significantly larger pore sizes. The Matrimid nano-fibers showed a contact angle of 130°, which was much higher than that of the Matrimid phase inversion membrane (i.e., 85°). The DCMD tests showed higher permeate fluxes for the nanofiber membrane compared to the phase-inversion membrane. The nanofibrous sample with polyester support also showed comparable fluxes with the nanofiber-only membrane. The high flux and high salt rejection (99.99%) of the nanofibrous membrane is attributed to its highly porous structure, high hydrophobicity, and narrow pore size distribution with high interconnectivity.

In a recent study [173], a new triple-layer hydrophilic–hydrophobic MD membrane for desalination by AGMD was fabricated via immersion precipitation method and electrospinning. The triple layer membrane consists of a top selective layer of electrospun PVDF nanofibers, a middle layer that is made of cast PVDF by immersion precipitation method, and a bottom hydrophilic PET support layer. PVDF (17 wt%) and polyvinylpyrrolidone (PVP) were dissolved in DMAc/ethanol solvent system by magnetic stirring. The PVDF solution was then cast onto a PET support layer with a casting knife, and then coagulated in a water bath at 25°C. After several refreshing of new fresh water in the bath, the casted film was immersed into 50% ethanol and 50% n-hexane bath, and then dried in ambient air. Electrospinning of 17 wt% PVDF in DMAc/ethanol solvent was carried out separately at 16 kV, a TCD of 15 cm and a feed rate of 2 mL/h. A volume of 10 mL was electrospun resulting in a thickness of 20 μm. After drying, the electrospun membrane was heat pressed onto the casted dual film at 160°C and at an applied pressure of 100 kPa. This forms a triple-layer membrane. The fabricated samples were then subjected to different characterization techniques and AGMD test. An effective membrane area of 0.015 m² and an air gap of 3 mm were used. Feed solutions of 3.5 wt% NaCl were used at a feed flow rate of 1.8 L/min. The feed and cooling temperatures were varied from 30 to 80°C and 15 to 20°C, respectively.
Fig. 26 shows the SEM images of the triple-layer membrane and their respective contact angles. It can be seen that after heat pressing, the three layers were compounded into one membrane with three distinct layers (Fig. 24b). The top layer (Layer 3) is made of nanofibrous layer with a thickness of 25 μm. The middle layer (Layer 2) was cast PVDF (thickness = 100 μm) and the support layer (Layer 1) was made of PET (thickness = 50 μm). One can clearly see the differences in pore size and morphologies (Fig. 24a) of the different layers. Even though both Layers 2 (cast film) and 3 (nanofibers) were made from similar solution, the different fabrication methods resulted in different morphological and surface characteristics. The nanofibers showed highly porous structure made from intersecting ultrafine fibers (mean pore size = 0.54 μm), while the cast film depicted the usual film-like structure with small pores (mean pore size = 0.12 μm). No pore size distribution measurements were reported. Contact angle measurements showed very high CA of 145° for nanofiber layer, 92° for cast film, and 30° for PET layer. Thus, the triple-layer membrane had decreasing CAs through its depth. The high hydrophobicity of the nanofibers can be attributed to its rougher structure compared to smoother cast film, as CA is dependent on surface roughness and surface energy.

The triple-layer membrane was compared to dual-layer (i.e., only the cast PVDF film on PET without nanofibers) and nanofiber-only membrane. The LEP of nanofiber-only membrane was found to be low at 40 kPa. This could be attributed to the wider pore sizes and the very thin thickness of 50 μm. The low LEP suggests possible pore wetting over time so that the operation will be limited to low feed and permeate flow rates. The triple-layer membrane obtained the highest LEP of 350 kPa from all membrane samples, which was 60% higher than the LEP of dual-layer (220 kPa). This high LEP could be attributed to the higher thicknessness of the triple-layer membrane as well as its high hydrophobicity, which prevents the water from wetting the pores.

Membrane distillation tests were carried out using an AGMD set-up. Using 3.5 wt% NaCl as feed, it was found that the nanofiber-only membrane at very low thickness was not suitable for AGMD because of its fast decline in salt rejection within the first hour of operation. Thus, focus was on the comparison of dual- and triple-layer membranes. The triple-layer membrane showed consistently higher permeate flux at increasing feed water temperature compared to the dual-layer membrane (Fig. 25a). This is interesting because the triple-layer membrane, which has higher thickness, is supposed to have higher mass transfer resistance that could lead to lower flux. However, the results showed otherwise. This could be explained by the fact that the presence of top selective nanofiber layer has increased significantly the hydrophobicity of the whole membrane, thus giving more resistance to pore wetting, and increasing the vapor transport across the membrane. Additionally, the nanofiber thickness, which is 25 μm did not present so much difference in terms of its effect on mass transfer resistance as the nanofibers are also highly porous and have interconnected pores. Higher salt rejection was observed for the triple-layer membrane, maintaining > 99.95% salt rejection regardless of the feed water temperature. Long-term tests (40 h) showed very stable flux performance and salt rejection (Fig. 25b) for the triple-layer membrane, while the dual-layer membrane showed decreasing salt rejection after 10 h, which suggests a pore wetting phenomenon. The triple-layer membrane configuration has promising results for AGMD mode. Its good flux and salt rejection performance are a result of the specific function that each layer serves. The nanofiber selective layer has high hydrophobicity that only allows water vapors to pass through, and due to its highly porous structure, it can lessen the heat loss across the membrane. The middle cast film layer increases the LEP of the membrane because of its smaller pore sizes, and the PET support layer helps draw water vapor by absorption due to its hydrophilic property.

### 4.5. Other applications

Jafaar and Sarbatly [174] discussed the feasibility of electrospun nanofibrous membrane for desalination of geothermal water. They used geothermal water from Sabah, Malaysia, which has an inside water temperature of 60 °C. This high temperature of geothermal water makes it suitable for MD without needing high amount of energy to evaporate the feed water, thus reducing the cost of water production. Even though nanofibers possess excellent properties such as high porosity, controllable thickness and interconnected open pore structure, they still suffer from low LEP values, leading to wetting of the pores especially in VMD set-up. It was suggested to use an AGMD or a DCMD set-up, and keep the higher hydrostatic pressure at the permeate side rather than at the feed side.

Feng [175] attempted to separate ethanol from water by VMD technique using a PVDF nanofibrous membrane. Ethanol at different temperatures (40–60 °C) and concentrations (20, 40, 60 and 80 wt%) was fed to the system and the effect on the permeate flux was investigated. The results showed that the flux increased with an increase in ethanol feed concentration and also with an increase in feed temperature. In another study by Feng et al. [176], electrospun PVDF nanofibrous membrane was used to remove volatile organic compound (VOC) from water using SMGD. Chloroform was used as a typical VOC. The presence of different concentrations of chloroform from 0 to 2000 mg/L did not affect
<table>
<thead>
<tr>
<th>Reference</th>
<th>Polymer</th>
<th>Solution</th>
<th>Electrospinning details</th>
<th>Membrane thickness (µm)</th>
<th>Mean pore size (µm)</th>
<th>Porosity (%)</th>
<th>Contact angle (°)</th>
<th>MD configuration</th>
<th>Feed solution property (wt %)</th>
<th>Permeate solution property (wt %)</th>
<th>Permeation flux (kg/m² h)</th>
<th>Salt rejection (%)</th>
<th>LEP (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feng et al. [55]</td>
<td>PVDF (Kynar761, Elf-Chem USA)</td>
<td>18 wt% PVDF in DMF</td>
<td>V: 18 kV; FR: 2 ml/h; TCD: 18 cm</td>
<td>150 (Fiber diameter = 500 nm)</td>
<td>0.15</td>
<td>–</td>
<td>–</td>
<td>AGMD (Ac = 2 mm)</td>
<td>1%, 3.5%, 6% NaCl</td>
<td>0.350</td>
<td>Temp = 15-60, 40-80</td>
<td>22</td>
<td>1.2</td>
</tr>
<tr>
<td>Francis et al. [172]</td>
<td>Matrimid 5218 (Hunstman)</td>
<td>18 wt% in NMP</td>
<td>V: 30 kV; FR: 15 µl/min; TCD: 17 cm; H: 50-60°C (dried 60°C for 12 h)</td>
<td>2.15 µm</td>
<td>0.05</td>
<td>130</td>
<td>–</td>
<td>DCMD</td>
<td>Seawater</td>
<td>1 L/min</td>
<td>10-56</td>
<td>99.99</td>
<td>–</td>
</tr>
<tr>
<td>Su et al. [147]</td>
<td>PVDF (Mw=275,000), PVDF-co-HFP (Mw=55,000)</td>
<td>23 wt% PVDF in 8/2 DMF/acetone; 17 wt% PVDF-co-HFP in 8/2 DMF/acetone</td>
<td>V: 30 kV; FR: 1 ml/h; TCD: 15 cm</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>DCMD</td>
<td>–</td>
<td>–</td>
<td>0.39</td>
<td>0.105-0.245</td>
<td>40</td>
</tr>
<tr>
<td>Prince et al. [138]</td>
<td>PVDF Kynar761 (ArkemaPte., Singapore)</td>
<td>– 12 wt% PVDF in DMAc/acetone (2:3 w/w); with 0, 2, 4, 8 wt% Cloisite 20A clay (Southern Clay Products Inc., TX, USA)</td>
<td>V: 16 kV; FR: 1 ml/h; vol: 10 ml</td>
<td>300 (25)</td>
<td>0.58</td>
<td>81-82</td>
<td>128-154.2</td>
<td>DCMD</td>
<td>3.5% NaCl</td>
<td>1.8</td>
<td>0.32</td>
<td>50-80</td>
<td>17</td>
</tr>
<tr>
<td>Lalia et al. [146]</td>
<td>PVDF-HFP (KynarPowerflex LBG, Mw=450,000 g/mol)</td>
<td>10, 12, 15 wt% in acetone/DMAC (7:3); drying at 50°C for 24 h in conventional oven</td>
<td>V: 20 kV; FR: 1 ml/h; TCD: 15 cm; N: 18 G (di = 838 µm); H: 60°C; temp: 25°C; hot-pressing at 200°C using household iron</td>
<td>110-150 (65-112 After hot press)</td>
<td>0.26-1.49</td>
<td>60-92</td>
<td>120-140</td>
<td>DCMD</td>
<td>10 g/L NaCl</td>
<td>0.32</td>
<td>30-50</td>
<td>24</td>
<td>0.32 m/s</td>
</tr>
<tr>
<td>Essalhi and Khayet [86]</td>
<td>PVDF (Sigma)</td>
<td>25 wt% in acetone/DMAC (2:8)</td>
<td>V: 24 kV; FR: 1.23 ml/h; TCD: 27.7 cm; H: 363°C; T: 23°C (1); drying in oven at 80°C for 30 min</td>
<td>144.4-1529.3 Fiber diameter: 1-1.3 µm</td>
<td>2.9-5.2</td>
<td>85-93</td>
<td>137.4-141.1</td>
<td>DCMD</td>
<td>0, 12, 30, 60 g/L NaCl</td>
<td>8.33 Hz (500 rpm)</td>
<td>40-80</td>
<td>20</td>
<td>8.33 Hz (500 rpm)</td>
</tr>
<tr>
<td>Liao et al. [139]</td>
<td>PVDF Kynar HSV 900 (high Mw); PVDF Kynar 761 (low Mw) (Arkema Inc., Singapore)</td>
<td>5-15 wt% dissolved in DMAc or DMF/acetone (6:4); with or without 0.004 wt% LiCl</td>
<td>V: 25 or 28 kV; FR: 1.23 ml/h; TCD: 12 or 15 cm; dried 60°C under vacuum overnight; hot press between two glasses and put in oven at 170°C for 1 h</td>
<td>71 µm (42 µm after heat press)</td>
<td>0.18-0.91</td>
<td>71.4</td>
<td>53.7 (53.7 after heat press)</td>
<td>136-142</td>
<td>DCMD</td>
<td>3.5 wt% NaCl</td>
<td>60</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>Liao et al. [152]</td>
<td>PVDF Kynar HSV 900 (Arkema Inc., Singapore)</td>
<td>5 wt% PVDF dissolved in DMAc/acetone (6:4); added 0.004 wt% LiCl</td>
<td>V: 28 kV; TCD: 12 cm; ST: 3 h; dried 60°C under vacuum overnight; hot press between two glasses and put in oven at 170°C for 1 h</td>
<td>48-52</td>
<td>0.18-0.34</td>
<td>68-79</td>
<td>138-158</td>
<td>DCMD</td>
<td>3.5 wt% NaCl</td>
<td>0.4</td>
<td>60</td>
<td>20</td>
<td>0.6</td>
</tr>
</tbody>
</table>
the hydrophobicity of the surface. SGMD test was carried out using nitrogen as sweep gas and the feed temperature was varied from 30 to 60 °C. The chloroform concentration was found to drastically decrease especially in the first hour of operation with a decrease of 80% from its initial value. This signifies the rapid removal of VOC from water, wherein the good performance is attributed to the hydrophobicity of the membrane, appropriate pore size, and the high surface area provided by the nanofibers.

The excellent properties of carbon nanotubes have also been utilized as membrane for desalination in the form of bucky paper membrane. Carbon nanotubes possess good hydrophobicity, excellent mechanical, thermal and electrical properties, and are known to exhibit fast fluid flow through their interior. A series of studies [177–179] were conducted using a self-supported CNT bucky paper for desalination by DCMD. Fig. 26 shows SEM images of the CNT bucky paper that look like nanofibers in their structure. They demonstrated the desalination feasibility of the CNT bucky paper, which possess high surface contact angle (113°), high porosity (90%) and low thermal conductivity. The rejection rate was 99% and the flux rate was 12 kg/m² h. The main limitation of its long-term use is the delamination problem and formation of micro-cracks. In a subsequent study [179], the durability of CNT bucky paper was improved by UV/ozone-treatment and modified with alkoxy-silane. Higher contact angle (140°) and LEP were obtained. Furthermore, by coating a thin layer of PTFE on the CNTs, the hydrophobicity of the bucky paper was improved up to 155°. High rejection rate (> 99%) was achieved with an improved lifespan and vapor permeability. Goh et al. [180] reviewed the prospects and hurdles of the use of CNT in desalination.

5. Membrane characteristics and MD performance comparison of nanofibrous membrane to other MD membrane structures

Table 8 presents a summary of studies conducted using nanofibers for MD. It is interesting to note that most of the studies using electrospinning for MD application only utilized PVDF as main polymer for electrospinning. One main reason is its ease of dissolution with common solvents, and easy electrospinnability. The performance of electrospun nanofibrous MD membrane has been promising so far. Still, a lot of studies are needed to be conducted to optimize the nanofibrous membranes for different operating parameters of the MD process. In comparison with flat-sheet and hollow fiber membranes, nanofibrous membrane can be fabricated at a lower thickness and higher porosity, without sacrificing much of the mechanical integrity. The thickness of flat-sheet membranes tested in laboratory setting is usually from 25 to 184 µm, while the thickness for hollow fibers and electro-spin nanofibers is in the range 25–1550 µm and 48–1529.3 µm, respectively. Flat-sheet membranes reported in literature showed a maximum flux rate of 45 kg/m² h, while advances in material selection and fabrication technique for hollow fibers obtained a flux rate up to 100 kg/m² h [29]. The maximum flux rate of nanofibrous MD membrane was 85 kg/m² h so far, using a newly synthesized membrane material as reported by Maab et al. [167] (see Table 9). Aside from having high porosity, the nanofibrous membrane boasts of low tortuosity, due to the interconnected structure of the pores, thus higher permeate flux could be attained. One important aspect of nanofibrous membranes is the increased hydrophobicity primarily due to their rougher surface structure compared to conventional membranes. The nanofiber membranes are deposited with intersecting fibers, forming bumps on the surface. When a hydrophobic membrane such as PVDF is used, making rougher surfaces leads to increased hydrophobicity. Here, the distance between bumps on the surface are narrow enough, which increases the probability of air pocket formation.
between the bumps, thus increasing the hydrophobicity of the surface. This is in contrast with the conventional flat-sheet and hollow fiber membranes, wherein their surfaces are generally smoother than nano- or microfiber membrane; as such there is lesser air pocket formation and larger areas for adhesion of water to the flat surface. As presented in a recent study [173], the provision of a thin nano-fiber layer on top of a cast PVDF film has resulted in increased permeate flux with stable salt rejection compared to the cast PVDF layer only. This is mainly attributed to the increased hydrophobicity of the surface due to the nano-fibers. Other studies find ways to enhance the hydrophobicity of the membrane. Electrospun nanoporous PVDF membrane containing Cloisite 20A clay NPs showed superhydrophobic surface with a maximum contact angle of 154.2°. Superhydrophobic glass membranes fabricated by Ma et al. [181] showed better anti-fouling and flux performance compared with polymeric membranes. Superhydrophobic surface with contact angle of 166° was realized for a flat-sheet PVDF membrane containing fluorosilanized TiO2 NPs [42]. However, it did not translate well to its permeate flux performance in DCMD mode. This result suggests that having superhydrophobic property does not automatically lead to improved flux performance. One study using PVDF hollow fiber membranes with lower hydrophobicity but with uniform PSD obtained a stable DCMD performance for 30 days [182]. Other studies prepared hydrophobic membranes but still suffered wetting due to capillary condensation. Generally, nanoporous membranes have larger mean pore sizes than flat-sheet or hollow fiber membranes (Table 8). Even so, electrospun nano-fibers have higher contact angles because of the rougher surfaces compared to flat-sheet and hollow fibers, thus it is possible to use larger pore sizes without much issues on pore wetting [167]. However, long-term MD tests are still lacking for the nano-fiber membrane. The smaller pore sizes of phase inversion membranes compared to electrospun nanofibers make them suitable for much higher temperature-driven vapor difference, without suffering decrease in salt selectivity.

Pore size distribution of a membrane is an important parameter that is often neglected in experimental and modeling studies. Most studies assume a uniform pore size, which is not the case for all membranes. The PSD of MD membranes usually follow a log-normal distribution. Woods et al. [59] reported a geometric mean pore size of 0.22–0.45 μm with a PSD geometric standard deviation of 1.1–1.2 of four commercial membranes. Kim [183] indicated that a broader distribution of pore sizes should generate lower vapor flux compared to a mono-dispersed (narrow) distribution with the same pore size. For electrospun nanofibrous membranes, it was reported that the bubble point pore size and the mean pore size of the interfiber space decrease with the decrease in fiber diameter [184]. Consequently, the PSD also becomes narrower. Wang et al. [185] investigated the effect of thickness and fiber diameter on the pore size and PSD of electrospun PAN nanofibrous membrane. They found that smaller fiber diameter leads to smaller maximum and mean pore sizes and narrower PSD. Furthermore, as the thickness of the electrospun layer got thicker, smaller mean pore sizes and narrower PSD were observed. This is attributed to the continuous deposition of nanofibers on top of other nanofibers that effectively intersect and divide more pores, thus smaller pore sizes are formed. However, at a certain thickness, the changes in PSD and mean pore sizes reach a plateau.

The PSD of electrospun nanofibers were found to be slightly wider than the PSD of other conventional MD membranes. Additionally, the pore sizes of the nanofiber membrane are generally bigger than those of conventional MD membranes. However, some recent studies have shown comparable pore sizes and PSD between nanofibrous membranes and commercial membranes. Liao et al. [152] showed similar PSD of I-PVDF nanofiber membrane to a commercial PVDF flat-sheet membrane. In fact, the mean pore size of the I-PVDF membrane was even smaller than the commercial membrane. The narrow PSD along with low thickness and superhydrophobic property of I-PVDF led to much higher permeate flux performance of I-PVDF compared to a commercial PVDF membrane. Lalia et al. [140] also found comparable narrow PSD between hot-pressed 2 layered PVDF-HFP nanofibrous membrane compared to a commercial PVDF membrane. Even the pore sizes were similar for both membranes. The DCMD test showed better vapor flux and high LEP for the nanofibrous membrane. The study of Francis et al. [172] showed narrower PSD but with larger pore sizes for nanofibrous Matrimid membrane compared to the phase inversion membrane. Stable salt rejection of 99.99% was obtained for both nanofiber and phase inversion membranes despite the differences in pore sizes. The PSD of nanofibers can be controlled by manipulating the process and solution parameters for electrospinning as well as post-treatment conditions. Proper comparison of different membranes should take into account similarities in parameters and characteristics used such as the kind of MD configuration, the membrane material used, similar thickness of the membrane, porosity, PSD, etc.

### 6. Future perspectives and concluding remarks

The availability of novel and advanced materials and techniques opens up a lot of possibilities in the materials and water science and engineering areas that could find promising application in membrane-based applications. In particular, electrospinning technique for the production of ultrafine nanofibers, which possess excellent properties and could be tailored for different applications, presents many possibilities for the fabrication or modification of existing conventional materials, especially membranes. In MD studies, the recent years have seen a surge of research focusing on membrane design, aside from modeling and theoretical studies. As membrane structure is an important determinant of the performance of an MD membrane, thus finding the appropriate membrane structure and design and its fabrication are very important. Electrospinning is a simple yet versatile technique and has been used extensively in the biomedical and energy fields, and recently, in water treatment applications. The published works on the use of electrospinning to fabricate membranes for MD have so far been only limited to conventional single-nozzle electrospinning and mostly utilizing PVDF as polymer. As the use of nanofiber by electrospinning is still in its infancy for MD application, there is still a lot of room for improvement. Several routes are open for research to improve the performance of electrospun nanofibrous membrane for MD application.

It is known that PTFE has higher hydrophobicity than PVDF. Thus, so far, no studies have been conducted yet on the use of PTFE and PP as nanofibrous membrane for MD. This issue may be solved
by finding appropriate solvents for the said polymers or by utilizing different electrospinning configurations. For example, by using a coaxial electrospinning, a non-electrospinnable polymer can be electrospun as a sheath layer in a coaxial nanoﬁbre set-up, thus, PTFE and PP can then be electrospun with PVDF and increase the hydrophobicity of the MD membrane. Additionally, since PP is very difﬁcult to dissolve, PP can be electrospun using a melt electrospinning set-up, wherein no solvent is needed. In a recent study [186], PP was successfully electrospun in solution or melt form using a modiﬁed electrospinning set-up. The electrospun PP mat was found to have superhydrophobicity up to contact angle of 151°, which is much higher compared to commercial PP nonwoven web (CA = 104°) and compression molded PP ﬁlm (CA = 112°).

So far, only single-component nanoﬁbrous structure (i.e., only one polymer) is reported for MD membranes. As electrospinning is quite versatile, one can actually conﬁgure the system to fabricate a multi-component nanoﬁbrous membrane using multi-nozzle electrospinning set-up. Multi-nozzle electrospinning could be an excellent method to fabricate hybrid materials containing mixed properties of each component polymer. A dual-layer or even triple-layer composed of hydrophobic/hydrophilic layers could also be explored using nanoﬁbres. As observed by other studies, dual-layer could provide good permeate ﬂux in ﬂat-sheet membranes and hollow ﬁber membranes. The provision of high porosity and low tortuosity nanoﬁbrous membrane could possibly result in much better permeability, and this type of membrane is ought to be explored.

There are many nanoparticles that can enhance the hydrophobic behavior of electrospun nanoﬁbres such as carbon nanotubes. Incorporation or decoration of nanoparticle in/on the electrospun nanoﬁbrous support layer can enhance the mechanical strength and thermal stability of the membrane, and enhance its hydrophobicity. Several routes of surface modiﬁcation to improve the hydrophobicity of the membrane should be investigated. Almost all of the conducted studies recently using nanoﬁbres utilized a DCMD conﬁguration. Thus, there is a need to explore the use of nanoﬁbrous membrane to other MD conﬁgurations as well. And the energy cost and the effect of operating parameters need to be investigated more. Moreover, the fouling formation and mitigation of foulants in MD membranes should be extensively studied. Long-term tests should be conducted to see the effect on the stability of the nanoﬁbrous membranes.

MD has been studied for more than 40 years now, however, it is not yet fully used commercially. In recent years, the vast array of MD research is making MD more ready for commercial viability. Still further experimental and theoretical research is needed to improve its performance. Equal focus on both experimental and theoretical research on the effect of operating parameters and membrane design is a must. Based on this review, nanoﬁbrous membrane fabricated by electrospinning presents a promising alternative in the design of MD membrane. However, it still needs continued effort to optimize the membrane design in terms of the trade-off in thickness, permeation ﬂux, thermal efficiency, and mechanical integrity. The recent published results have shown promising direction for nanoﬁbrous membrane in water puriﬁcation and desalination.

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References


