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Membrane Distillation for Desalination and Current Advances in MD Membranes

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ABSTRACT

Desalination is a great technique to address the growing demand for water because it is essential for humans. Water treatment and desalination are two common uses for the membrane-based, non-isothermal MD (Membrane Distillation) process. It works at low pressure and temperature, and heat from waste and solar energy can meet the process's heat requirements. In MD, dissolved salts and nonvolatile contaminants are rejected as the vapors go through the membrane's pores and start condensing at the permeate side. However, because to the lack of a suitable and adaptable membrane, biofouling, wetting and water efficacy are the main problems for MD. Many researchers have recently worked on membrane composites and attempted to create effective, appealing, and unique membranes for membrane distillation. This review article talks about water shortages in the 21st century, the rise of desalination, the use of membrane distillation (MD), recent developments in membrane distillations, developments in pilot scale MD technologies, New developments in membrane fabrication and modification, the desired properties of membranes, and desalination membranes.

Keywords: Desalination, Membrane distillation, membrane, biofouling, water efficacy

1.0 INTRODUCTION

The 21st century faces global difficulties related to the water crisis and water scarcity [3] . A third of the world's population experienced moderate to severe water stress at the start of this century [4]; this number will climb to 50% by 2030 [5] or even two-thirds of all people on the planet. In 2025, it is predicted that, compared to early 2000s levels, the annual worldwide accessibility of clean water supplies will fall by 40% (from 6600 to 4800 m^3) [6]. More recently, an MIT research found that by 2050, up to 5 billion people might be exposed to water stress at least to a considerable extent [7]. The primary causes of increasing water scarcity in the near future include population expansion and rapid urbanization, as well as growing industrial development, conflicting requirements, contamination of conventional water sources, climate change, and rising costs of obtaining fresh water from traditional sources [8, 9].

The supply of freshwater has been significantly or even permanently reduced during the past few decades due to overuse or contamination of

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water sources [10]. This has caused the water levels in many basins, particularly those in dry and semi-arid areas, to drop quickly. Along with this, the so-called "hydraulic paradigm" has come under growing scrutiny [6]. This term applies to state-led, centralized schemes from the 20th century that made use of sophisticated engineering, such as water transfers and dams, to control rivers and increase the amount of water readily accessible to address the world's growing water requirements and harsh weather. Growing discontent Because to the ecological, social, and economic effects of large-scale water projects, there has been a gradual, albeit uneven, and by no means total, collapse of the hydraulic paradigm among locals, scientists, and environmental activists [11], combined with the government's unwillingness or inability to maintain substantial investment for infrastructure development. There has been a significant paradigm shift in the water sector from water management to water governance, with the state no longer playing a central role and taking almost all of the culpability for the water cycle. This has allowed for the participation of non-governmental players and the private sector [12].

The membrane distillation (MD) method is a thermal separation technique that may be used to treat a variety of fluids, including brackish water, seawater, radioactive wastewater, mining water, wastewater, and reverse osmosis (RO) brine (concentrate) [13, 14]. Regarding seawater desalination, membrane distillation (MD) is a promising approach. The low operating temperature, fewer harmful effects on the environment, and high rejection performance of non-volatile elements in MD mean that it typically needs less hydraulic pressure than RO [15]. The hydrophobic membrane in the MD process is situated between the low-temperature permeate and the high-temperature feed. Since the membrane is hydrophobic, only gas molecules can pass through it. As a result, the MD process may be used to treat salt water and wastewater, resulting in potable water and a concentration consisting of the same elements as the mother liquid, but at a feed side. The vapor pressure gradient (P = Pf - Pp) caused by the temperature difference between the feed (f) and the permeate (p) is the major force at work here [16].

Four basic configurations of MD are categorized based on the process through which the condensed vapor permeates the membrane. (VMD), (DCMD), (SGMD), and (AGMD) [45-47]. In DCMD, the hot solution (feed) makes direct contact with the hot membrane side's surface. Thereafter, the vaporized water is transferred from the warmer feed side to the cooler permeate side, where it condenses. Transfer of water vapor over a membrane is facilitated by a vapor gradient, which results from a pressure differential between the inside and outside of the membrane. DCMD is shorthand for the standard MD configuration unless otherwise noted [48]. The feed solution in AGMD is in constant contact with the membrane's warmed face. Multiplying membrane thickness by air gap length yields the total vapor diffusion length. The membrane's hot side is separated from the condensing side by a layer of static air. Since there is air between the membrane and the condensation chamber, water vapor may be able to pass through [49]. SGMD involves using a non-reactive gas to transport vapor from the permeate compartment within the membrane to the condensing compartment outside the membrane area. [50]. The VMD configuration creates a vacuum on the membrane's side that permeates. The water vapor condenses when it is forced beyond the barrier. Heat loss is greatly reduced on with this setup [51]. The DCMD has proven to be the most appealing of the four configurations because of its high permeate flux [47]. The DCMD technique is used to treat wastewater [52] the desalination of water, color-tainted textile wastewater [53] , rubber wastewater [54], and water polluted with radioactive and heavy metals [55].

2.0 DESALINATION TECHNOLOGIES

In part due to the demise of the hydraulic paradigm and the subsequent shift to water governance, "demand-side management" has emerged [17], i.e., changing the focus to how water is used and letting other water technologies in [18]. Desalination is promoted in this scenario as a practically limitless, cost-effective [6], flexible [19], and independent of rainfall [20] containing the detrimental changes in water availability as a result of climate change depends critically on water technology [21, 22]. In a world where most major cities—roughly 75% of them—and half of the people are situated within 60 kilometers of the shore, [6], desalinated water is promoted as "the only extra sustainable source of fresh water now accessible." [23] to meet the Global North's growing needs for water, both in terms of quantity and quality [6] and to achieve the Global South's Millennium Development Goals [24]. Whether it's to get beyond environmental barriers like shortages or to provide ultrapure water for certain operations, desalination is presented as a fast remedy for the industrial sector. Ultrapure water, also known as ultra-filtered water, is utilized in the microelectronics and energy sectors, among others, since it has been processed according to very stringent rules that remove almost all traces of impurity. Desalination may also be used to purify polluted industrial wastewater [6], such as the wastewater produced during hydraulic fracturing, which is employed in the exploration and production of unconventional gas and oil [25]. Future predictions indicate that agriculture will also be a significant user of desalination water [26].

It is probable that only in some locations of the globe, such as the Mediterranean basin, and under certain conditions, would desalinate water be cost effective for high-value items. Desalination, it is said, may also help stop the depletion of traditional water supplies like groundwater [27], and thereby boost river ecosystem productivity. To solve the water issues of the twenty-first century, desalination has sprang as a techno-social solution [28]. The desalination techniques that are now in use around the world are shown in Figure 1.

The two basic ways for desalinating water are membrane and thermal [29]. Thermal techniques include multistage flash (MSF) and multiple-effect distillation (MED). The latter, known as membrane electrodialysis (MED), is now the most widespread desalination method because of its high thermodynamic efficiency. Recovering heat from condensed steam requires the cooperation of several cells working to lower pressures and temperatures. Nonetheless, MSF has a global reputation for reliability and longevity, making it the most used thermal process. Brine heaters work by sending water through a series of heat exchangers to get the temperature up. Patterns of rapid decompression cause steam to develop in a cyclical fashion (it "flashes" into steam). Condensation is a method for recapturing latent heat.

Vapor compression distillation (VCD) is often used in smaller-scale desalination facilities because it is an energy-efficient method that requires less space and water than traditional distillation methods. The most widely used membrane technique nowadays is reverse osmosis used to purify water via filtration through semi-permeable membranes, which remove salts and other contaminants (RO). RO is capable of overcoming the water's osmotic pressure because it uses such high hydraulic pressure [6]. Table 1 lists the expenses and energy needs for several desalination techniques.

The membranes' tiny holes make it simple for the solvent (H_2O) to pass through, but they make it difficult for solutes to get through from the membrane's under-pressure side. The RO procedure produces both filtered water and saltwater, a very salty solution. The recovery rate of a desalination process is the percentage by which the output water is greater than the input water. This figure often exceeds 60% for the economic environment. Another method of desalination that employs selective ion-exchange membranes is electrodialysis (ED). Compared to membrane processes, the energy requirements of thermally based processes (MVC, MED,and MSF) are much higher (RO, FO, and ED). Energy demands for thermal desalination processes are not affected by salt concentration, in contrast to membrane processes [30].

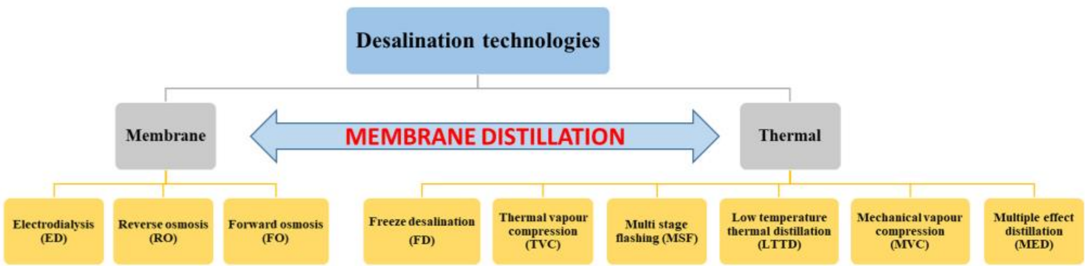

Figure 1 classification of desalination technologies [1]

Table 1 summarizes the costs and energy requirements of several desalination methods

Desalination Technology	Energy (kWh m^{-3})	Price (USD m^{-3})	References
MSF	021–059	04	[31]
MED	015–057	01	[32]
MVC	07–015	-	[33]
	03–022	0.66	[34]
ED	01–03.5	-	[33]
Sea water RO	03–06	0.2–0.7	[35]
Brackish water RO	0.5–03	0.53–0.99	[36]
FO	10–068	0.6	[37]

One of the most well-known advantages of membranes is the significant reduction in energy required in comparison to thermal methods. Energy requirements for RO are stable at 3–4 kWh/m^3 for saltwater or drop to 0.5–2.5 kWh/m^3 for brackish water, whereas those for MSF and MED range from 10–16 kWh/m^3 [38]. In any scenario, distribution expenses may result in greater energy needs for the "final" water that is provided to the consumer. capacity to treat feedwaters other than saltwater, including brackish water, subterranean water, and wastewater as well as the modularity of membrane technology, which enables future size expansions or reductions based on demand trends, are great benefits of membrane technology over thermal methods. Moreover, experimental techniques aim to be more economical and efficient with energy. As an illustration, forward osmosis (FO) [39, 40] operates at a lower pressure than RO and uses less energy as a result. Distillation using membrane (MD) [39, 41] since its introduction in the 1960s, a thermally driven separation method employing microporous membranes to handle very salty water has only been used in prototype form [40]; As a commercial technology, it is now showing potential. Research and development in the desalination industry is centered on a wide variety of novel membrane and material types, aquaporins, carbon nanotubes, nanoengineered membranes, and ion concentration polarization are just a few examples [6, 39].

3.0 RECENT DEVELOPMENTS IN MD CONFIGURATIONS

When attempting to overcome issues with MD nowadays, two factors are taken into account: membrane design and module configuration. As was previously mentioned, advancements in MD membrane materials are not very useful if module and configuration design is not also prioritized. The majority of new and enhanced configurations aim to increase vapor flux and thermal energy efficiency. Some examples of modified MD configurations include material gap membrane distillation (MGMD), vacuumed air gap membrane distillation (VAGMED), or sub-atmospheric AGMD, submerged membrane distillation (SMD), conductive gap membrane distillation (CGMD), permeate gap or liquid gap membrane distillation (PGMD or LGMD), [flashed-feed-VMD [vacuum-enhanced DCMD, and vacuum multi-effect membrane distillation (V-MEMD) [76, 77]. PGMD/LGMD and V-MEMD have both already been released on the market in a pilot scale module, among the MD configurations previously described. Vacuum is used in several stages and effects, similar to the traditional multi-effect distillation (MED) process, in the V-MEMD configuration type of vacuum-mediated distillation [78]. Each of these new MD setups is briefly described in this section.

3.1 Vacuum-Multi Effect Membrane Distillation

In the V-MEMD technology, energy is recycled several times. Between the water space and the vapor space inside the plastic module, a Teflon microporous membrane was used. The permeate vapors are driven from the feed solution side to the vapor space through the membrane pores by the partial vapor pressure differential that results from the circulation of the hot feed solution through the water space. A thin polypropylene foil in the subsequent stage separates the feed solution from the vapor area. The vapors in the foil frame will heat the feed solution in the water gap, which will then condense. The Vacuum Multi-Effect Membrane Distillation design is shown in Figure 2. Condensation heat is transferred through the foil and transformed into feed evaporation heat, which creates additional vapor in the vapor channel [76, 79, 80].

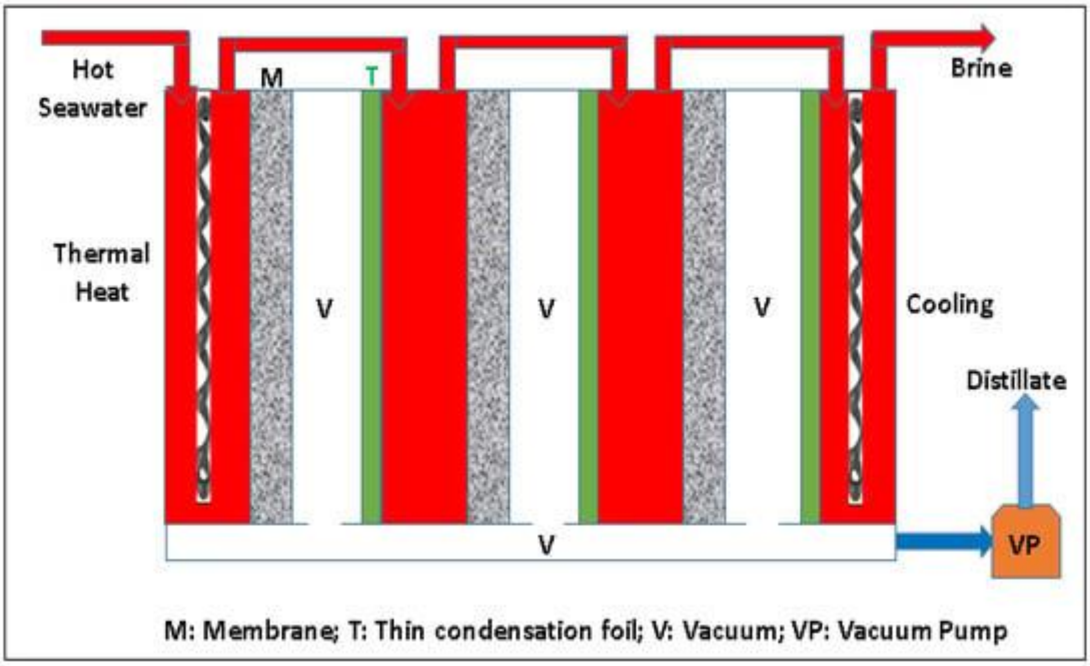

Figure 2 Schematic of the Vacuum Multi-Effect Membrane Distillation. Reproduced with permission from ref [76]

Permeate that has condensed will enter a distillate channel. MEMSYS created pilot V-MEMD configuration modules, which are used in a variety of production capabilities across various nations. Zhao and colleagues claim that the Memsys V-MEMD system, which uses solar energy or waste heat sources to produce water of excellent quality, is small and extremely energy-efficient. They looked at how well 2-stage and 4-stage systems performed. It is discovered that the GOR of 2-stage and 4-stage systems are, respectively, 1.84 and 2.79. Additionally, they looked at the performance of 2-stage systems with 7, 9, and 17 frames, and discovered that while the flux decreased as the number of frames increased, the GOR remained consistent in all three cases. Memsys was purchased by New Concepts Holdings Limited (NCHL) in 2016. Depending on the feed water types and quality, they offered conventional models with capacities ranging from 3 to 24 tons/day of distillate production. In addition to the regular models, they are able to build customized systems with a daily capacity for producing 50–1000 tons of distillate [81].

3.2 Material Gap Membrane Distillation

The MGMD procedure was introduced by Francis and his coworkers. It is a new MD configuration where various materials are inserted into an AGMD module's air gap. An AGMD module's air gap creates a significant amount of mass transfer resistance. The permeate flux may be increased by reducing the mass transfer barrier and enhancing the condensation process in specific materials that filled the air gap. The MGMD module's schematic is shown in Figure 3. In the MGMD setup, materials including sand, polyurethane, conductive materials, water, etc. are used. Conductive gap membrane distillation (CGMD) refers to the MD module or process that uses conducting materials [76]. The method is known as water gap, liquid gap, or permeate gap membrane distillation (WGMD, LGMD, or PGMD) when water or permeate is utilized in the air gap of an AGMD module. Francis *et al*. filled the air gap of an AGMD module with various materials at various feedwater temperatures and found that the water vapor flux increased by around 200–800%. Sand, polypropylene, polyurethane, and water in varied thicknesses were the materials employed in this investigation . It was observed that the conducting materials can enhance the permeate flux whereas, the insulating materials such as polypropylene and polyurethane have no significant influence on the permeate flux. This is because of the occurrence of heat transfer hindrance which dominates over the air gap reduction [76].

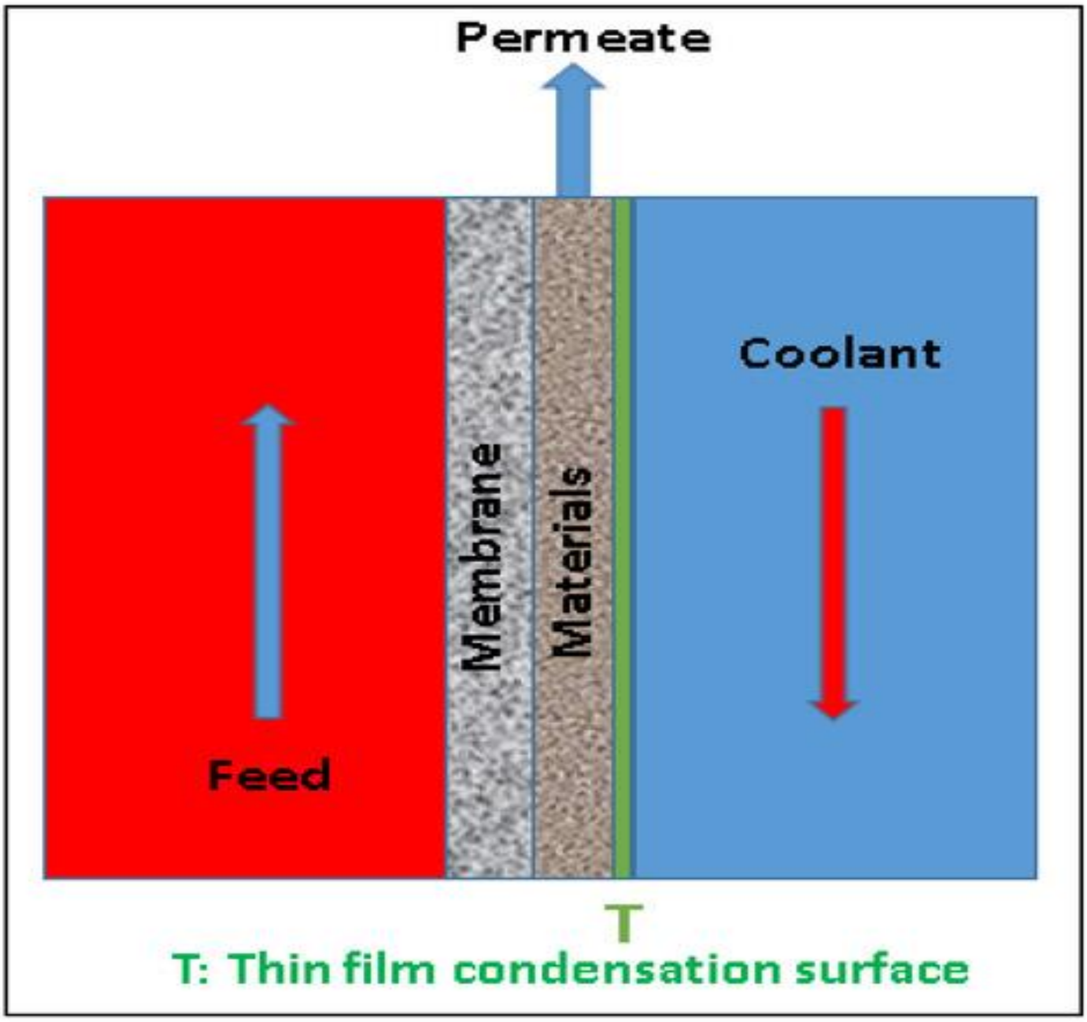

Figure 3 Schematic of a material gap membrane distillation (MGMD) module. Reproduced with permission from ref [76]

The highly thermally conductive materials inserted in the air gap of an AGMD module can greatly increase the permeate flux, according to research done by Cai *et al*. in 2020 on the transport analysis of the MGMD process [82]. Following up on MGMD research, a different research team from the Massachusetts Institute of Technology, USA, expanded on this work by inserting conductive metallic meshes into the air gap of an AGMD module and comparing the results with the PGMD procedure. They discovered that PGMD has a gain-output ratio (GOR) or energy efficiency that is 20% higher than that of an AGMD system of equal size, and that CGMD can have a GOR that is twice as high as that of a PGMD system under similar operating conditions [76].

3.3 Vacuumed AGMD and DCMD

Vacuumed air gap membrane distillation (VAGMED) is an AGMD process that is carried out in sub-atmospheric circumstances or with the application of controlled vacuum in the air gap of an AGMD module, according to Ghaffour and coworkers [83]. According to the simulation and experimental results of this paper, when non-condensable gases are removed from an AGMD's air gap and the gap is kept at the feed temperature's saturation pressure, the permeate flux is increased by three times. Due to the corresponding mass and heat transfers in a multi-stage process, the feed temperature decreases from stage one to stage two, and the vacuum in the air gap of the module can be adjusted in line with the saturation pressure of the feed solution. Additionally, they focused on how effective process staging and correct engineering may increase the value and effectiveness of the MD process. This system has a lower likelihood of membrane pore wetting than traditional VMD. Figure 4 depicts a schematic of a multi-stage VAGMED procedure. This study also briefly discusses the impact of staging on the permeate flux in the VAGMED system and its relationship to membrane cost [84].

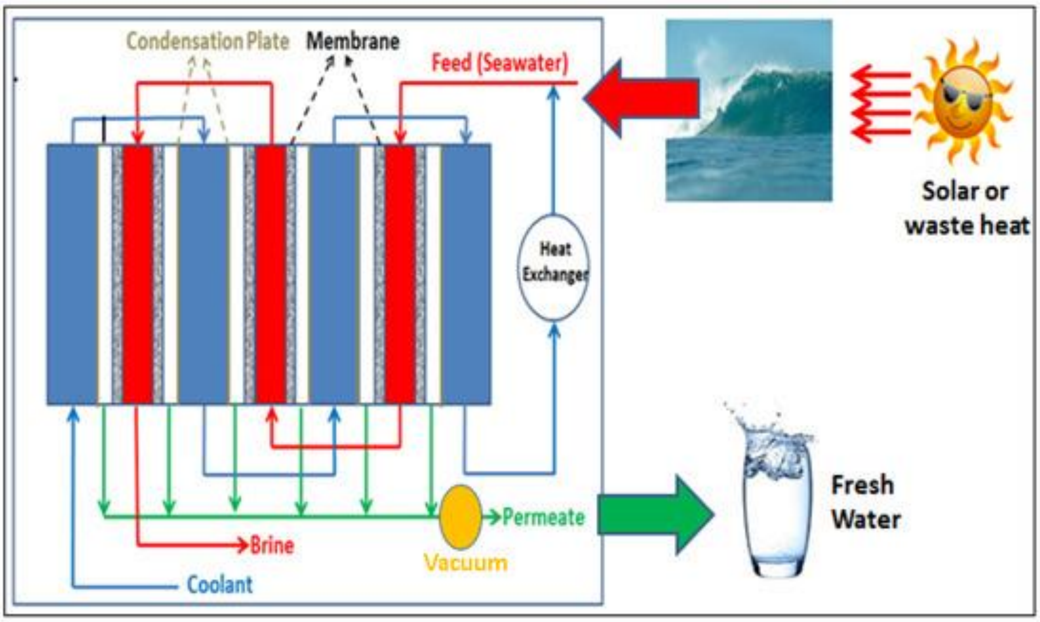

Figure 4 Schematic of a multi-stage VAGMED process. Reproduced with permission from ref [76]

Naidu and colleagues presented a novel vacuum-enhanced DCMD (V-DCMD) technique in which they used experimental data and theoretical models to examine the behavior of fouling and transport phenomena. The permeate flux was increased by 37.6% with V-DCMD compared to DCMD setup [85].

3.4 Submerged Membrane Distillation

SMD is a newly developed configuration for an MD process. The membrane module is immersed in a feed solution tank or a coolant stream during the SMD process. In comparison to other MD arrangements, the design and manufacturing of modules in an SMD architecture are quite straightforward. A significant benefit of SMD, aside from module simplicity, is that it may be used with ease in other common MD configuration modes, like DCMD, VMD, and SGMD. Using hollow fiber membranes, Francis and colleagues conducted lab-scale testing on the SMD process and discovered that the permeate flux is comparable to that of the other standard MD configurations. A schematic of an SMD process arrangement using a hollow fiber membrane module is shown in Figure 5. The SMD technique can also use a flat sheet membrane with a closed plate-and-frame module. Figure 10 depicts the SMD process in DCMD mode, where a hot feed stream passes through the lumen side of the membrane while an open membrane module is immersed in the cold stream. It is also feasible to design in a different approach, for example, by immersing the membrane module in a hot feed stream while passing a cooling stream via the membrane's lumen side [76, 86].

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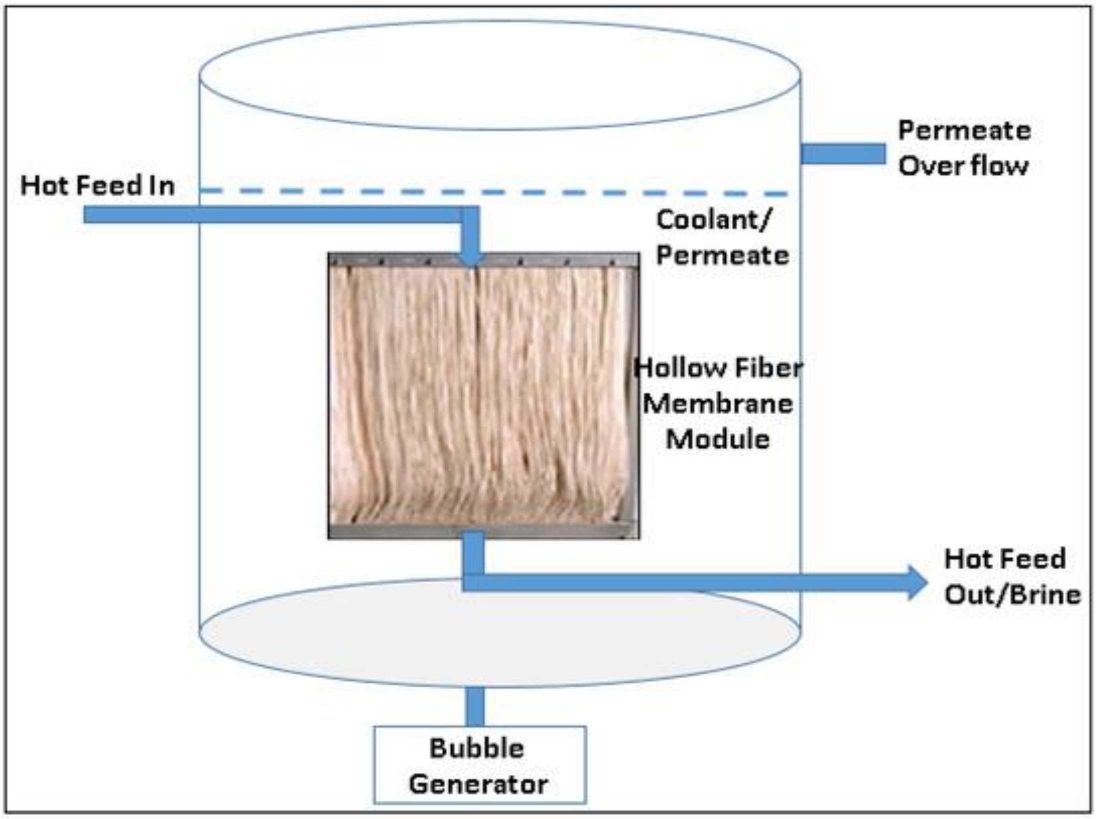

Figure 5 Schematic of Submerged membrane distillation (SMD) process. Reproduced with permission from ref [76]

3.5 Flashed-Feed VMD

The Flashed-feed VMD (FF-VMD) configuration is another intriguing and innovative VMD architecture that was introduced by Al Saadi and colleagues. A innovative technique for reducing the temperature polarization effect and improving water vapor flux is the flashed-feed VMD configuration. In FF-VMD, the feed solution is flashed into the feed chamber through a very small hole instead of coming into contact with the membrane to reduce the TP effect. Therefore, under equal operating conditions, the flashed-feed VMD configuration produces enhanced permeate flux up to 3.5 times (200 LMH) higher than the standard VMD process. Figure 6 shows a very basic concept of the FF-VMD membrane module. In this study, the hot feed stream was kept from coming into close contact with the membrane surface in order to dissociate the TP effect from the membrane mass transfer coefficient. This investigation has led to the conclusion that in a traditional VMD design, the heat transfer coefficient regulates the resistance of permeate flux [87].

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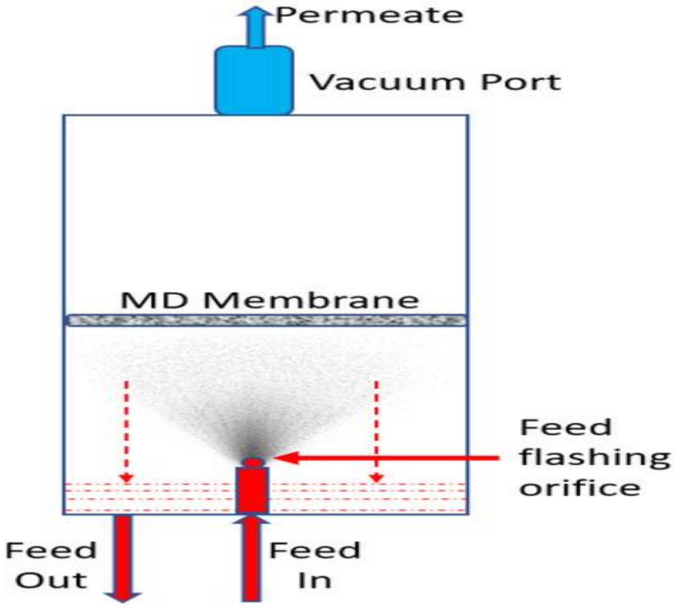

Figure 6 A schematic of the FF-VMD membrane module. Reproduced with permission from ref [76]

3.6 Dead-End Membrane Distillation

For sustainable and energy-efficient desalination, Mustakeem *et al*. recently published a unique dead-end MD (DE-MD) module arrangement. With the help of a localized heating element placed at the feed chamber, the feed solution is heated in this system inside the membrane module. The permeate flux could be increased by intermittently flushing the feed solution to lessen the TP effect. With this new MD module design, specific energy consumption lowered by up to 57%, permeate flux increased by up to 45%, and GOR value raised by up to

132 ±12%. Figure 7 displays a schematic representation of the DE-MD module. The use of DE-MD could also reduce conventional heat losses and membrane fouling problems in the MD process. Studies using conjugate heat transfer models show that localized heating techniques result in a more effective procedure and a uniform heat transmission across the membrane [88, 89].

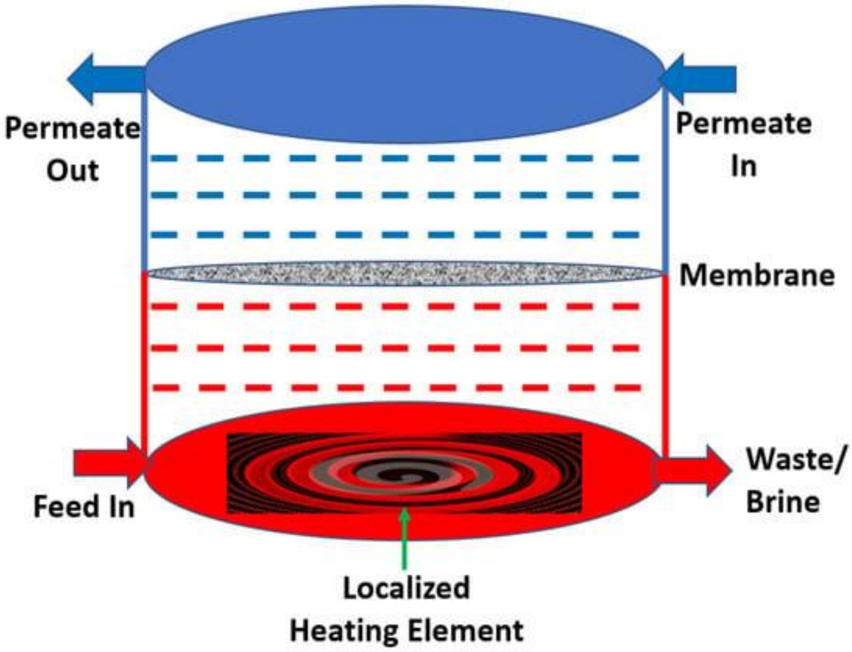

Figure 7 Schematic representation of DE-MD Module. Reproduced with permission from ref [76]

4.0 DEVELOPMENTS IN PILOT SCALE MD TECHNOLOGIES

Carab Improvement AB (Stockholm, Sweden), Fraunhofer ISE- Sun based Springs GmbH (Freiburg, Germany), TNO—Memstill (Amsterdam, The Netherlands), Aquastill (Sittard, The Netherlands), Aquatech (Hackettstown, NJ, USA), Memsys GmbH (Schwabmünchen, Germany), KmX Enterprise (Markham, ON, Canada), Memsift Developments (Pandan Circle, Singapore) and Econity (Gyeonggi-do, Korea) are a few commercial MD pilot innovation engineers. Scarab created an AGMD film module while, Sun oriented springs, Memstill, and Aquastill created LGMD/PGMD layer modules in spiral-wound plan utilizing level sheet layers. In any case, it is exceptionally vital to specify that a few MD pilot plants coordinates with renewable sun oriented vitality have been effectively introduced and worked, as of late [76].

In 2009, the Fraunhofer Institute for Solar Energy Systems in Freiberg, Germany, spun off Solar Spring GmbH. For solar-driven MD desalination applications, Winter *et al.* [90] created spiral-wound AGMD and PGMD modules. Swedish business Scarab developments AB was established in 1973. In 1981, they received a patent for the plate-and-frame AGMD module design modular flat sheets. Scarab granted Xzero of Sweden a license to utilize their technology for the semiconductor secto [91]. For zero liquid discharge (ZLD) and minimal liquid discharge (MLD) facilities, Aquatech is a US-based company that offers advanced VMD (AVMD) MD modules. In spite of the typical MD designs, the flat sheet membrane solely serves as a demister and does not come into contact with the feed solution. For "method and apparatus for the advanced vacuum membrane distillation," they submitted a patent application[92]. MD prototype modules based on hollow fiber membranes were recently introduced by the US-based KMX Technologies LLC and the Singapore-based Memsift Innovations. Hollow fiber membranes can offer modules with a small footprint and a large surface area. The temperature is controlled by the Carnote cycle, which is based on the Joule-Thomson effect in the Memsift MD process. The KMX technique uses PTFE hollow fiber membranes configured in a VMD for the treatment of generated water, acid mine drainage, and lithium recovery [2]. Table 2 appears the diverse MD pilot frameworks introduced and worked with distinctive MD arrangements and generation capacities.

Table 2 MD pilot systems deployed in different parts of the world

Company and country	**Configuration**	**Application**	**References**
Econity—Global MVP (South Korea)	PVDF Hollow Fiber VMD module	active membrane area of 5.3 m^2. With 99.99% rejection of inorganic salts, 18 LMH flux at 75 °C.	[93]
Scarab AB-Xzero (Sweden, Spain)	AGMD PTFE membrane with flat sheet Plate and Frame	Municipal wastewater used as feed, 2.3 m^2 membrane area. recovery of 35%. After 370 hours of nonstop operation, there was a significant flux decline. synthetic brackish water, seawater desalination, and 2.8 m2 membrane area. 6.5 LMH	[94, 95]
Aquastill Low-density polyethylene membrane(Australia and Spain)	Spiral-wound AGMD Spiral-wound V-AGMD	1<LMH, 7.2 m^2 membrane area. Using natural and artificial seawater as feed. up to 9 GOR 7.2 m^2 and 24 m^2 membrane areas in two pilot modules. application of seawater desalination. 1.35–4.2 LMH	[96, 97]

Company and country	Configuration	Application	References
Memsys PTFE membrane(Singapore, Qatar, Saudi Arabia and Greece)	Plate and Frame V-MEMD	Seawater desalination powered by solar and waste heat (<1 m3/day) Seawater and Thermal brines (<1 m^3/day) Four stage-single effect system optimized for 43–46 °C feed Artificial Saline Water Desalination (30–50 LMH)	[78, 79, 98, 99]
Memstill(Singapore, Netherlands)	Flat Sheet AGMD	Seawater Pollution Desalination Desalination of Brackish Seawater Unclean Brackish Water	[100]

5.0 MD SPECIALIZED APPLICATIONS

There are numerous uses for the MD process in the reclamation of freshwater in addition to seawater desalination. One of these is brine management, or brine treatment, where the MD process can be combined with traditional desalination facilities like MSF, MED, and RO and use the brine from these facilities to extract freshwater. The industry could benefit from the MD process to lower the volume of salt and lessen the challenges associated with brine disposal because MD can function at very high salinities. Membrane distillation crystallization, also known as MDC, is a technique that can be used with MD to recover the precious minerals in brine in zero liquid discharge (ZLD) or minimum liquid discharge (MLD) processes). The oil and gas sector produces a large amount of wastewater each day. One potential specialized application for the MD process is the treatment of this produced water. MD method could create ultrapure water for the pharmaceutical and electronic sectors by rejecting nearly all salts and nonvolatile impurities [101].

6.0 MD TECHNOLOGY FIELD TESTING

The main pilot/field studies of MD technology for water desalination carried out over the previous ten years. With the main objective of advancing the MD to TRL scale of 8 or 9, various research organizations from various nations participated in these efforts to enable wide-scale applications of the technology. In order to emphasize certain applications, vendors, module configurations, and important process performance challenges, the researchers also went over relevant case studies [2].

6.1 MD for Desalinating Seawater

The proprietary Memstill air gap flat sheet MD technology (Figure 8) was put to the test in the field in direct contact mode by a nine-party consortium led by Netherlands Organisation for Applied Scientific Research (TNO) and Keppel. An array of hydrophobic PTFE membranes and impermeable condensers arranged parallel to one another make up a single Memstill design. The seawater is first preheated in the condenser before additional heat is added. Through the hydrophobic membrane, the water vapor from the ocean condenses to create freshwater. Numerous studies were conducted using a 24 m^3/day pilot system (Figure 13) in various places: Singapore, Rotterdam, and Antwerp [102, 103]. All MD systems produced water that was of exceptional quality and had a salt rejection rate of greater than 99.9% [2].

Figure 8 Memstil pilot unit in Singapore. Reproduced with permission from ref [2]

6.2 MD COMBINED WITH SOLAR ENERGY FOR DESALINATION OF SALTWATER

Fraunhofer created an MD system with a 5-120 l/h capacity (Figure 9) for the "MEMDIS" project, which was funded by the European Union. It was field tested in Spain [104]. To provide the MD system with the necessary electrical and heat energy, the system was combined with solar energy (collectors and photovoltaic modules). The feed for the pilot unit was pretreated seawater through the use of cartridge filters. The equipment was used sporadically for about two years. In order to facilitate effective heat transfer, the hydrophobic PTFE membrane channels were set up in a spiral wound pattern, with a consistent temperature difference generated across the entire membrane surface area. Through the membrane, the water vapor traveled before condensing in the distillate channel. Overall, the membranes achieved > 99% salt rejection while the MD unit was operated at a feedwater recovery rate of up to 44% [2].

Figure 9 Pilot facility of Fraunhofer system in Spain. Reproduced with permission from ref [2]

6.3 Thermal Desalination Plant Brines to be Desalinated by MD

For the Middle Eastern region to be sustainable, saltwater desalination is essential for producing water. The most popular desalination techniques include multistage flash (MSF), multieffect distillation (MED), and reverse osmosis (RO), many of which are connected to power plants to take advantage of the thermal energy and electrical needs. Large volumes of rather hot, concentrated brine are produced by desalination plants in the Middle East and are then released back into the water. Without incurring considerable additional capital expenses, MD has the capacity to recover additional water from the concentrated brine of currently operating desalination facilities. In order to demonstrate pilot scale MD performance at a full-scale thermal desalination plant in Qatar, the ConocoPhillips Global Water Sustainability Center (GWSC) and an industrial-academic consortium that included Qatar University (QU) and Qatar Electricity and Water Company (QEWC) started an ambitious MD research program in 2012. The issues related to long-term performance, process economics, and particular field conditions were addressed [105].

Memsys (Germany, multieffect VMD) and Xzero (Sweden, AGMD), two MD providers, were chosen for the field experiment after a technical examination. The vendors designed and constructed the pilot units, which were then transported to Qatar to be used at a large-scale thermal desalination facility (Figure 10). The study offered a rare chance to compare MD systems side by side in real-world scenarios [99].

Figure 10 Memsys (a) and Xzero (b) pilot units at a desalination plant in Qatar. Reproduced with permission from ref [2]

6.4 **MD for Hypersaline Brine Concentration**

Germany tested a spiral wound AGMD module made by Solarspring (Figure 11) with salt chloride solutions with a concentration range of 0 to 240 g/L NaCl [106]. The distillate capacity of the pilot unit was 25 L/h (Figure 16). The pressured air that was blown into the air gap of their AGMD module was new since it enhanced the drainage of the sluggish distillate, reduced membrane wetting, and increased distillate conductivity. PTFE with PP backing makes up the hydrophobic membrane. The feed flow rate, condenser inlet temperature, and condenser output temperature in the pilot research were all maintained at 300 L/h, 25 °C, and 80 °C, respectively. When the feed salinity was increased from 0 to 240 g/L, the membrane flux reduced from 2.1 to 0.7 LMH. The distillate flow and GOR were both decreased by air blowing by 1.4% and 4.1%, respectively [107].

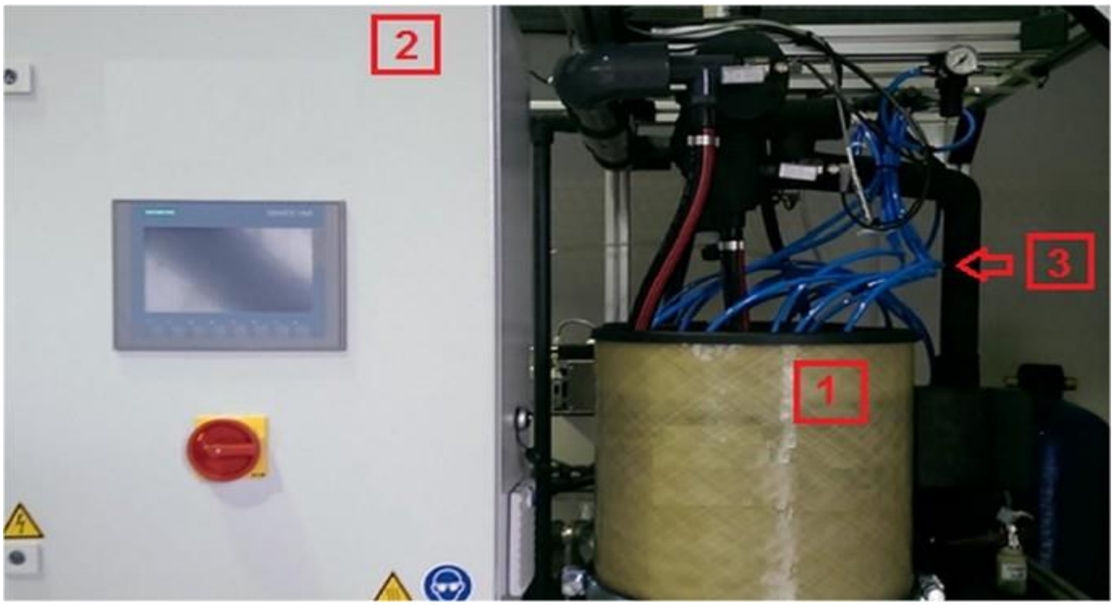

Figure 11 Solarspring MD pilot unit for treatment of hypersaline water with blower arrangement (1, membrane

6.5 Desalination of Hypersaline Groundwaters using MD

In order to treat inland hypersaline groundwater for prospective use in fracking of shale reservoirs, the Memsys pilot unit from the aforementioned study was shipped to Texas (USA). To illustrate a ZLD process, the MD pilot unit was combined with a multieffect humidification-dehumidification (HDH) unit (Figure 12). Canadian company Saltworks Technologies Inc. provided the HDH pilot unit. A new desalination technique called HDH mimics the natural water cycle by heating water to create vapor streams, which are then condensed to create distilled water. For the transfer of both heat and mass, air is used as a carrier gas. For hydraulic fracturing, the high-quality water can either be produced water or combined with a low-saline solution. Canadian company Saltworks Technologies Inc. provided the HDH pilot unit. A new desalination technique called HDH mimics the natural water cycle by heating water to create vapor streams, which are then condensed to create distilled water. For the transfer of both heat and mass, air is used as a carrier gas. Both units achieved > 99.9% TDS rejection, with the feed water salinity of the MD system being 6.3% total dissolved solids (TDS) and the MD brine being 10.2% TDS. MD and HDH had specific energy consumption (SEC) of 260 and 220 kWh/m^3, respectively [2, 108].

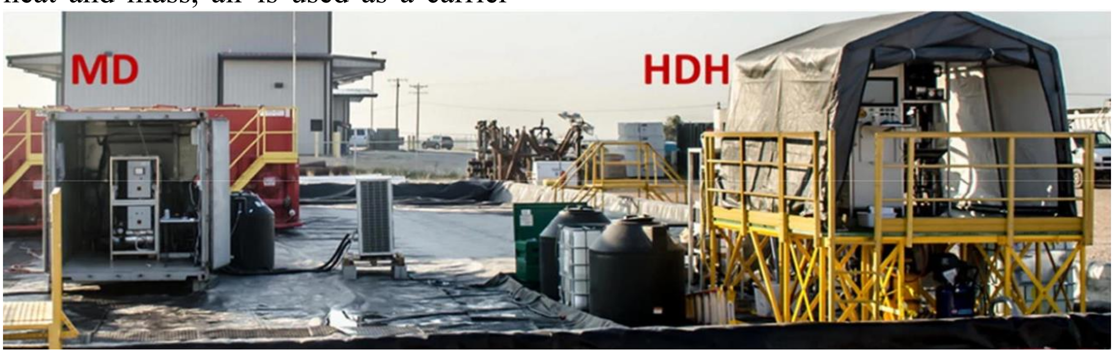

Figure 12 Pilot facility of MD-HDH pilot unit. Reproduced with permission from ref [2]

6.6 MD for Seawater Desalination with Improved Heat Recovery

In Spain, a prototype VMD study based on the Memsys concept was assessed for saltwater desalination. Thermal energy was provided by the 1 m3/day pilot unit in combination with solar energy collectors. To heat the seawater and increase energy effectiveness, creative changes were made in the condenser portion. The other innovation was the use of internal passageways rather than an exterior siphon to transmit vapor between effects. As a result, the flow of the distillate was increased and non-condensable gases were eliminated. The module was made of PP, and the membranes were made of PTFE. Even though the system was able to generate a high flux (8.5 LMH) at a hot feed temperature (75 °C), seasonal changes in seawater temperature caused a decline in productivity of about 40%. Additionally, membrane fouling brought on by calcium scaling decreased production by 50%; however, cleaning with citric acid was able to restore the flux [108].

7.0 NEW DEVELOPMENTS IN MEMBRANE FABRICATION AND MODIFICATION

The selectivity and permeability of membrane-based processes are significantly influenced by the membrane structure. However, there are presently no suitable membranes available that are made expressly for use with membrane contactors. Currently, PVDF, PFTE, or PP membranes developed for MF or UF investigations make up the majority of the membranes used for MD and MCr studies [109, 110]. But certain qualities need to be improved. Better hydrophobicity is required for higher efficiency in MD and MCr. greater porosity, sufficient pore size, and a more narrowly distributed pore size. Additionally, these membranes don't moisten well with more complicated feed solutions during the MD and MCr processes and have low permeability. In order to use MCs, new membranes must be created particularly for that purpose. Despite the fact that phase inversion is the primary approach utilized to create membranes suited for MCs applications, other techniques have been developed in more recent years to improve the synthesis and modification of polymeric membranes [111].

To create membranes for MCs applications, 3D printing and electrospinning techniques have been introduced. However, 3D printing technology is still in its infancy and has a number of drawbacks, particularly in terms of controlling membrane pore size. Due to their intriguing properties, electrospun nanofiber membranes have attracted a lot of attention recently as prospective MD membranes. These electrospun membranes exhibit numerous benefits, including very high porosity, excellent hydrophobicity, very strong interconnectivity, and a very high surface to volume ratio, which makes them intriguing candidates for desalination applications [112, 113].

Eletrospinning can be done using polymer melt or solution, and the properties can be changed by adjusting the process's variables, the material's properties, and the post-processing step's application. Due to the ability to employ polymer melt rather than solution, this new process opens up the prospect of producing membranes using a wide range of polymers. The nanofibers can have many functional components inserted into them either during or after spinning, giving the fibers multiple uses. Electrospun nanofiber membranes have also been used in a few lab-scale applications, according to current literature [64, 114-116].

Composite membranes made of various materials allows for the creation of membranes with properties appropriate for MD. Direct contact MD has used bilayer hydrophobic/hydrophilic porous composite membranes. While the hydrophobic layer is kept in touch with the feed aqueous solution, the hydrophilic layer is brought into contact with the permeate liquid. Utilizing a variety of techniques, composite membranes were created either in situ during membrane formation or by altering already-existing membranes through coating, grafting, plasma surface modification, etc [117]. A triple layer membrane that included a bottom hydrophilic polyethylene terephthalate (PET) support layer, a middle layer made by immersion precipitation, and a thin hydrophobic electrospun nanofibrous layer coated on PVDF microporous layer gave good performance in MD. In comparison to a bilayer membrane, a triple-layered membrane displayed higher LEP values, a greater water contact angle, and a nanofibrous layer that was hydrophobic in nature [118, 119].

The creation of composite hollow-fiber membranes appropriate for MD use has also gained attention recently. In specifically, dry/wet spinning by a triple-orifice spinneret was used to create dual-layer hollow-fiber membranes. The spinneret's annular middle and outer channels were used to circulate both spinning solutions, such as hydrophobic and hydrophilic solutions, as well as the bore fluid, which was extruded through the spinneret's central channel. The effect of introducing things like methanol (MeOH) and fluorinated silica particles into the outer dope solutions constituted of PVDF/NMP and polyacrylonitrile (PAN)/hydrophilic cloisite NAJVEG/NMP was investigated [120]. in a different work. The outer layer of the hollow-fiber membranes was made of the same polymer solution as the inner layer, but with PTFE particles added to the PVDF/NMP/EG solution. When 30% by weight of PFTE particles were added to the outer layer in this instance, a morphology free of macrovoids and a thin outer layer were achieved. In particular, the electrospinning method used to create innovative membranes, a number of research groups began to investigate nanotechnology. Electrospinning was used to create nanofibers with two layers, which DCMD then evaluated for desalination [121].

To increase the membranes' surface hydrophobicity, membrane surface coating is used. The main disadvantage of this method is the instability of the coated layer, which may come off during the procedure due to the weak physical connection between the membrane and coated layer, as well as the significant danger of closing the pores and/or shrinking their size. Crosslinking via solid-vapor contact or chemical treatment was used in some instances. Because the membrane surface is altered by the covalent bond formed between the grafted chains and the membrane, surface grafting is advised. Covalent bonding contact of the graft chains on the membrane surface prevents their delamination, providing long-term chemical stability of the grafted chains, in contrast to the physically surface coating technique [122, 123].

Recently, various membranes with changed surfaces have been created and used in MD technology. Using CNTs, self-supporting bucky-paper membranes were created, and they were then sputtered with a thin layer of PTFE on both sides to boost the membrane's hydrophobicity and mechanical stability without changing the pore size or porosity. This composite membrane, which consists of four layers a PTFE layer, a CNT BP layer, a PTFE layer, and a PE support performed well in MD testing [110]. Another technique for creating superhydrophobic PVDF membranes for MD applications involves using an airbrush to apply a solution of polydimethylsiloxane and hydrophobic silica (Si02) nanoparticles to the membranes. The final membrane was successfully tested in DCMD, and compared to the polymeric membrane, it showed superior antifouling properties [124]. Due to the intense fluorination of the membrane surface by fluorine functional groups, this approach was also employed to increase the membrane's hydrophobicity. For instance, an asymmetric hydrophilic polyethersulfone (PES) flat-sheet membrane that is appropriate for DCMD application has been rendered hydrophobic [125].

Due to its remarkable mechanical, electrical, and thermal capabilities, high aspect ratio, and light weight, CNT was employed to manufacture membranes for MCs application in order to enhance their properties and performance. CNTs were initially thoroughly investigated as standalone materials or as filler components of polymer composites for various applications. Due to their high hydrophobicity, large void volume percentage, high specific surface area, and relatively low heat transfer by conduction, self-supporting CNTs membranes made by vacuum filtering were suited for MD application. However, standalone CNTs membranes are vulnerable to deterioration during MD testing [126, 127]. While also giving the membrane new properties. Other studies have been conducted in an effort to immobilize the CNTs on support without letting fluid movement carry them away [128]. Over the past 50 years, membrane technology has developed significantly due to improvements in materials, creative module design, and a growing comprehension of the related transport phenomena. More recently, 2D materials often symbolized by graphene and its derivatives, have drawn a lot of interest and are widely seen to have enormous potential [129]. The thermal characteristics of the PVDF-HFP membrane were changed by the addition of CNTs and graphene particles. Despite the fact that CNTs and graphene worked as nodules inside the composite framework, there were very minor modifications in membrane architecture with the addition of these particles. These particles can stiffen materials, which decreases membrane compressibility while increasing surface roughness, contact angle, and effective heat transfer surface [130].

To alter the contact angle and surface energy of polymer membranes, hydrophobic macroparticles have been added to polymer mixes. Compared to membranes made entirely of polymers, the final products demonstrated better MD performance. Due to the reduced microscopic area of contact between the liquid and the membrane, these modifications enable higher surface hydrophobicity, lower contact angles, and decreased thermal conductivity [131]. Other methods have recently been employed to change the hydrophilic membranes' surface and turn them superhydrophobic. Fluorolinkperfluoropolyether (PFPE) was used to modify the surfaces of commercial membranes, such as polyamide (PA) and polyethersulfone PES, with variable pore sizes utilizing dip-coating and in situ polymerization techniques. The DCMD test of the resulting hydrophobic/hydrophilic membranes confirmed the stability of the coating and the successful operation of the membranes [132].

8.0 WATER DESALINATION-BASED ON ARTIFICIAL INTELLIGENCE

The availability of conventional water sources is decreasing more and more every day [133, 134]. Thus, recent developments in water supply technology and their ever-improving efficacy are crucial to addressing the current global water crisis. This study used computational methods to analyze how the NaCl can be filtered into the water using graphene nanopores with various functionalizations and diameters [135]. The pore sizes varied within the range of 1.5–55 Å2. To investigate the effect of the pores' chemistry on desalination dynamics, the study was conducted on pores passivated with hydroxyl groups, which are typically hydrophilic. This research established that desalination performance is more sensitive to pore chemistry and size. The hydrophobic nature of hydrogenated pores reduces the water flow by imposing additional order to the system. In contrast to hydroxylated pores, the limited-hydrogen bond allows a higher salt rejection.

Alwatban *et al*. conducted a computational fluid dynamic simulation to study the effects of the membrane properties and the system performance's operational parameters: the membrane porosity, the membrane thickness, the pore size feed flow rate, and the feed temperature. A laminar model was utilized to characterize the weather, the velocity, and the concentration range in the empty channels while net spacers were used to reduce polarization. The simulation results highlight that the pore size and the porosity are increased, while the intensity of temperature, the permeation flux, and the concentration of polarization increase as the thickness decreases. The presence of the spacers raises the performance of the membrane flux by more than 50% and reduces polarization by 30% [136]. On the other hand, Osman *et al*. compared the simulated results of a transition predictive model that was solved through a mathematical algorithm developed into the MATLAB code with the experimental results of the treatment for the recovery of salt and water through reverse osmosis (RO) from the wastewater of the petrochemical industries in South Africa. The model might potentially be utilized as a process design tool because it could accurately predict the water flux values [137].

Esfandiari *et al*. explored a low-energy continuous Direct Contact Membrane Distillation (DCMD) system for water desalination using a 2D computational fluid dynamic model. This model could predict the amount of freshwater produced by the under-consideration system and contains all phenomena equations (momentum, energy, and mass transfer). Three domains, including membrane, cold, and hot channels, were used to write the phenomenon equations. MATLAB software was used to discretize the domains with the finite volume methods and to solve the system. Additionally, the effects of various parameters were investigated, revealing that the system's performance is influenced by the temperature and velocity of the input currents [138].

Essentially, all these applications listed above are about the use of Computational Fluid Dynamic (CFD), without the use of an AI tool, even if some studies deepened this novel aspect into the membrane applications. Yusuf *et al*. the use of Molecular Dynamic Simulation (MDS) and AI tools, which have been used in Decision Support Systems (DSS), ANNs, FL, and GA, as well as some developing developments in sustainable membrane water treatment. Compared to deterministic solutions, MDS and AI techniques are more effective at resolving actual issues. Therefore, both methods should be developed into 3D form, although there is currently insufficient study in this area. The membrane selectivity and performance indicators may both be enhanced by the 3D method. In addition, although the use of AI to membrane-based desalination is still in its early stages, it may eventually be enhanced to better manage the water resource. A DSS is essentially a framework that guides the user in analyzing a vast amount of data from the water plant in order to identify the best solutions [139].

9.0 ATTEMPTS TO MAKE MD MEMBRANES WITH THE NECESSARY PROPERTIES

Several studies have focused on optimizing maximum LEP, large flux, and reduced fouling rates since these are seen to be the most important criteria for successfully scaling up MD, however all of the characteristics are crucial for MD applications [140]. Finding a fair equilibrium among the elevated permeability and LEP of the membranes is one of the basic issues encountered by research teams on MD. Large holes provide reduced wetting resistance at the expense of high permeability since MD centers on porous membranes, and vice versa. As a result, researchers studying membranes have emphasized the significance of optimal pore diameters and the necessity to consider other aspects that may contribute to the achievement of the aforementioned features [124]. This section discusses the research initiatives that have been undertaken to develop MD membranes with the requisite properties, with a particular emphasis on achieving maximum LEP, maximum permeability, and reduced fouling rates.

9.1 Liquid Entry Pressure (LEP)

A high LEP for water means that the membrane has a strong capacity to prevent any water liquids from penetrating the pores. The most important causes is the development of many linked microporous holes. It could start the process of improving the flow of permeate vapor in membrane distillation [125]. LEP is the pressure needed to force a liquid (water in the this case) through a hydrophobic barrier and cause it to wet [141], is often used to assess the wetting resistance of a membrane. The Smolder's process is the one used most often to calculate LEP [142]. The dynamic approach for determining LEP was devised; in this method, the pressure of the recirculating feed is gradually raised while vacuum is concurrently provided to the permeate side. The motion of a liquid meniscus in the permeate side tube indicates that the LEP has been reached. A balance that is positioned underneath the permeate reservoir may then be used to quantify the permeate flow of the wetted membrane at various pressures

[141]. Whenever the membrane's LEP against a particular liquid is exceeded by membrane pressure (P), membrane wetting results [143].

$$\Delta P \geq LEP$$

In other words, LEP is the lowest pressure at which liquids may pass through a membrane pore (i.e., the greatest membrane pressure that a membrane pore can withstand [144, 145].

$$LEP = \frac{B\gamma_L \cos\theta}{r_{max}}$$

where γL is the liquid's surface tension θ is the apparent contact angle (CA) between both membrane surface and feed solution. rmax is the membrane's maximum pore size, and B is the pore geometry coefficient (for example, B = 1.0 for a circular pore and stretched membranes like PTFE with small curvature radius has B value of 0.4-0.6).

9.2 Mechanical Strength

This quality is essential to resist the significant stress and pressure applied to the membrane during module assembly and MD operation. A membrane's long-term performance may be impacted by pore collapsing and membrane breakdown due to insufficient mechanical strength. Because they cause mechanical weakness in the membrane, macrovoids are undesirable in membranes. According to some reports, structures that resemble sponges prevent the growth of large voids [146]. Several methods have been used to enhance the performance of the mechanical strength of membrane. It has been demonstrated that the application of nano additives enhances tensile strength and addresses membrane-breaking problems [147]. Moreover, the mechanical strength of the membrane is influenced by the membrane's structure. Guidelines for creating a membrane with adequate mechanical strength include wall thickness of membranes 100-200 m and pore diameter less than 0.2 µm [148].

9.3 Pore Tortuosity

The average length of the holes in relation to the thickness of the membrane is known as membrane tortuosity. A value of 2 is typically considered for the tortuosity factor in MD investigations and to estimate the transmembrane flow [15, 149-151] although a value as high as 3.9 was also observed [152]. The word "tortuosity" refers to the pore structure's divergence from a straight, meaning that the pores have a cylindrical form that is perpendicular to the membrane surface. More tortuosity causes poorer permeability since it is inversely related to the permeate flux [152].

9.4 Porosity

MD flux is greatly influenced by membrane porosity, also known as membrane void volume. More evaporation surface area may be found in membranes with increased porosity. The porosity of the MD membrane typically ranges from 30 to 85%. It is commonly accepted that regardless of the MD structure, membrane porosity increases lead to larger permeate flows. It should be noted that high porosity membranes have reduced conductive heat loss because the gases trapped inside the holes of the membrane have conductive heat transfer coefficients that are orders of magnitude lower than those of the hydrophobic polymer employed to manufacture the membranes [153-155]. The loss of membrane performance might occur as a consequence of diminished mechanical integrity, which should be kept in mind when one increases the porosity. MD membrane porosity has been estimated to range from 35% to 93% [156, 157]. Porosity, as opposed to other membrane features, has the greatest impact on DCMD performance, according to other studies [152, 158].

9.5 High Permeability

The membrane must be thin in order to get a high MD permeability [68, 159, 160] A high turnover rate per unit of time is evident from an economic perspective as high flux. Each factor that affects the shape and size of the holes has an impact on how permeable the membrane is because water vapor can only travel through the pores and not the membrane matrix. The largest fluxes recorded are 102 kgm^{-2} h^{-1} and 98.6 kgm^{-2} h^{-1} in studies by Aljumaily *et al*. and Wang, Teoh, and Chung, respectively [58, 161]. Bonyadi and Chung [162] The membrane made using a weak coagulant mixture of 80% methanol and 20% water possessed an additional permeable structure compared to the membrane made with water as the coagulant. (strong). To save money and the environment, methanol might not be the best coagulant to use in large amounts throughout the manufacturing process. In their analysis of how combined solvents affect the structure of PVDF-HFP, Garca-Fernández, Garca-Payo, and Khayet [163] discovered that larger pores resulted from an increase in the trimethyl phosphate ratio, which in turn increased permeate flow. Chang *et al* [164] employed non-toxic triethyl phosphate (TEP) to create a more porous, spongy layer in PVDF membranes in an attempt to transition membrane manufacture towards greener procedures. According to Silva *et al*. [165]

5 wt% PVP in PVDF membranes achieves a balance between high flux and effective salt rejection. Due to the membrane's very high permeability, they discovered that 2 wt% PVP caused a poor salt rejection. By increasing the PVP content to 5 wt%, the dope solution's viscosity rose, creating a denser membrane with fewer macrovoids that was effective enough to produce high flux and good salt rejection. A greater polymer solution concentration causes the liquid-liquid demixing to take longer, increasing viscosity, which creates sponge-like holes in phase-inversed membranes that lower permeate flow. In MD membranes, a satisfactory flux is typically produced at a polymer content of 16–18 wt%. In research by Garcia-Payo, Essalhi, and Khayet [166], it was discovered that as the pores were more condensed, the permeate flow decreased. Electrospun MD membranes are prized for their high porosity (over 80%), which produces a high flux, in compared to phase-inversed membranes [167].

9.6 Thermal Conductivity

Due to heat losses, high membrane thermal conductivity (km) reduces flow and energy efficiency [168, 169]. Thus, kilometers ought to be as little as feasible. Thermal conductivities for the majority of commercial MD membranes fall between 0.04-0.07 Wm^{-1} K^{-1} [170, 171]. It is possible that the thermal conductivity of a membrane might decrease with increased porosity because of the existence of air or water vapor with such a small thermal conductivity inside the pores. Besides that, bi or layered membranes having layers that are both hydrophobic and hydrophilic may be employed [172]. For optimal mass transfer, the hydrophobic layer must be as thin as possible, whereas conductive heat transfer must be restricted in order for the hydrophilic layer to be thick enough to prevent noticeably raising mass transfer resistance [170, 173]. Factors including the membrane's composition, thickness, and porosity may have an impact on the thermal conductivity of the membrane. Compared to ceramic membranes, Polymeric membranes conduct heat poorly (0.1–0.5 $Wm^{-1} K^{-1}$) [171, 174].

10.0 DESALINATION MEMBRANES

10.1 Graphene Desalination Membranes

Advanced desalination membranes may be built using graphene nanoparticles, which come in two basic forms: monolayer and stacked multilayer [175].

10.1.1 Monolayer Graphene Desalination Membranes

Due to the presence of the cloud of delocalized electrons from its -orbitals, pure graphene is impermeable, It thus stops even helium with a molecular radius of 1.3 Å from going through [176, 177]. Yet, simulations reveal that graphene membranes (GMs) can outperform existing desalination membranes (DMs), displaying orders of magnitude greater permeability and selectivity, by including holes of regulated size, density, and functionality [178]. Graphene with subnanometer-sized holes is shown in Figure 13 as a RO membrane.

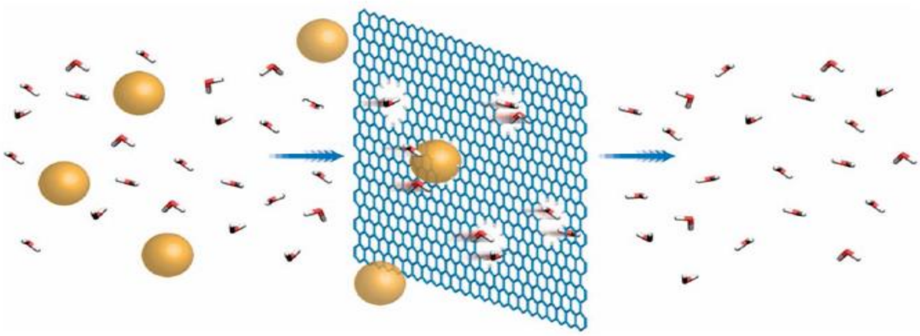

Figure 13 as a RO membrane, graphene with subnanometer-sized holes is shown in. In this mechanism, salt water (left), under high pressure, separates into two components: salt ions (golden spheres), which are blocked, and water molecules (red and white), which flow through the membrane [179]. Copyright 2016 Nature Publishing Group

Nanoporous graphene has been predicted to be one of the most desired materials for water desalination by molecular dynamics simulations due to its remarkable water flow rate of approximately 66 $l.cm^{-2}.day^{-1}.MPa^{-1}$ and 99% salt rejection depending on pore size and chemistry [180]. However, a conventional RO membrane may only have a water permeability of 0.01 to 0.05 $lcm^{-2} day^{-1}MPa^{-1}$, while providing the same salt rejection efficiency [181]. The initial capital cost and continuous operational expenses of desalination facilities are greatly decreased due to graphene's unusually high-water permeability, which is brought on by its atomic thickness. So, the creation of a highly selective and simultaneously permeable membrane for water desalination is promised by the regulated development of holes in a graphene structure with regard to size, density, and functionality. These benefits have prompted scientists to examine the graphene's filtering abilities both experimentally and virtually [182].

Size exclusion and dehydration effects processes are the most significant salt rejection methods because the suitable size for a water molecule (0.26 nm) is larger than the hydrated diameter of several ions in water, such as Na^+ (0.72 nm), K^+ (0.66 nm), Ca^{2+} (0.82 nm), Mg^{2+} (0.86 nm), and Cl^- (0.66 nm) [183]. Simulations using molecular dynamics indicated that graphene membranes with sufficiently narrow nanopores might completely block the passage of salt ions [184]. According to these investigations, the critical nanopore diameter for removing NaCl ranges from 0.6 and 0.8 nm, depending on the hydration radius of the ions. Along with the size exclusion effect, the nanopore chemistry and electrical charge of the nanopore edge also have an impact on ion rejection [183].

O'Hern *et al*. created a 25mm^2 graphene composite membrane by transferring a monolayer of CVD graphene onto a porous polycarbonate substrate. Their method makes use of monolayer graphene membranes with intrinsic holes. The size-selective transport of molecules through the membrane was aided by the intrinsic 1–15 nm diameter holes in the CVD graphene. 83% of the pores had a diameter of less than 10 nm, according to the scanning transmission electron microscopy analysis of the pore size distribution. The diffusion of molecules of various sizes, such as KCl, tetramethylammonium chloride, Allura Red AC (496 Da dye), and tetramethylrhodamine dextran (70 kDa), through the membrane was experimentally studied by the authors. The graphene composite membrane permitted the diffusion of tetramethylrhodamine dextran but prevented the penetration of KCl and tetramethylammonium chloride (12 nm). The bigger tetramethylrhodamine dextran molecules had a significantly poorer diffusive transport than the smaller ones. Measurements using scanning transmission electron microscopy confirm pore sizes are typically between 1 and 10 nm , which is consistent with the Stokes-Einstein molecular diameters of Allura Red and tetramethylrhodamine dextran, which are 1 and 12 nm, respectively. The observed permeability was consistent with estimates made by the continuum model for graphene with 0.012–0.61% porosity and 1–10 nm intrinsic pore size, or 0.025–0.15%. The authors asserted that monolayers of CVD graphene may be made large enough to allow for selective molecule transport [178].

10.1.2 Multilayer Graphene Desalination Membranes

High water permeability is just one of the numerous benefits of single-layer graphene membranes, but producing spill-free, large-area membranes with regulated pore density and size on an industrial scale remains difficult [185, 186]. Layered GO nanosheets could be used to create DMs to address this issue. Due in significant part to their structure—a single-atom-thick layer with a lateral dimension close to tens of micrometers—these nanosheets are incredibly stacked. The stable interlayer hydrogen bonds between the GO sheets form a freestanding membrane that is kept together [187]. In addition, chemical oxidation and ultrasonic exfoliation of graphite may be used to create GO nanosheets on a large scale at cheap cost. This process offers to produce stacked membranes at a low cost and with industrial applicability. Lastly, 2D graphene offers higher flexibility and solution processibility, as well as exceptional chemical and thermal stabilities. [188]. Figure 14b demonstrates how two neighboring graphene sheets may be separated by 2D nanochannels and formed as highly ordered films [187, 189]. The 2D channels of this arrangement allow water to permeate while rejecting unwanted solutes. Moreover, the GO nanosheets' inclusion of functional groups containing oxygen, such as carboxyl groups, permits functionalization and thus permits associated charge-based interactions with water contaminants [190]. Multilayer GO structure is a prime choice for the production of improved ionic and molecular sieving membranes for desalination due to its array of promising properties [184, 191, 192].

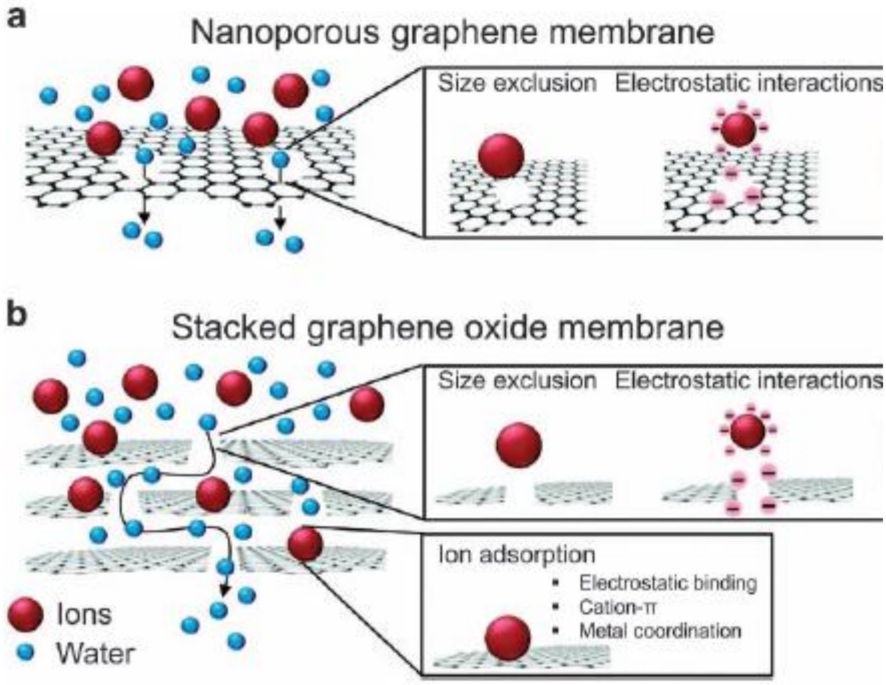

Figure 14A illustrates the separation mechanisms of two graphene membranes: (a) a monolayer membrane with controlled-sized nanopores, and (b) a multilayer membrane made of stacked GO sheets. (Reprinted with permission from Perreault *et al*.[193] Copyright 2016 The Royal Society of Chemistry)

10.2 Bridged Polysilsesquioxane Membranes

Polysilsesquioxanes (PSQs) are often synthesized by hydrolyzing trialkoxysilanes or condensing trihalosilanes to yield the [RSiO1.5]n chemical formula, which is the general formula for organic-inorganic hybrid materials. PSQ properties are intermediate between those of silicone and silicate, based on their unit structure (i.e., three Si-O bonds and one Si-R bond on one silicon atom). Due to its very stable three-dimensional siloxane (Si-O-Si) construction, PSQs are highly resistant to heat, chemicals, and mechanical stress. Because of their adaptability, reactivity, photoactivity, and wide variety of applications—from thermal and mechanical fillers to electronic and optical materials and even ceramic precursors—organic compounds constitute a class of their own (R). PSQ monomers are depicted in two classes in Figure 15. One reactive trialkoxysilane moiety is present in class one monomers. BPSQs (bridged polysilsesquioxane membranes) made from class 2 monomers have attracted considerable attention in recent years owing to their intriguing features, such as high porosity, that are difficult to create with basic class 1 monomers. Class 2 monomers, on the other hand, contain two or more trialkoxysilane units. [194-196]..

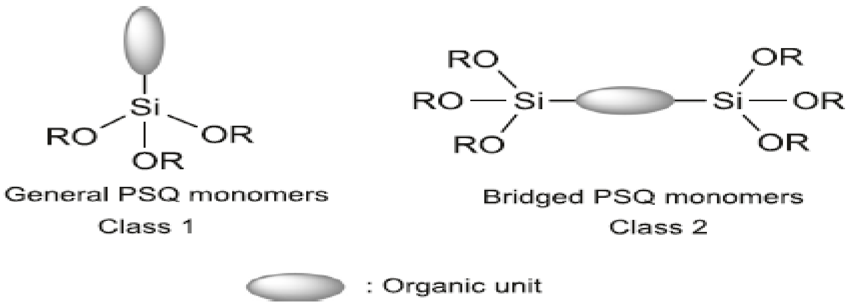

Figure 15 Chemical structures of polysilsesquioxane monomers

Lin *et al*. and Loy and Shea were the first to examine PSQs based on class 2 monomers [198, 199]. Next Corriu *et al*. investigated the gel's polymerization behavior, appearance, and chemical composition and showed that the gel's characteristics were significantly influenced by the bridge architectures of class 2 alkoxysilane monomers [200]. Sol-gel produced bridging PSQs have been studied for their potential as adsorbent materials, catalyst, and heat insulators due to their very high porosity and low density. This method has so far been applied to many class 2 monomers [201, 202].

The materials based on BPSQ can also be used to create separation membranes. As a primary illustration of separation membranes using a BPSQ-based separation layer, Castricum *et al*. produced a copolymer consisting of bis(triethoxysilyl) ethane (BTES-E1) and methyltriethoxysilane and documented its use to n-butanol dehydration. In contrast to silica membrane, this membrane, interestingly, demonstrated high-temperature endurance at 90 °C under humid circumstances [203, 204]. The Si-C bonds in the PSQ network's resistance to hydrolysis, which raised the membrane's hydrothermal stability, were responsible for the durability. According to Kanezashi, Tsuru, and colleagues, a bridging PSQ made by homopolymerizing BTES-E1 had greater porosity, which led to increased membrane gas permeance in comparison to the similar non-bridged PSQ membrane made from a normal class 1 monomer (i.e., methyltriethoxysilane) [205, 206]. BTES-E1-derived membranes may be employed as RO membranes for water desalination with great thermal stability and chlorine resistance, demonstrating the high potential of bridged PSQs as robust RO membrane materials [197]. To further increase porosity and improve water permeability, ethenylene and ethynylene were added to BTES-E1 as C2 spacers in place of ethylene [207, 208]. According to this finding, the bridge construction is crucial in adjusting separation qualities. Similar bridging PSQ-based membranes have also been investigated for use in other separation applications, such as gas separation.[209, 210]. Although having strong characteristics, these bridging PSQ membranes have less water permeance than traditional PA membranes. To boost water permeability without sacrificing selectivity, our research team has spent the last ten years exploring the creation of bridging silsesquioxane membranes using a variety of class 2 monomers (i.e., salt rejection for water desalination). PSQ monomers from the class 2. Sol-gel processing has been used to create RO membranes from a variety of class 2 bridged trialkoxysilane monomers. As was indicated before, bridging PSQ membranes made from ethylene- and ethenylene-bridged monomers (BTESE1 and BTES-E2) showed RO characteristics with strong thermal stability and chlorine resistance [197]. Through collaborations with this group, they developed ethynylenebridged monomer BTES-E3 [208]. Membrane water permeance increases in the following sequence when the monomer C2 bridge's unsaturation number rises: BTESE1, BTES-E2, and BTES-E3. Yet, in the same sequence, the salt rejection was somewhat reduced. Since stiffness would prevent the creation of tiny rings, adding a rigid bridge might result in pores growing larger. The polar -electron systems seen in BTES-E2 and BTES-E3 may also improve membrane hydrophilicity.

Water permeability and NaCl rejection are generally the two factors that may be used to evaluate the membrane's desalination performance. The introduction of a carefully designed bridging unit is required to improve both characteristics since these parameters often have a trade-off relationship. To build a high-performance desalination RO, the monomer structure must be optimized. A core unit and spacers that connect the core and the reactive form the bridging units [197].

10.3 Electrospun Nanofiber Membranes (ENMs)

MD membrane development now has access to a wide range of resources because to enormous advancements in nanotechnology. Since it is utilized to create membranes with high interconnected porosity, mechanical durability, tuneable hydrophobicity, and thickness, the electrospinning technology for creating nanofibers from a polymer solution has attracted an unprecedented amount of interest [173]. A lot of research has been done on ENMs and MD performance. Feng *et al.* originally showed electrospun PVDF membranes for the AGMD procedure. Subsequently, Essalhi *et al.* thoroughly investigated the impact of membrane thickness and polymer concentration on desalination using the DCMD technique. Using solutions with different concentrations, they created PVDF nano-fibrous membranes. With a feed stream containing 3 wt% NaCl, the resulting membranes had a rejection factor of around >99.99 [211]. Many adjustments have been documented to increase the MD performance efficiency of ENMs, including hot press treatment [212], loading nonfunctionalized/ functionalized nanomaterials [213], blending approach [214], surface modification [215] and so on. Heat pressing is a post-processing method that improves the mechanical and morphological properties of ENMs by putting them under a certain amount of pressure and heat for a certain amount of time while keeping their hydrophobicity and porosity. The performance of PVDF electrospun nanofibrous membranes with respect to pore size distribution was thoroughly investigated by Liao *et al*. using heat-press post-treatment and electrospinning process variables (spinneret moving speed, humidity, and polymer dope compositions containing inorganic additives) [216].

The same research team recently suggested a simple method for electrospinning a dual-layer silica/PVDF microporous composite membrane for the first time, and the membrane performances were better than those of standard PVDF nanofibrous membranes that had previously been reported [217]. The addition of functionalized nanomaterials helps boost the MD performance of ENMs, by modifying the roughness and surface chemistry (anti-wetting capabilities) of ENMs. For instance, A.K. An *et al*. improved the hydrophobicity and DCMD performance of PH ENMs by adding PFTS modified TiO_2 nanoparticles (Figure 16). The resulting membranes performed better at handling high salinity water (7 wt% NaCl, which is equivalent to RO concentrate) and had greater mechanical stability [218, 219].

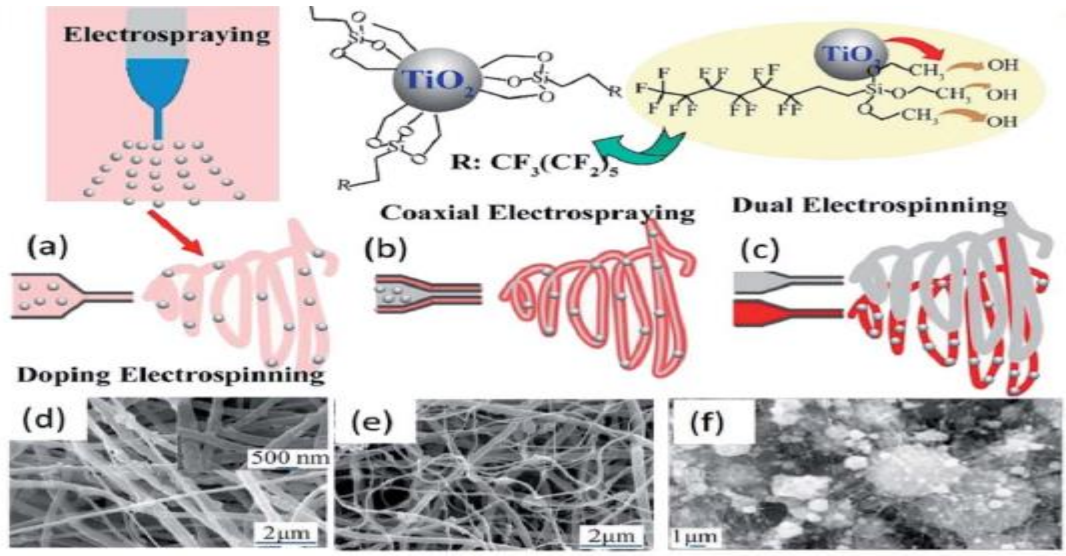

Figure 16 shows a schematic representation of the creation of 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (PFTS) functionalized TiO2 nanoparticles using a variety of techniques, including direct doping, co-axial electrospinning, dual electrospinning, and electrospinning in combination with electrospraying. It also shows SEM images of TiO2-polyvinylidene fluoride [218]

To increase the superhydrophobicity of PVDF ENMs for DCMD performance, Li *et al*. used SiO2 nanoparticles that have been treated with octadecyltrichlorosilane (OTS). Comparing their membranes to commercial PVDF membranes, they showed a 5–6 times greater vapour flow (Figure 17).

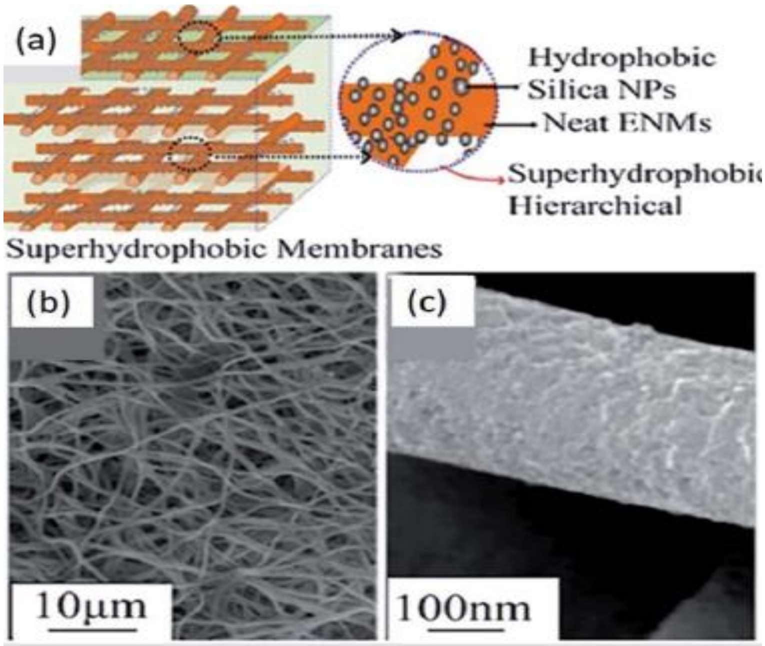

Figure 17 Superhydrophobic PVDF ENMs for DCMD application; (a) diagrammatic depiction of OTS-modified SiO2 nanoparticles integrated superhydrophobic PVDF ENMs; (b) and (c) SEM images of SiO2-PVDF ENMs. [218]

A superhydrophobic membrane with a contact angle (CA) of 158 was successfully developed by Z.Q. Dong *et al*. for a VMD application by grafting fluoroalkylsilane (FAS) onto glutaraldehyde crosslinked electrospun PVA nanofiber. Their membranes for desalinating high salinity water were chemically stable and performed (70%) better than a conventional polytetrafluoroethylene (PTFE) membrane [220]. By adding FAS-SiO2 nanoparticles (from 0 to 8 wt%) to PVDF solution, the same research team created PVDF-silicon dioxide (SiO2) ENMs that are even more superhydrophobic (CA 161°C). They discovered that when used for VMD, PVDF-SiO2 ENMs with greater FAS-SiO2 nanoparticle contents exhibited much better wetting resistance than membranes with lower FAS-SiO2 contents. For a feed solution containing 3.5 wt% NaCl, all PVDF ENMs, with or without FAS-SiO2, demonstrated a twofold increase in salt rejection efficacy over a commercial PTFE membrane. A metal-organic framework (MOF-F300) was added to PVDF ENMs (Figure 18) in another recent study to improve DCMD performance for handling 3.5 weight percent NaCl feed solution. Superhydrophobicity (CA of 138 °C_) was given by MOF doping with an increase in surface roughness from 285.28 to 661.80 nm. Hence, a greater impact on flux performance of PVDF ENMs was observed [221].

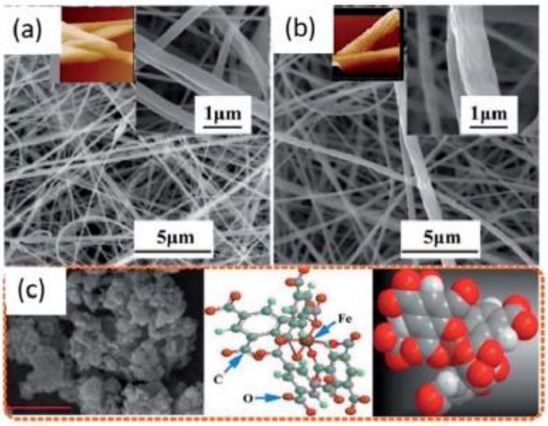

Figure 18 Metal organic framework (MOF-F300) incorporated PVDF ENMs (d) for DCMD performance; (a), (b) and (c) SEM images of MOF-F300- PVDF ENMs [218]

In recent research, PH ENMs were combined with covalently modified and fluorinated MWCNTs to produce 3D MD ENMs (Figure 19). Superhydrophobicity was enhanced by fluorination of MWCNTs with FTES, which resulted in a decrease in the number of hydrogen and -OH groups in MWCNTs through hydrolysis and condensation. The MWCNTs' dispersal was enhanced by the covalent modification. These membranes in DCMD showed around 60% higher water flow than the typical PVDF membrane for desalination of a 3.5 wt% NaCl solution [222].

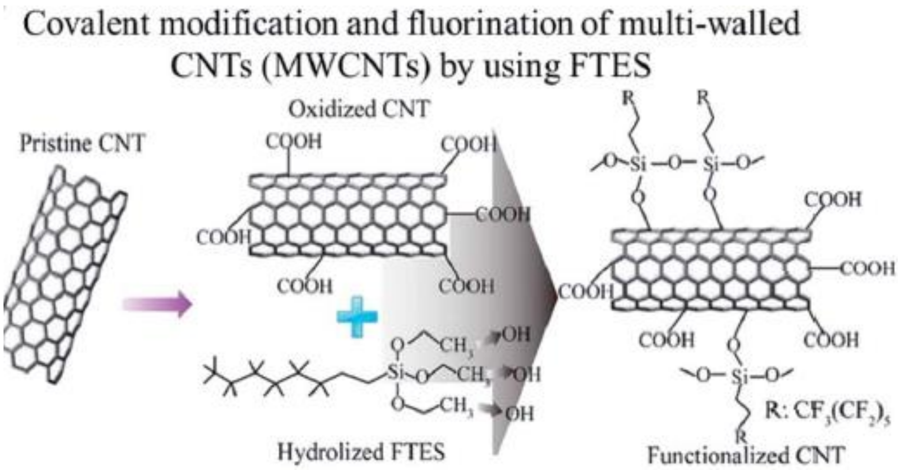

Figure 19 is a schematic showing how 3D PH ENMs are built utilizing FTES of MWCNTs to undergo covalent modifying and fluorination for DCMD use. Reproduced from ref. [223] with permission from Elsevier, copyright 2019

With the purpose of enhancing ENMs' functionality in MD applications, several groups investigated surface modification. Guo F. *et al*. coated poly(1H,1H,2H,2H perfluorodecyl acrylate) (PPFDA) on poly(trimethylene hexamethylene terephthalamide) (PA6-3-T) ENMs utilizing started chemical vapor deposition (CVD) approach to better understand the relationship between nanofiber width and flux performance. The resulting membranes, with fiber diameters varying from 0.25 to 1.8 mm, underwent salt rejection testing utilizing the AGMD procedure and a 3.5 weight percent NaCl solution. When the feed solution and condenser plate were 25–40 °C apart, they saw an increase in permeate flow from 2 to 11 kg m^{-2} h^{-1}. Liquid entry pressure (LEP) rose as a result of the membranes' enhanced hydrophobicity and decreased porosity (from 84 to 69%).[224]. Shon *et al*. investigated the impact of the length of the CF4 plasma surface modification on PVDF ENM AGMD performance. They discovered that the newly generated CF2-, CF2 and CF3 links gave the membrane's surface an omniphobic quality and reduced surface energy. This increased the membranes' resistance to wetting in the presence of low surface tension liquids such ethylene glycol, mineral oils, and methanol [225]. YC Woo *et al*. investigated the AGMD performance of double-layered ENMs made of a hydrophobic active PH layer and various hydrophilic bottom layers made of PVA, Nylon-6, and PAN. The active layer's CA was 140°C _, whereas the CA of the bottom ENM layers was less than 90°C. The AGMD performance of dual-layered ENMs was improved by the wettability of bottom hydrophilic ENMs [218, 226].

10.4 Two-dimensional Metal Organic Framework Membranes

Water desalination is a reliable method of producing fresh water and a practical solution to water scarcity due to the availability of saline water on earth [227]. Reverse osmosis (RO) techniques are used by most water desalination plants to remove ions and other unwanted substances [228]. Traditional membranes are still widely employed, although there are drawbacks, including sluggish water conveyance and high capital expenses because of energy loss during the desalination process [229]. Alternatives to these membranes that are being studied entail creating nanosized pores with dimensions ranging from a few Angstroms to several nanometers wide by drilling holes in ultra-thin membranes. When water penetration occurs, atomically thin membranes have much less friction than conventional membranes [178, 230]. Due to its single-atom thickness, graphene as a 2D membrane has a substantially greater water flow than zeolite membranes [135, 231]. Molybdenum disulfide (MoS2), a different 2D material, has been demonstrated to be more effective than graphene because of its hourglass-shaped pore structure, which increases water flux [232]. With the development of nanotechnology, research into 2D membranes and other nanomaterials is being investigated in order to find more effective ultra-thin membranes. Scientists' interest in materials having intrinsic porosity for water desalination has increased in recent studies [233, 234]. Pore drilling and other post-processing techniques are unnecessary for porous 2D materials. Hence, they may maintain their structure while improving the pore-membrane area ratio [233]. It is found that the covalent organic framework TpPa-1 with 25 offset-eclipsed layers and the graphene-like carbon nitride (g-C2N) have high water flux and efficient ion rejections among naturally porous materials [233, 234].

Another category of materials having intrinsic porosity of angstrom size is metal-organic frameworks (MOFs) [235]. Several MOFs have been investigated as possible desalination and ion/gas separation possibilities [236]. According to reports, Cu3(BTC)2 membrane exhibits exceptional selectivity and high penetration while separating H_2 gas [237]. Another recent study demonstrates that UiO-66 membrane may be produced for the desalination of water [238]. Additionally, ZIF-8 and UiO-66 membranes are claimed to create rapid selective transport of alkali metal ions [239]. As the ion rejection rate of a membrane during desalination is significantly influenced by the size of the hole [232, 240], In addition to having holes that are small enough to reject ions, the optimal material for water desalination should also have pores that are big enough to allow for quick water transfer. The Hexaaminobenzene (HAB)-derived 2D MOFs, among other 2D conductive MOFs [241], been thoroughly investigated for energy storage purposes [242]. Nanopores in conductive MOFs layers have an area of roughly 43.3 2 and a diameter of 8. (Figure 20) They are the best membranes for water desalination due to the size of their holes and the experimental ability to fabricate a few layers of 2D MOFs 34–36 [243, 244]. According to Zhonglin Cao, one of the biggest challenges the world is now experiencing is providing access to clean, drinking water. Using energy-efficient nanoporous materials for water desalination may become possible as nanomaterials research advances. In this work, they showed how conductive metal-organic frameworks (MOFs) that are extremely thin may effectively reject ions while yet allowing for significant water flux. They identified the ideal ion rejection rate using two-dimensional multi-layer MOF by molecular dynamic modeling. 2D MOFs' naturally porous structure allows for water permeability that is 3 to 6 orders of magnitude greater than that of conventional membranes. As compared to single-layer nanoporous graphene or molybdenum disulfide (MoS2), few layers of MOF membranes demonstrate an order of magnitude greater water flux without the need for pore drilling. Water permeation simulations, water density/velocity profiles at the pore, and water interfacial diffusion close to the pore all corroborate the good performance of 2D MOF membranes. A potential answer for energy-efficient water desalination is provided by the water desalination capabilities of MOF [245].

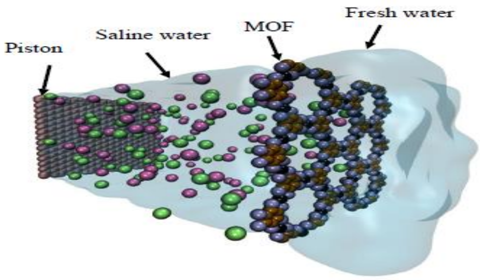

Figure 20 shows a schematic of a typical simulation box, which includes a graphene piston, salty water containing potassium and chloride ions, a membrane (MOF, graphene/MoS2), and a piece of fresh water [245]

11.0 CONCLUSION AND FUTURE OUTLOOK

After many years of ongoing research to understand the idea of MD and its issues. Yet, there should be a lot of obstacles removed. According to the most recent advancements, MD is usable in a variety of applications, including desalination and wastewater treatment. The commercialization of this method can benefit significantly from the production of high-quality MD membranes with properties including maximum hydrophobicity, great permeation flux, reduced fouling propensity, strong mechanical strength, poor thermal conductivity, and higher LEP. Low water flux, wetness, and the weak mechanical qualities of MD membranes are some of the barriers to its widespread commercialization. Water efficacy, biofouling, and a shortage of appropriate modules are just a few of the issues affected its performance. Research work and investigations are required in this exciting research area in order to go forward and address a variety of challenges associated to the MD process.

12.0 APPENDIX

All abbreviations and their full names are included in the appendix.

Abbreviations	**Name**
AGMD	air gap membrane distillation
AG	air gap
BTESE	Bis(triethoxysilyl)ethane
CP	concentration polarization
CVD	chemical vapor deposition
CNT	Carbon nanotube
DCMD	direct contact membrane distillation
ENM	electrospun nanofibrous membrane
ED	electrodialysis
FAS	fluoroalkylsilanes
FO	forward osmosis
GO	graphene oxide
MOF	metal organic framework
MWCNT	multi wall carbon nanotube
MEE	multiple effect evaporation
MoS_2	molybdenum disulfide
MED	multiple-effect distillation
PP	polypropylene
PES	polyethersulfone
PE	polyethylene
PTFE	polytetrafluoroethylene
PVDF	polyvinylidene fluoride
PSQ	polysilsesquioxanes
BPSQs	bridge polysilsesquioxanes
Abbreviations	**Name**
PFTS	perfluorooctyltriethoxysilane
RO	reverse osmosis
SGMD	sweep gas membrane distillation
TP	temperature polarization
VMD	vaccum membrane distillation

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