Functional nanomaterial based membrane in membrane distillation for water reclamation

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Abstract

Membrane technologies have been expanded to treat seawater, brine water, wastewater, and polluted water to provide clean water. In membrane distillation (MD) application, a membrane with low surface free energy is preferable to prevent membrane wetting. Thus, the pristine membrane was often modified with functional material to enhance the membrane performance during operation. In this paper, the mechanism of MD is briefly described according to different membrane configurations. Additionally, case studies for pilot plant MD were discussed. This is followed by the membrane fabrication techniques, functional material used for membrane modification and application of functional membrane in MD system. Finally, a future outlook and conclusion were made based on the review.

Keywords: Membrane distillation; Pilot plant; Nanomaterial doped membrane; Surface modification; Membrane performance; Long term stability

1. Introduction

Our earth’s surface is covered with 70% of water but only 3% of the water is freshwater [1]. At the present, more than one billion people lack access to safe water [2]. In Asia, it was reported that a total of US$1.2 trillion in economic losses from 1970 to 2019 were due to water stress [3]. Over the past ten decades, the world’s water demand has increased by 600% which is equal to a 1.8% each year [4]. As reported by UN-endorsed projections, by the year 2030, freshwater demand will surpass the water supply by 40%. The growth of water demand is due to the increase in population, fast development of the economy, climate change, pollution, poor water infrastructure and human activity [5,6]. Fig. 1 illustrates the concept of a clean water crisis due to increasing water demand and decreasing water availability. The global water scarcity issue has been affecting environmental sustainability, food production, public health and industrial efficiency [7–9].

The global view of the area with water stress is shown in Fig. 2. Although water infrastructure such as the aqueduct, cistern, rainwater harvesting and dams brought advantages to billions of people, however, these strategies are not sufficient to address the water crisis. It is crucial to ensure adequate water resources for humans’ well-being and survival. One of the solutions to address the water shortage issue is to invest in technologies such as wastewater recycling, solar water filtration, desalination plant and membrane filtration to meet the expanding water demand.

Membrane distillation (MD), a developing water reclamation technology adopting brackish water and seawater has attracted attraction from researchers and industry due to its exceptional advantages such as the capability to
treat high salinity feed with high salt rejection (~99%) thus producing high-quality water. MD is a thermally driven membrane process that required a temperature between 30°C to 70°C and pressure near atmospheric pressure for operation [11]. During MD operation, a microporous membrane with hydrophobic nature was selected to segregate between the hot feed stream and cold permeate stream [12]. The temperature difference between circulating feed and permeate creates a vapor pressure gradient along the membrane which became the driving force of evaporated water vapor at the hot feed to transport through the hydrophobic membrane. The water vapor that is transported through the membrane pores would condense on the cold side and generate clean water [13]. Due to the low temperature required during the MD process, sustainable sources such as waste heat, solar and geothermal can be employed to heat the feed stream [14]. Therefore, MD has been applied in numerous applications such as brackish and seawater desalination [15–17], wastewater reclamation [18–20] and resource recovery [21–23].

Researches often report on the factors which hinder the development of MD due to high thermal energy demand, low permeate flux compared to other membrane technology, membrane wetting, membrane fouling, complexity in transport process compared with reverse osmosis process and insufficient commercial membrane for MD application. In fact, it is expected that MD is at the boundary of commercialization for industrial application after decades of research has been conducted on MD. Nevertheless, most of the research is at the lab scale or bench scale where the active membrane areas are insufficient for industrial application. Most of the bench-scale research with favorable results often could not be reproduced in the full-scale plant when the operating parameters have been magnified [24]. In addition, the scale-up process in MD complicates both mass and heat transfer of MD process [25,26]. Thus, pilot plants for MD research to obtain useful operational data are the key to MD industrialization. Unfortunately, the current research on full-scale MD plants is still insufficient.

The conventional MD is still far from performing at a level that would spur rapid acceptance by the desalination industry due to limitations such as temperature polarization and membrane fouling and wetting issue which lead to low vapor flux at prolonged operation [27]. Hence, membranes are often modified to optimize the MD process. The purpose of surface modification is to achieve preferable properties during operations. Commercial membranes or pristine membranes are often modified to mitigate issues such as membrane wetting and fouling, poor hydrophobicity and low mechanical strength [28,29]. Membrane can be modified
via surface coating, electrospinning and plasma treatment. Among the modification techniques, coating is the most widely used technique in membrane modification due to its easy handling and less cost. In addition, membrane that was modified via coating almost fit all membrane configurations. Unlike electrospinning and plasma treatment, both modifications are used in direct contact membrane distillation configuration by preference [30]. Membrane modified with electrospinning to improve antiwetting and antifouling of the membrane [31]. On the other hand, membranes modified with plasma treatment were utilized in organic separation and actual effluents [30].

The expanding interest in functional materials allowed researchers to develop high-performance MD membranes. Nanoparticles (NP), carbon nanotubes (CNT), and graphene are nanomaterials selected for MD membrane modification [32] because they provide membrane with excellent properties such as high permeate flux, long-term stability, antiwetting, antifouling and chemical resistance [33,34]. Hence, nanomaterial has been widely adopted to enhance membranes’ physico-chemical which later helps in the improvement of MD performance. CNT and graphene-based membranes are considered carbon-based membranes with numerous functionalities especially in the enhancement of water transport properties which are then utilised by researchers in actual seawater conditions [35]. However, most nanomaterials face challenges during membrane fabrication such as stability of NP, NP size uniformity, synthesised techniques, scaling up of NP for application and environmental concerns [36,37]. When the nanomaterials are coated or embedded in MD membrane, it is crucial to ensure the stability of NP on/in the membrane active layer to prevent NP pass through the membrane to the permeate side during MD operation which could deteriorate the water quality. Therefore, strong chemical interaction or bonding between nanomaterial and the membrane has to examine before proceeding with water treatment application.

This paper presents recent studies in MD membrane modification techniques and functional materials used for MD membrane modification. This article starts with the discussion of the MD mechanism, followed by case studies for the pilot unit for the MD system and current practice in MD is reviewed. Next, membrane modification techniques such as surface coating, electrospinning and plasma treatment are introduced. This is followed by a comprehensive review of materials used to fabricate functional membrane and their application with a different configuration of MD. Lastly, a brief outlook and conclusion based on modification of functional membranes for future research related to water reclamation are provided. It is expected that the systematic elucidation in this paper will enlighten readers with the understanding of MD fabrication techniques with functional materials for the application in the MD system which eventually inspires them to further investigate novel MD membranes for water reclamation.

2. Membrane distillation for desalination

2.1. Mechanism of membrane distillation

In MD system, a membrane with low surface free energy is necessary, thus, MD membrane should be made from a hydrophobic polymer which is hydrophobic. The most commonly used polymer for MD application is polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE) and polypropylene (PP) [38]. However, there is a lack of commercial membrane for MD with wetting and fouling resistance and high-performance. Therefore, hydrophobic polymers are selected due to their characteristics such as easy modification, scale-up, fabrication and low costs [39]. Fabrication such as phase inversion, electrospinning, sintering, extrusion stretching and other technologies have been adopted to the synthesized membrane [40]. Except for polymeric membranes, materials such as metals, carbon nanotubes and ceramic have also been discovered for MD desalination studies [41].

Four major MD configurations have been developed which are air-gap membrane distillation (AGMD), direct contact membrane distillation (DCMD), sweep gas membrane distillation (SGMD) and vacuum membrane distillation (VMD). Among these configurations, DCMD is the most commonly used configuration in the desalination and wastewater treatment process mainly due to its ease of operation [42]. Besides, it was found that the DCMD configuration is the most ordinary mentioned configuration in literature and lab-scale studies for water recovery. Nevertheless, DCMD has a high thermal conductivity which experienced heat loss through convection via the membrane matrix and pores [43]. The introduction of AGMD is due to the limitation of DCMD in heat loss via conduction and also additional expenses for the add-on condenser in the SGMD system [26].

In an AGMD system, the hot feed remains contact with the membrane surface meanwhile the evaporated vapor that passed through the membrane pores will enter a stationary air-gap and then be condensed on a chilled plate. With the design of an air-gap in MD system, heat loss due to membrane conduction is reduced, yet, the presence of an air-gap would increase the resistance of mass transport. Consequently, under the same operating conditions, AGMD has a lower permeate flux when compared to the DCMD system [44]. The introduction of an air-gap allowed permeate to condense at the cooling plate without contact with the membrane surface, thus, it is applicable in the field where other MD configurations were limited.

In an SGMD configuration, condensation of vapor happened on the outside of the membrane module with the aid of an additional external condenser to collect the vapor. To create a sweeping flow to collect vapor at the distillate side, inert gas was utilized. Compared with AGMD, SGMD has higher mass transport and lower heat loss due to the sweeping flow [45]. Therefore, sweeping gas flow and feed temperature are the most important operating parameter in controlling the permeate flux [46,47]. The configuration of VMD is almost similar to AGMD where permeate is collected outside of the membrane module in a condenser. Instead of sweeping gas, a vacuum pump is employed at the permeate side to assist the vapor transport via vacuum suction. The presence of a vacuum pump could reduce mass transfer and increase membrane permeability. Hence, in the VMD configuration, conduction heat loss was insignificant [48]. Table 1 shows the working principle of MD configurations with their advantages and disadvantages.
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<th>Configuration</th>
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<th>Pros and cons</th>
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| Air-gap membrane distillation | Hot feed contact with membrane surface meanwhile the evaporated vapor that passed through the membrane pores will enter a stationary air-gap and then condensed on a chilled plate | Pros:  
- Heat loss due to membrane conduction reduced  
- Recovery of latent heat on a chilled plate  
- Permeate condense without contact with the membrane surface  
Cons:  
- Air-gap increase the resistance of mass transport  
- AGMD has a lower permeate flux compared to DCMD |
| Direct contact membrane distillation | Both hot feed and cold permeate are in contact with the membrane and its surface facing the hot feed. The evaporated vapor is transported via membrane pores and condensed at the cold permeate side | Pros:  
- Easy to operate  
- Simple MD design  
- High permeate flux  
Cons:  
- High heat loss via membrane conduction |
| Sweep gas membrane distillation | Inert gas was utilized to create a sweeping flow to collect vapor at the distillate side. Vapor condensation takes place on the outside of the membrane module with the aid of an additional external condenser to collect the vapor | Pros:  
- Higher mass transport and lower heat loss due to the sweeping flow  
Cons:  
- Additional expenses for the add-on condenser and sweep gas during operation |
| Vacuum membrane distillation  | A vacuum pump is employed at the permeate side to assist the vapor transport via vacuum suction. Vapor condensation takes place on the outside of the membrane module with the aid of an additional external condenser to collect the vapor | Pros:  
- A vacuum pump could reduce mass transfer and increase membrane permeability  
- Heat loss via conduction was insignificant  
Cons:  
- Additional expenses for the add-on condenser and vacuum pump. |

Adapted from Lyly [49].
2.2. Membrane distillation in full-scale plant

MD technology developers have installed MD pilot plants since the 2000s. In the year of 2006, the first MD pilot plant demonstration was carried out at Senoko Incineration Plant, Singapore where the capacity of the plant was 1 m$^3$/d [50]. Later in the year 2011, two pilot plants were installed in Singapore by two different MD technology developers. One was installed at Jurong Island with a capacity of 100 m$^3$/d and another one was a solar-powered plant at Marina Barrage with a capacity of 1 m$^3$/d. In the year 2014, the first seawater desalination plant for drinking water using waste heat from a power generator was set up at Gulhi, Maldives which could produce 10 m$^3$/d of drinking water. The largest MD full-scale plant was designed with a capacity of 400 m$^3$/d for brine treatment and was constructed in South Korea under the Global MVP program [51]. In 2019, the MD pilot plant desalination project has been launched in the Middle East which focuses on operation and maintenance technologies and the employment of renewable energy [52]. The development and progress of MD technology are slow when compared with other membrane technology especially the reverse osmosis (RO) process. The latest highest production of desalination plants reached 65,500,000 m$^3$/d [53].

One of the main drawbacks of the commercial implementation of MD is its high thermal energy consumption which gave a big impact on the operation cost. Therefore, thermal efficiency analysis for MD has to be studied on a pilot scale. According to Kim et al. [54], the minimum theoretical energy for MD desalination is 7.67 kWh/m$^3$ while only 1.05 kWh/m$^3$ for the RO process. However, MD still draws researchers’ attention because low-grade heat sources can be utilized for MD operation. Additionally, MD could treat water with high salinity where it cannot be operated with the RO process [52]. Woldemariam et al. [55] analyzed the energy demand for a pilot-scale AGMD system in treating pharmaceutical effluent. Three cases of heat supply to the feed were demonstrated which were utilized of external waste heat, direct heating and heat integration between the hot and cold side of the AGMD system. In the case of utilizing external waste heat and direct heating, the thermal required was 692 and 735 kWh/m$^3$ respectively while the thermal required for heat integration between hot and cold sides was 105 kWh/m$^3$. Although heat integration between the hot and cold sides in the AGMD system is possible, yet, the permeate flux was low where investment is necessary for a larger membrane surface area.

The improvement of heat consumption was further evaluated with vacuum-enhanced AGMD which was carried out by Andres et al. [56] in the latest thermal energy study using a spiral-wound module. The 2.7 m long spiral wound module achieved a heat efficiency of 49 kWh/m$^3$. However, the downside of this pilot-scale V-AGMD was the permeate quality where salinity at the permeate side increased due to the use of vacuum. In large-scale MD plants, heat is still a major problem, this can be further proven in the VMD pilot plant study by Jia et al. [57]. The heat demand for a VMD plant using 8 PTFE hollow fiber was 748.1 kWh/m$^3$ to treat radioactive wastewater. However, it was found that heat loss of the hollow fiber module in an axial direction was significant during operation due to temperature polarization.

In addition, almost all of the membranes used in the current MD pilot plant study are commercial membranes. The use of modified membranes in pilot plant studies is remarkably scarce. However, membrane modifications are important to address the MD issues such as low permeate flux, temperature polarization, membrane-fouling problem and membrane long-term stability. Membrane modification with different techniques results in different membrane properties which could improve the MD performance. It is difficult to have a single perfect membrane that could address all the issues in the MD system. Hence, the current study on the modification of membrane was conducted to achieve desirable MD performance and results.

3. Functional membrane

3.1. Membrane surface modification techniques

3.1.1. Surface coating

There are a few methods for surface coating such as dip-coating, grafting and sol–gel. Fig. 3 shows the schematic drawing for membrane modification techniques for dip-coating, surface grafting and plasma treatment. Among the methods, it was found that the grafting method can easily produce membrane surfaces with superhydrophobic or omniphobic character depending on the crosslink produced from grafting [58,59]. Porous membrane that is modified via a dip-coating method usually results in high permeate flux due to coating with hydrophilic material on a hydrophobic surface [60]. It is the easiest method for membrane modification because it does not involve many steps, not required harsh temperature, pressure and energy during modification. Thus, dip-coating is considered the most feasible technique for scaling up for industrial applications. Yet, the coating method could not precisely control some membrane characteristics such as porosity and pore size which is also a concern when it comes to industrial application. Sol–gel methods were adopted to fabricate membranes with a less porous surface [61]. Membrane fabricated via sol–gel has significant improvement in mechanical strength and membrane structure [62]. However, it required costly material and two steps which are the formation of sol and gel respectively during fabrication. Hence, this method is seldom applied in the membrane modification of commercial membranes.

3.1.2. Electrospinning

Electrospinning can produce a membrane with oleophobic, superhydrophobic and omniphobic characteristics depending on the nature of the dope solution [66]. The electrospun membrane possessed characteristics such as high water and oil contact angles, LEP and permeate flux [67]. In addition, electrospinning can be controlled by adjusting the composition and material used for dope solution and explosion time under spinning [68], therefore, membrane that fabricates via electrospinning is consistent in terms of membrane characteristics such as hydrophobicity, thickness, porosity and pore size. Fig. 4 shows a schematic diagram of
Comparing the cost between the coating method and the electrospinning method, electrospinning has a lower modification cost due to the low volume of dope solution for modification and is fully utilized to embed on the membrane surface and membrane matrix [69]. However, for the coating method, large amounts of substances and solvents were prepared and after membrane coating, the extra coating solution was discarded which increase the modification cost. Nevertheless, electrospinning techniques involve expensive initial costs for the robust equipment setup and facing scale-up challenges mainly due to nozzles clogging and stability of spinnerets during continuous operation [70].

### 3.1.3. Plasma treatment

For the formation of plasma during plasma treatment, high temperature and pressure are required which make the modification become difficult and costly compared with other modification methods [72]. Therefore, plasma treatment is the least studied modification method in the last few years. Fig. 5 shows a schematic diagram for a plasma treatment process. Plasma modification is greatly affected by the duration of membrane exposure [73]. The desired membrane characteristics are modified by utilizing different attachments and gases to create radicals on the surface of membrane. The fabricated membrane via...
plasma treatment is more robust due to the bonding formation between the modified agent and membrane surface [74]. Nevertheless, plasma treatment is a high-speed process that could effectively enhance membrane characteristics such as porosity, pore size and surface roughness [75]. The high porosity of membrane would result in higher permeate flux during operation.

3.2. Functional nanomaterial doped membrane

3.2.1. Nanoparticles

Research involving MD membrane modification with NP has been studied extensively to solve issues related to porosity, fouling, flux and wetting. NP are materials which have a size less than 100 nm but larger than molecules and atoms. Membrane that has been modified with NP could increase membrane surface roughness. Membrane with high surface roughness enables the minimal contact of water droplet on membrane surface which then results in the improvement of hydrophobicity of membrane. Besides, NP such as silicon dioxide (SiO2), titanium dioxide (TiO2) and silver (Ag) has antibacterial property which impedes biofouling [77].

SiO2 nanoparticles that are used in membrane modification have been explored as a material to dramatically improve the permeate flux of MD system. This can be proven in the SiO2 modified membrane study by Zhang et al. [78], SiO2 and polydimethylsiloxane (PDMS) were added into PVDF polymer solution to fabricate SiO2-PDMS-PVDF hollow fiber membrane via phase inversion. PDMS was used to create physical cross-linking between SiO2 nanoparticles and PVDF polymer membrane. The effect of the concentration of SiO2 on membrane property and performance was investigated. It was found that membrane that doped in with 1% of SiO2 is more favorable for VMD system due to its high permeates flux and antiwetting properties. Despite that, SiO2-modified membranes have weak mechanical strength and low LEPw with the increase of SiO2 particles in the membrane matrix which would affect the membrane’s long-term stability. Hence, in the study of Zhou et al. [79], multi-walled carbon nanotubes (MWCNT) as a reinforcement additive was used together with SiO2 particles during membrane modification to improve the mechanical properties and durability of membrane. MWCNT and SiO2 particles with different natures which are superhydrophobic, hydrophobic and hydrophilic were blended in the PVDF polymer solution respectively. Membrane that was modified with 2 wt.% of MWCNT and 7 wt.% of hydrophilelic SiO2 has the best performance in the VMD system which gave a permeate flux value of 4.55 LMH with 99.8% of salt rejection. Since SiO2 is a stable particle, it can act as a core and the surface is being modified with a functional material. This can be found in the study of Lyly et al. [27] where a thermoresponsive membrane by modifying SiO2 particles with temperature-responsive polymer poly(N-isopropylacrylamide) (PNIPAM) was developed. The fabricated membrane exhibited antifouling properties and demonstrated self-cleaning abilities during membrane cleaning. The feed temperature was altered during membrane cleaning to stimulate the PNIPAM on the membrane surface. The actuation of the SiO2-PNIPAM on the PVDF membrane successfully repelled organic foulants such as bovine serum albumin (BSA) and sodium alginate (SA) that fouled on the membrane surface. The fabricated thermoresponsive membrane was tested under long-hour operation, the flux remain at 10.32 LHM for 120 h of operation with 99.9% of salt rejection.

TiO2 nanoparticles are hydrophilic in nature, thus, introducing TiO2 hydrophilic nanoparticles would cause a decrease in hydrophobicity and eventually lead to membrane wetting during MD process. Therefore, TiO2 is often functionalised with fluorosilane moieties to reduce its hydrophilic behaviour by decreasing its surface energy. Lee et al. [80] functionalised TiO2 nanoparticles with fluorine coating additives 1H,1H,2H,2H-perfluoro-octyltriethoxysilane (FTES) and coated them on PVDF-HEP membrane surface by electrospraying. The membrane has good permeability with 40 LHM for 2 d of operation with 7 wt.% of NaCl and 99.99% of salt rejection. In another similar modification study, the fabricated superhydrophobic TiO2-PVDF-HFP (hexafluoropropylene) membrane has shown antifouling properties towards algal organic matter where the membrane could recover its hydrophobicity by simply flushing with water for 30 min [81]. Besides, TiO2 nanoparticles have been used to modify photocatalytic graphene oxide (GO) membrane to remove concentration polarization during DCMD operation. TiO2 could be coated on top of a hydrophobic PVDF membrane to produce a self-cleaning GO-PVDF photocatalytic membrane. The modified membrane achieved 96% of flux recovery after 8 h of UV radiation in a photocatalytic reactor [82].

Ag nanoparticles are toxic towards microorganisms such as bacteria, fungi and viruses [83,84], therefore, they can be adopted in water treatment applications. Ag is capable to enter the cells wall of microorganisms to destroy the cell envelopes and inhibit the growth of microorganisms [85]. Membrane that is dosed with Ag nanoparticles could function as a preventive measure that helps to hinder the biofilms formed on the membrane surface and pores. This was proven in the study by Chew et al. [86]. The fabricated Ag-PDA/PVDF hollow fiber membranes were immersed...
in a bacterial solution for 120 h and it was observed that a negligible amount of bacteria was attached to the membrane surface. Thus, the Ag-PDA/PVDF membrane possessed anti-bacterial properties. The study on optimum loading of Ag particles in membrane is crucial to prevent high loading of Ag which could eventually block the membrane pores and affect the water flux. Most of the literature on fouling studies in MD is dominated by organic and inorganic fouling and scaling, the literature report on MD biofouling is limited due to microorganisms could not survive at high temperatures and high salinity during MD operation. However, studies have shown that the release of algal organic matter (AOM) from microorganisms could attach to the membrane surface, induce membrane fouling and affect the MD water flux [87]. Additionally, discharged wastewater consists of thermophilic bacteria in high concentrations which can survive at elevated temperatures (>80°C). Besides, Ag nanoparticles have a strong plasmonic heating effect which causes the conversion from light to heat. It is suitable to apply in MD system to heat the membrane surface due to the low operating temperature (<70°C) on the hot side. The photothermal membrane has been successfully demonstrated by Ye et al. [88]. In their study, a double layer Ag-PVDF/PVDF membrane to study the photothermal performance of membrane under UV assisted DCMD system was fabricated. It was found that 20 wt.% of Ag loadings in membrane have the best photothermal performance which could reach up to 92.3°C under 1 min of UV light. Furthermore, the fabricated photothermal membrane exhibits superior durability for 60 h of operation without pore wetting. The thermoplasmonic property of Ag which acts as nano-heaters can restrain the temperature polarization in MD operation [89].

### 3.2.2. Carbon nanotubes

CNT and graphene are carbon-based low dimension nanomaterial that has been used in MD modification [90]. They possessed properties such as high thermal conductivity, tuneable hydrophobicity, high strength, high specific area and good permeability for MD membrane [91]. The use of CNT or graphene in MD enhanced the membrane performance in terms of permeability and fouling propensity. The loading of carbon-based nanomaterial should be low because there is a possibility that the overloading of thermal conductive carbon nanomaterial would cause temperature polarization [92].

CNT has gained attention from researchers due to its excellent properties. CNT-based membranes are suitable to apply in MD systems owing to their high electrical and thermal stability, good permeability, antiwetting, antibacterial, good mechanical behaviors lightweight and easy to clean [93,94]. The water flux performance with CNT modified membrane improved due to the rapid diffusion capability of CNT along the membrane surface. Additionally, the presence of CNT on membrane surface could increase conductive heat transfer from the feed to membrane surface which could decrease the thermal polarization effect [95]. Yet, fabrications of CNT polymeric membrane face challenges such as agglomeration of nanoparticle CNT in aqueous solution or easily re-aggregate in polymer solution during electrospinning fabrication due to long fabrication time. Agglomeration of CNT would result in beads forming on membrane and blocking the membrane pores, which eventually affect MD performance. However, the agglomeration of CNT could be minimized by adopting spraying method [96]. The anti-fouling property has been demonstrated in the study of Gupta et al. [97] where a CNT-based membrane achieved high permeability with no biofouling. They observed that there is no biofilm formation on membrane surface by utilising the *E. coli* and *G. stearothermophilus* contaminated water in a DCMD process.

#### 3.2.3. Graphene and its derivatives

Graphene is hydrophobic in nature which could enhance membrane wetting and fouling resistance and mechanical strength which is necessary for MD system [98,99]. On the other hand, modification of membrane with oxidised graphene renders membrane with hydrophilicity that could prevent membrane fouling [100]. Graphene oxide (GO) is amphiphilic in nature and consists of epoxide and carboxyl groups which show good conducting and tensile strength [101]. In MD process, GO are able to assist water molecules transport via the hydrophilic–hydrophobic gateway. The presence of epoxide and carboxyls group act as a hydrophilic gate in GO that attracts water to the hydrophobic carbon layer [102]. Based on the capture and slip flow theory, the formation of gaps between GO layers allows water to slip to the permeate side which results in a flux increment [103]. Besides, GO became a potential candidate in water separation applications due to its antibacterial properties against harmful microorganisms in water such as *E. coli* and *S. Aureus* [104,105]. Therefore, studies on the incorporation of GO in polymeric membranes have been conducted by researchers in water separation process.

The increase of GO concentration in MD membrane would render the membrane with increased water permeability, tensile strength and hydrophilicity. An effect of GO concentration on member properties has been conducted by Camacho et al. [106]. In a fabrication work conducted by Intrchom et al. [107], they utilize the hydrophilic nature of GO and modified the commercial PTFE membrane by casting these hydrophilic GO on the permeate side to enhance the permeate flux. The DCMD setup has a high permeate flux (~48LMH) for 60 d of DCMD operation with no detection of GO and salt at the permeate side. On the other hand, in the work reported by Mao et al. [108], the nature of GO-based membrane towards organic and surfactant fouling was studied. The membrane was modified by embedded with SiO₂ and grafted with hexadecyltrimethoxysilane (HDTMS) to increase membrane roughness via vacuum filtration method. Varying the oxidation temperature during GO membrane fabrication could affect the membrane permeate flux. This was proven in the work of Xu et al. [109], where they observed that 70°C of oxidation temperature would increase the epoxy group and decrease in hydroxyl group in GO which then enhanced membrane permeate flux. Table 2 shows the summarised modified membrane with NP and their significant results.
3.3. Application of functional membrane distillation in long-term stability study

Table 3 summarized the application of MD with different membrane configurations in a long-term study. In a pilot-scale AGMD study by Duong et al. [110], low-density polyethylene (LDPE) membranes were used for long-term study using the actual seawater. Although the salt rejection was up to 99% for 7 d of operation, it was found that the permeate flux was low with only 0.6 LMH. Due to the lack of commercial MD membrane with good performance, modification of membrane is required to produce a robust MD membrane. During membrane fabrication via phase inversion process, Azeem et al. [111] utilized polydimethylsiloxane (PDMS) to support PVDF polymer to create a sandpaper-like texture. The increase in water contact angle (WCA) was due to an increase in surface roughness. The modified membrane has a stable permeate flux of 21 LMH for 50 h with 7 wt.% of NaCl solution with 99.99% of NaCl rejection. However, it is also preferred that the feed was treated before MD process to increase the permeate flux and reduce the scaling propensity. Rioyo et al. [112] treated the RO concentrate feed with lime soda ash to demineralize the feed before operating with AGMD system. The AGMD operates with a commercial PVDF membrane and for 30 h of operation, the flux was between 0.72–1.38 LMH.

Among the fabrication method, it was found that membranes that fabricate via electrosprinnning often produce superhydrophobic membranes where WCA are more than 150°. The electrosprinnning of PVDF-HFP superhydrophobic membrane with a WCA of 156.6° ± 1.38° exhibits antiwetting and antifouling properties. The membrane has a stable and high permeate flux of 38.8 LMH for 40 h when tested with 3.5 wt.% of NaCl with 99.9% of salt rejection [113]. Membrane can be modified with nanoparticles to further increase the WCA. In a study performed by Li et al. [114], PVDF membrane was modified with ZnO and resulted in a superhydrophobic membrane with antifouling properties due to a high WCA of 162.3°. The membrane was tested with 3.5 wt.% of NaCl for 68 h and the permeate flux was at the range of 10–15 LMH. Ceramic membrane is often employed during a long-term study due to its high durability. In 54 d of DCMD operation with polyetherimide (PEI) membrane that was modified with fluorinated polyurethane, the membrane has a high permeate flux of 23.8 LMH with 2.98 wt.% of NaCl solution with 99.9% salt rejection [115]. In another word, there is no membrane wetting occurring for 54 d of DCMD operation with FPS-PEI membrane.

Due to the sweep gas flow in membrane module, SGMD normally operates with robust ceramic membrane. Ceramic membrane was often modified to produce membrane with good permeability, resistance to fouling and high chemical and thermal stability. Salon membranes were modified with boron nitride (BN) to improve membranes’ chemical and thermal stability. It was observed that the BN-β-sailon membrane has a flux maintained at 5–6 LMH for 200 h with 4 wt.% of NaCl feed and the rejection was up to 99% in an SGMD mode [116]. Besides, PEI membrane was dip-coating with PDMS to produce a membrane with antifouling and good permeability. The PDMS-PEI membrane has a permeate flux of 18.23 LMH during a 5 d operation with 0.008 wt.% of dye water. The results showed the dye rejection was up to 100% [117]. Ceramic membrane could be modified to superhydrophobic conditions to obtain a membrane with strong physico-chemical and anti fouling properties. For instance, after γ-Y2SiO3, membranes were modified with α-SiN4, the membrane has a stable permeate flux of 6.58 LMH for more than 500 h of operation with 4 wt.% NaCl and the rejection was up to 99.9% [118].

Modification of membrane can be done before, during and after the membrane fabrication. In a membrane modification by Yadav et al. [119], the SiO2-PVDF membrane was first prepared via electrosprinning. The membrane was treated with acid before being further modified by fluorosilanization with fluoroalkysiliane (FAS). The FAS-Si-PVDF-A membrane possessed antiwetting and hood permeability properties. The membrane was tested with 3.5 wt.% of NaCl for 22 h and the flux was stable at 11.5 LMH. On the occasion of membrane modification, polyethylene glycol (PEG) was blended with PVDF-co-HFP solution and membrane was fabricated through a facile phase inversion process. This fabricated membrane has high thermal stability and it can last for more than 100 h of operation with 4 wt.% of NaCl in VMD mode and the permeate flux was stable at 19.72 ± 0.87 LMH with rejection up to 99.81% [120]. Besides, to improve the performance of membrane, commercial membrane is often modified before apply to MD system. PP membrane was modified with n-octyltrimethoxysilane (OTES) through dip-coating before being run in the VMD system. The membrane has a permeate flux of 19.72 ± 0.87 LMH for 30 h operations with 3.5 wt.% of NaCl and 99% of salt rejection [121].

4. Summary and outlook

Water recovery from industrial wastewater consists of complex materials such as salts, organic and inorganic fouling substances. Low surface energy material has been employed in MD technology due to low energy requirements, high rejection rate and high distillate quality. In view of this, membrane that can operate for a longer term with responsive properties is required. Besides, the development and advancement of membrane separation technology are remarkably correlated with functional nanomaterials which could effectively enhance membrane performance and are expected to have potential application in complex wastewater treatment. Membrane modification for MD application become challenging due to the application of MD is not solely for desalination purpose. The choice of membrane modification process should fit the MD system and industrial scale-up consideration. From a chemical engineering perspective, the main challenge faced in membrane modification is combining the chosen materials and the desired properties which are economically feasible, easy to fabricate, effective towards application and low cost. Low-cost and efficient membranes are the potential to use for MD on an industrial scale. As a point of view, membranes that fabricate with a simple and low-cost method such as coating are suitable to mitigate MD operational issues for desalination and water recovery of wastewater that involves large volumes. Additional improvement of membrane properties through facile coating methods such as antifouling,
<table>
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<td>SiO$_2$-PDMS-PVDF hollow fiber membrane</td>
<td>SiO$_2$-PDMS</td>
<td>Non-solvent induced phase separation (NIPS) method</td>
<td>VMD</td>
<td>- Hydrophobic asymmetric membrane with antiwetting properties&lt;br&gt;- Stable permeate flux of 44.27 LMH for &gt;9 h operation with 3.5 wt.% of NaCl&lt;br&gt;- Salt rejection up to 99.9%</td>
<td>[78]</td>
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<tr>
<td>SiO$_2$-MWCNT-PVDF membrane</td>
<td>SiO$_2$-MWCNT</td>
<td>Non-solvent induced phase separation (NIPS) method</td>
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<td>[79]</td>
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<tr>
<td>SiO$_2$-PNIPAM PVDF/PTFE flat sheet membrane</td>
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<td>- Free radical polymerization (SiO$_2$-PNIPAM) &lt;br&gt;- Phase inversion (SiO$_2$-PNIPAM PVDF/PTFE membrane)</td>
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<td>[27,87]</td>
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<tr>
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<td>[80]</td>
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<tr>
<td>TiO$_2$-GO-PVDF membrane</td>
<td>TiO$_2$</td>
<td>Non-solvent induced phase separation (NIPS) method</td>
<td>DCMD</td>
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<td>[82]</td>
</tr>
<tr>
<td>TiO$_2$-PVDF-HFP membrane</td>
<td>TiO$_2$-FTES</td>
<td>- TiO$_2$ functionalised with FTES&lt;br&gt;- Electrospinning of PVDF-HFP membrane&lt;br&gt;- Electrospraying of TiO$_2$ on PVDF-HFP membrane</td>
<td>DCMD</td>
<td>- Superhydrophobic membrane with antiwetting and antifouling properties&lt;br&gt;- Stable permeate flux of 38 LMH for 120 h operation with real seawater&lt;br&gt;- Salt rejection up to 99.99%</td>
<td>[81]</td>
</tr>
<tr>
<td>Ag-PDA/PVDF hollow fiber membrane</td>
<td>Ag-PDA</td>
<td>- Deposition of PDA&lt;br&gt;- Deposition of Ag on PDA/PVDF membrane</td>
<td>DCMD</td>
<td>- Hierarchical Janus membrane with antiwetting, antifouling and anti-bacterial&lt;br&gt;- Deposition of Ag on membrane prevent the formation of biofilm&lt;br&gt;- Janus membrane has a stable flux of ~17.67 LMH for 1 d operation with 3.5 wt.% of NaCl&lt;br&gt;- Salt rejection up to 99.99%</td>
<td>[86]</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Surface/Preparation Method</th>
<th>Process/Condition</th>
<th>Additional Properties</th>
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</thead>
</table>
| Ag-PVDF/PVDF double layer membrane | - Electrospinning of PVDF nanofibrous membrane  
- Electrospinning of AgNO₃-PVDF on PVDF nanofibrous membrane  
- Dip AgNO₃-PVDF/PVDF into NaBH₄ ethanol solution to reduce AgNO₃ to Ag | UV-DCMD                                                                          | - Fabrication of photothermal membrane with 20 wt.% of Ag  
- Stable flux performance with 3.5 wt.% of NaCl solution for 60 h of continuous UV-DCMD operation  
- Temperature could reach up to 92.3°C under 1 min of UV light on photothermal membrane,  
- Salt rejection up to 99.99% |
| Ag-PVDF membrane                   | - Non-solvent induced phase inversion process                                                                 | VMD                                                                              | - Photothermal membrane with enhance thermal efficiency and  
water flux  
- Stable flux of ~257 LMH with 0.5 M of NaCl solution for 60 h  
- Salt rejection up to 99.99% |
| CNT-COOH/PVDF membrane             | - Spraying of CNT-COOH on PVDF membrane                                                                 | DCMD                                                                             | - Janus membrane with hydrophilic surface and hydrophobic  
bottom was fabricated  
- Antifouling property when tested with high concentration of  
oil content emulsion  
- Thermal polarization effect reduced due to introduction of  
CNT that has heat transfer property  
- Salt rejection up to 99.99% |
| CNT/PVDF nanofiber membrane        | - Electrospinning of PVDF  
- Spraying of CNT on PVDF membrane                                                                 | VMD                                                                              | - Superhydrophobic composite membrane with improved  
permeability  
- 20 g/m² of CNT on PVDF membrane has a stable flux of  
28.4 LMH for >26 h of operation  
- Salt rejection up to 99.99% |
| CNT-PVDF/PTFE flat sheet membrane  | - Coating of CNT-PVDF on PTFE laminated membrane                                                                 | DCMD                                                                             | - CNT-PVDF/PTFE membrane has anti-microbial property with  
no biofilm formed on membrane surface  
- CNT-PVDF/PTFE membrane has a water flux of 22.3 LMH for  
2 h with endotoxin and bacteria contaminated water  
- Endotoxin removal up to 99.9% |
| GO-PVDF membrane                   | - Phase inversion process                                                                 | DCMD                                                                             | - GO was modified at the permeate side to enhanced overall  
flux by improved condensation process at permeate side  
- Stable flux performance of ~48 LMH with 3.5 wt.% of NaCl  
solution for 60 d of DCMD operation  
- Salt rejection up to 99.99% |
| SiO₂-GO based membrane             | - Vacuum filtration method                                                                 | VMD                                                                              | - Hydrophobic membrane possessed antifouling property  
towards with organic foulants and surfactant  
- Stable flux performance of 15.59 LMH with 3.5 wt.% of NaCl  
solution for 170 h of VMD operation  
- Salt rejection up to 99.99% |
| GO/PDA/PVDF membrane               | - Evaporation deposition of GO on PDA/PVDF membrane                                                                 | DCMD                                                                             | - GO/PDA/PVDF membrane flux increase by tuning the  
oxidation temperature  
- Stable flux performance of 17.80 LMH with 0.1 wt.% of NaCl  
solution for 12 h of DCMD operation  
- Salt rejection up to 99.99% |
<table>
<thead>
<tr>
<th>Membrane module</th>
<th>Membrane</th>
<th>Membrane fabrication</th>
<th>Membrane characteristics</th>
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<tbody>
<tr>
<td>AGMD LDPE</td>
<td>Membranes</td>
<td>Commercial membrane</td>
<td>Average pore size 0.3 μm</td>
<td>Hydrophobic membrane with antiwetting and anti fouling properties</td>
<td>[110]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Thickness 76 μm</td>
<td>Stable permeate flux of 0.6 LMH for 7 d operation with actual seawater</td>
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<td></td>
<td></td>
<td></td>
<td>Porosity 85%</td>
<td>Salt rejection up to 99%</td>
<td></td>
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<tr>
<td>PVDF membrane</td>
<td>with PDMS support</td>
<td>Non-solvent induced phase separation process (NIPS)</td>
<td>WCA 150° ± 1.7°</td>
<td>Superhydrophobic membrane with sandpaper-like texture support</td>
<td>[111]</td>
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<td></td>
<td></td>
<td></td>
<td>Average pore size 0.26 μm</td>
<td>Stable permeate flux of 21 LMH for 40 h operation with 7.0 wt.% of NaCl</td>
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<td></td>
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<td></td>
<td>LEPw 2.1 ± 0.2 bar</td>
<td>Salt rejection up to 99.9%</td>
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<td></td>
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<td></td>
<td>Thickness 152 ± 13 μm</td>
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<td></td>
<td></td>
<td></td>
<td>Porosity 71.8%</td>
<td></td>
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<tr>
<td>PVDF membrane</td>
<td>Commercial membrane</td>
<td></td>
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<td>pH treatment with lime soda ash to demineralization of feed before AGMD process could increase permeate flux and reduced scaling</td>
<td>[112]</td>
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<td></td>
<td>Thickness 0.09–0.11 μm</td>
<td>Permeate flux of 0.72–1.38 LMH for 30 h operation with RO concentrate</td>
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<tr>
<td>DCMD PVDF-HFP</td>
<td>membrane</td>
<td>Electrospinning of PVDF-HFP</td>
<td>WCA 156.6° ± 1.38°</td>
<td>Superhydrophobic membrane with antiwetting and antifouling properties</td>
<td>[113]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Average pore size 0.94 ± 0.1 μm</td>
<td>Stable permeate flux of 38.8 LMH for 40 h operation with 3.5 wt.% of NaCl</td>
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<tr>
<td></td>
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<td></td>
<td>LEPw 1.49 ± 0.1 bar</td>
<td>Salt rejection up to 99.9%</td>
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<td></td>
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<td></td>
<td>Thickness 111 ± 5 μm</td>
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<td></td>
<td></td>
<td></td>
<td>Porosity 58% ± 2%</td>
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<tr>
<td>ZnO-PVDF</td>
<td>membrane</td>
<td>Electrospinning of PVDF-ZnO</td>
<td>WCA 162.3°</td>
<td>Superhydrophobic membrane with antiwetting property</td>
<td>[114]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Average pore size 0.40 ± 0.03 μm</td>
<td>Permeate flux of 10–15 LMH for 68 h operation with 3.5 wt.% of NaCl</td>
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<td></td>
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<td></td>
<td>LEPw 1.60 ± 0.03 bar</td>
<td>Salt rejection up to 99.9%</td>
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<tr>
<td>FPA-PEI membrane</td>
<td>Two-step solution polymerization of fluorinated polyurethane (FPA)</td>
<td></td>
<td>WCA 80.38°</td>
<td>Hydrophobic membrane</td>
<td>[115]</td>
</tr>
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<td></td>
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<td>Pe rmeate flux of 23.8 LMH for 54 d operation with 2.98 wt.% of NaCl</td>
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<td></td>
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<td></td>
<td>LEPw 4 bar</td>
<td>Salt rejection up to 99.9%</td>
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<tr>
<th>Membrane Type</th>
<th>Preparation Method</th>
<th>WCA (°)</th>
<th>Average Pore Size (μm)</th>
<th>LEPw (bar)</th>
<th>Porosity (%)</th>
<th>Notes</th>
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<tr>
<td>SGMD BN-β-sailon membrane</td>
<td>Phase inversion and sintering</td>
<td>145°</td>
<td>0.78</td>
<td>-</td>
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<td>Hydrophobic membrane with high chemical and thermal stability</td>
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<td>Chemical vapor deposition</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Stable permeate flux of 5–6 LMH for 200 h operation with 4 wt.% of NaCl</td>
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<tr>
<td></td>
<td>Chemical vapor deposition</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Salt rejection up to 99.9%</td>
</tr>
<tr>
<td>PDMS-PEI membrane</td>
<td>Spinning process (PEI membrane)</td>
<td>103.8° ± 0.26°</td>
<td>0.072</td>
<td>4.0</td>
<td>81%</td>
<td>-</td>
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<tr>
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<td>Dip-coating process (polydimethylsiloxane (PDMS)-PEI membrane)</td>
<td>Average pore size</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
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<td>Spin-coating (PEI membrane)</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>Permeate flux of 18.23 LMH for 5 d operation with 0.008 wt.% dye water</td>
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<tr>
<td></td>
<td>Average pore size</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Dye rejection up to 100%</td>
</tr>
<tr>
<td></td>
<td>WCA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Superhydrophobic membrane with antifouling and robust physico-chemical property</td>
</tr>
<tr>
<td></td>
<td>Other properties</td>
<td>Average pore size</td>
<td>-</td>
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<td></td>
<td></td>
<td>LEPw</td>
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<td></td>
<td></td>
<td>Porosity</td>
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<tr>
<td>α-Si$_3$N$_4$/γ-Y$_2$Si$_2$O$_7$ membrane</td>
<td>Tap casting and sintering</td>
<td>153°</td>
<td>0.9</td>
<td>2.3</td>
<td>-</td>
<td>Superhydrophobic membrane with antiwetting and good permeability</td>
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<tr>
<td></td>
<td>Other properties</td>
<td>Average pore size</td>
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<td></td>
<td></td>
<td>LEPw</td>
<td>-</td>
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<tr>
<td>VMD FAS-Si-PVDF-A membrane</td>
<td>Electrospinning of SiO$_2$ and PVDF (SiO$_2$-PVDF membrane)</td>
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<td>0.27 ± 0.30</td>
<td>1.43 ± 0.04</td>
<td>98 ± 5</td>
<td>Superhydrophobic membrane with antiwetting and good permeability</td>
</tr>
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<td>Acid pre-treatment (SiO$_2$-PVDF-A membrane)</td>
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<td>-</td>
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<td></td>
<td>Fluorosilanization with FAS (FAS-SiO$_2$-PVDF-A membrane)</td>
<td>LEPw</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Salt rejection up to 99.9%</td>
</tr>
<tr>
<td></td>
<td>Other properties</td>
<td>Thickness</td>
<td>-</td>
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<tr>
<td>PEG-PVDF-co-HFP membrane</td>
<td>Phase inversion process</td>
<td>100°</td>
<td>0.18</td>
<td>3.03 ± 0.17</td>
<td>76% ± 2.7%</td>
<td>Hydrophobic membrane with high thermal stability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average pore size</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Stable permeate flux of 19.72 ± 0.87 LMH for &gt;100 h operation with 4 wt.% of NaCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LEPw</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Salt rejection up to 99.81%</td>
</tr>
<tr>
<td>OTES-PP membrane</td>
<td>Phase inversion dip-coating of PP membrane</td>
<td>153°</td>
<td>160</td>
<td>-</td>
<td>70.12%</td>
<td>Superhydrophobic membrane with good permeability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WCA</td>
<td>-</td>
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<td>-</td>
<td>Permeate flux of 19.72 ± 0.87 LMH for 30 h operation with 3.5 wt.% of NaCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Other properties</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Salt rejection up to 99.99%</td>
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</table>
long-term stability and responsive membrane are potential membranes for MD operation. On the other hand, processes involving complex and high-value-added products could consider robust membranes where the robust techniques involve membrane modification such as electrospinning and plasma treatment. Both electrospinning and plasma treatment could be precisely controlled to achieve desirable features. To consolidate the industrial application of MD, it is crucial to develop a functional membrane with responsive properties and able to operate long-term. The evolution of membrane modification is always correlated with the reduction of environmental issues that further relate to a safe water supply. Ultimately, a stable antifouling membrane together with MD process design is key potential for pilot scale and industrial scale in MD development.

Acknowledgement

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References


