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Status of membrane distillation for water and wastewater treatment—A review

Bhausaheb L. Pangarkar[a,*], Mukund G. Sane[b], Saroj B. Parjane[a], Mahendra Guddad[a]

[a]*Chemical Engineering Department, Sir Visvesvaraya Institute of Technology, Chincholi, Sinnar, Nashik 422 101, India*
Tel. +91 2551 271 278; Fax: +91 2551 271 277; email: pbl_1978@yahoo.com
[b]*National Chemical Laboratory (NCL), Pune, India*

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ABSTRACT

Membrane distillation (MD) is a promising separation technique for water treatment. It is a nonisothermal process known since 1963. However, this technology still needs to be developed for its industrial implementation for different purposes. This paper presents a status review of MD based on the available published literatures and on preliminary analysis. The review covers the concept, membranes and modules design, configurations, performance parameters, fouling phenomena, the heat and mass transfer phenomena, applications, energy assessment, heat integration, and Memstill technology of MD process. Earlier study indicates that the permeate quality obtained by MD is stable and practically independent on the feed concentrations. The permeate flux is strongly affected by the feed temperature, feed flow rate, vacuum pressure in vacuum MD, and the boundary layer heat transfer coefficient. The permeate flux obtained in the literature of MD process is disagree by an order of enormity and hence better experimental work is needed. The less attention was found in the literature towards the removal of organic and inorganic toxic constituents from the groundwater by MD process.

Keywords: Membrane distillation; Membrane design; Membrane configuration; Fouling; Wastewater

1. Introduction

Availability of pure and clean water is very crucial for human survival. Fresh water is needed in agriculture, as a drinking water, and for various process industries. The fresh water scarcity is a growing problem all over the world. Only 1% of earth's fresh water is available for human to drink. Both rapid population growth and the impairment of existing freshwater sources cause many reasons to turn towards the alternative sources of water such as wastewater, brackish water, and seawater. These water sources could gain more importance compared to traditional water sources in near future.

In order to bridge the wide gap between the availability and the demand for freshwater, desalination of the available saline water has become a suitable alternative [1–6]. Wastewater reuse after purification would not only help to overcome water shortage, but it also decreases the volume of wastewater to be discharged, which is of high

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*Corresponding author.

importance in view of new legislations for wastewater discharge [3,7]. Desalination technique removes salts from salty water, and produces a water stream with a low concentration and a high concentration of salts. The World Health Organization has restricted the salinity of drinking water to be 500 mg/L [8,9]. A principle objective of wastewater treatment is removal of contaminants to such degree, so that the effluents can be reused for industrial or municipal purposes. For this reason, the application of several mutually supplementary technologies is required in wastewater treatment [10].

In recent years, membrane technologies such as microfiltration (MF), ultrafiltration (UF), nanofiltration, and reverse osmosis (RO) have become more attractive for drinking water treatment compared to conventional purification. The main benefits for membrane processes are (a) low-energy consumption, (b) accessible operation conditions, (c) simple maintenance, and (d) high construction compactness [8,11–15]. Wastewater treatment using membranes is experiencing a stable 15% annual growth. Practically, all membrane categories are used in wastewater treatment. However, MF and RO are the most representatives in this area [10]. Among various desalination technologies, MD is supposed to have a great potential due to low-energy requirement, low-cost, low-operational pressure as compared to RO and distillation [8,16–19].

MD is a thermal, vapor-driven transportation process through microporous hydrophobic membranes. It is a nonisothermal membrane separation process used in various applications such as desalination, environmental waste cleanup, food, etc. It is a low-cost membrane separation technology and energy-saving process with significantly lower requirements of pretreatment of feedwater. In this process, saline water is heated to increase its vapor pressure, which generates the difference between the partial pressure at both sides of the membrane. Hot water evaporates through nonwetted pores of hydrophobic membranes, which cannot be wetted by liquid water [8,20,21].

MD membranes are mainly made of polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF). Various methods may be employed to impose a vapor pressure difference across the membrane to drive a flux. The permeate side may be a cold liquid in direct contact with the membrane called direct contact membrane distillation (DCMD), a condensing surface separated from the membrane by an air gap called air gap membrane distillation (AGMD), a sweep gas blown across the membrane called sweep gas membrane distillation (SGMD), and a vacuumed permeate side called vacuum membrane distillation (VMD). AGMD and DCMD do not need an external condenser hence they are best suited for applications where water is the permeating flux. SGMD and VMD are typically used to remove volatile organic or dissolved gas from an aqueous solution [6,8,10,21–24].

The MD process has number of advantages. It can be performed at lower operating pressure and temperatures than the boiling point of feed solution. It requires less vapor space because large vapor space required by a conventional distillation column is replaced in MD by the pore volume of a microporous membrane. It is unlimited to high osmotic pressure and fouling. It permits a very high separation factor of nonvolatile solute and has potential applications for concentrating aqueous solutions or producing high-purity water. It can use any form of low-grade waste heat or it can be coupled with solar energy systems which makes it attractive for production of potable water from brackish water in arid regions [4,10,25–28].

Due to number of such advantages, MD has wide applications in industrial wastewater treatment and desalination of seawater or brackish water. The MD process enables the production of clean water from natural or wastewater, the quality of which impedes a direct application of the RO process. Therefore, MD process received worldwide attention from academia and industry in the last decade. Hence, MD is a promising; yet still emerging technology for water treatment [24,29,30]. MD process can be used for efficient purification of drinking water, which can remove all sorts of nonvolatiles. Currently, there is no commercial product available in the market, which is based on the MD process.

2. Membrane in MD

MD was first developed in the 1960s [31], but advances in the technology progressed very slowly due to its perceived poor performance, nonoptimal heat and flow conditions, and unavailability of suitable membrane. In the 1980s, MD research rose again and many novel MD modules were designed based on a better understanding of the mass and heat-transfer processes. More recently, fresh water resources becoming a problem world-wide, membrane manufacturers are now seeking to develop membrane specifically for MD [29–31].

Ballooning is the known problem in the membrane design which is caused by pressure differentials and is detected by measuring the pressure change as the solvent is added or removed from the solvent cell. This effect is due to the viscoelastic nature of the membrane used. Rapid membrane degradation can also be a problem if harsh solvents are used or if the membrane is not keep moistened. Careful preparation of the membrane is also needed in order to ensure no holes are present. Numerous enclosure wall systems as well as roof systems employ membranes that are not fully adhered, common examples being mechanically attached roofing membranes and house wraps in screen-type exterior wall systems. Under a negative air pressure differential, these membranes can deform or balloon. Ballooning of the membrane could affect many aspects of performance. For instance, it could change the volume of the air chamber in screen-type wall systems and would therefore, affect both the extent of screen pressure moderation and the nature of ventilation within the wall, e.g. ventilation drying and screen pressure moderation. There is a need to develop structural mechanics to model the membrane ballooning and to identify its implications [32,33].

2.1. Commercial membranes

The major requirement of MD membrane is that the membrane should not be wetted by the process liquids. To avoid liquid invasion of the pores, highly hydrophobic membranes with an appropriate pore size are used. The surface tension of liquid also affects wetting. Organic solutes present in an aqueous solution reduce the surface tension to the point where spontaneous membrane wetting occurs. At this point, the surface tension is called the critical surface tension at which MD is no longer possible. The second major considerations in membrane selection are pore size and porosity. High porosities are of special interest since the area available for evaporation is directly related to flux. However, high porosities are usually associated with large pore sizes, which are undesirable, as it increases the risk of membrane wetting. Membranes with 60–80% porosity and 0.1–0.5 μm pore size offer a suitable compromise. The thickness is an important characteristic of the membrane along with pore size and porosity. The thickness of the membrane is inversely proportional to the rate of mass and heat transport through the membrane. In MD process, a high mass transfer is favored and high heat transfer is considered to be a heat loss. Hence, the compromise should be made between the mass and heat transport by properly adjusting the membrane thickness [8,10,24,29,30]. Apart from the hydrophobic character of the membrane material, also the liquid surface tension, pore diameter, and the hydraulic pressure decide about the possibilities of the liquid penetration into the pores. Hence, the membranes used for various configuration of MD and their properties with literature references are listed in Table 1. The pore size of the membrane is used in the range of 0.1–0.45 μm, membrane thickness is in the range 30–175 μm and the porosity is 40–85%.

The commercial microporous hydrophobic membranes are made up of different polymers such as PP, PTFE, polyethylene (PE) and PVDF which can meet these requirements. All these membranes are available in tubular, capillary, or flat sheet forms used in MD experiments. Applying a thin hydrophobic coat upon a cheaper substrate is also a viable alternative [24,29,30].

The PTFE is an ideal material for MD membrane manufacturing since it exhibits one of the highest hydrophobic characters among polymers and also one of the best chemical resistance and thermal stability. The basic disadvantage of PTFE lies in its difficult process ability. Moreover, at present, commercial PTFE membranes are usually produced through complicated extrusion, rolling, and stretching or sintering procedures. PP exhibits excellent solvent resistant properties and high crystallinity. PP membranes are generally manufactured by stretching and thermal phase inversion. PVDF membrane exhibits good thermal and chemical resistance; however, this polymer easily dissolves at room temperature in variety of solvents including dimethyl formamide and triethyl phosphate. PVDF membranes are generally prepared by phase inversion method.

Tubular and flat sheet configurations are available in commercial membranes. The selection of a unit for a given application requires consideration of the type of separation problem, the f1uid phase involved, frequency of maintenance, compactness of the module, and the possibility of membrane replacement. Hollow fiber membrane (diameter <0.5 mm) provides high surface area per unit volume, making the flux density greater compare to other configurations.

Flat sheet membranes are used in cross-flow and stirred cells where the membrane needs to be easily removed for replacement and treatment. The packing density which is the ratio between the membrane area and the given packing volume is considered low for these modules. Therefore, flat membranes are usually incorporated into plate and frame or spiral wound modules. The biggest disadvantage of shell-and-tube modules is that, the damaged membranes cannot be replaced as easily as in flat sheet apparatus. Therefore, the membrane has limited life. Various modifications have been proposed to the standard shell and tube configuration, in order to promote mixing which reduces fouling and promote turbulence at the membrane surface [34].

Table 1
Review of the membrane used by some researchers

Ref.	MD configuration	Membrane material	Module	Company	r μm	ε%	δ μm
[108]	DCMD	PTFE	TF200	Gelman	0.2	80	178
[109]	DCMD	PP	Accurel PP	Microdyne	0.22	73	NA
[20]	DCMD	PP	Accurel	Microdyne	0.22	73	NA
[93]	DCMD	PP	NA	Membrana	0.2	NA	91
[18]	DCMD	PP	NA	NA	0.074	53.3	50
[101]	DCMD	NA	X-20	Celgard	0.6	NA	NA
[90]	DCMD	PP	NA	Osmonic	0.22	70	150
[90]	DCMD	PTFE	NA	Osmonic	0.45	70	175
[76]	DCMD	PVDF	GVHP	Millipore	0.11	75	125
[102]	DCMD	PVDF	NA	NA	0.2	75	60
[83]	DCMD	PVDF	NA	Millipore	0.25	75	126
[66]	DCMD	PVDF	GVHP	Millipore	0.22	75	110
[66]	DCMD	PP	AK20Nobel	Acurel	0.2	75	450
[26]	DCMD	PVDF	GVSP	Millipore	0.22	75	120
[103]	DCMD	PVDF	NA	Simens Water Tech. Australia	NA	NA	NA
[89]	DCMD	PTFE	TF200	Gelman	NA	60	NA
[89]	DCMD	PVDF	GVHP	Millipore	NA	70	NA
[69]	DCMD	PTFE	FGLP14250	Millipore	0.22	70	61
[79]	DCMD	PTFE	FGLP1425	Millipore	0.25	70	NA
[63]	DCMD	PVDF	GVHP22	Millipore	0.16	70	55
[63]	DCMD	PTFE	TF200	Gelman	0.156	60	NA
[104]	SGMD	NA	Liqui-cel	Celgard	0.03	40	30
[67]	SGMD	Silicon rubber	NA	Nagayangi	NA	NA	40
[67]	SGMD	PP	Liqui-cel	Celgard	0.04	40	40
[27]	SGMD	PP	NA	NA	NA	NA	NA
[82]	SGMD	PTFE	TF200	Gelman Sci	0.198	69 + 5	55 + 6
[105]	VMD	PP	NA	Membrana	0.2	75	163
[68]	VMD	PP	MD020TP2 N	Enka	0.2	75	155
[106]	VMD	PTFE	TF200	Gelman	0.2	60	60
[81]	VMD	PP	MD020TP2 N	Mycrodyn	0.2	70	NA
[84]	VMD	PP	NA	NA	0.29	NA	91
[84]	VMD	PP	NA	NA	0.4	NA	81
[84]	VMD	PP	NA	NA	0.51	NA	76
[17]	VMD	PP	NA	Membrana	0.2	75	163
[9]	VMD	PVDF	Microza	Ashi Chem	0.2	NA	NA
[101]	VMD	NA	X-20	Celgard	0.4	NA	NA
[94]	VMD	PVDF	Pall-Microza	NA	0.2	NA	NA
[19]	VMD	PP	NA	NA	NA	NA	53
[69]	VMD	PP	NA	NA	0.1	50	52.5
[22]	VMD	PTFE	NA	NA	0.1	NA	NA
[22]	VMD	PTFE	NA	NA	0.2	NA	NA
[22]	VMD	PP	NA	NA	0.1	NA	NA
[22]	VMD	PVDF	NA	NA	0.2	NA	NA
[107]	VMD	PTFE	TF200	Gelman	0.2	60	60
[85]	VMD	PTFE	NA	NA	0.2	NA	NA
[85]	VMD	PTFE	NA	NA	0.3	NA	NA
[85]	VMD	PTFE	NA	NA	0.4	NA	NA
[85]	VMD	PTFE	NA	NA	0.1	NA	NA

(*Continued*)

Table 1
(*Continued*)

Ref.	MD configuration	Membrane material	Module	Company	r μm	ε%	δ μm
[7]	VMD	PVDF	M09G0020	GVS	0.2	NA	199
[7]	VMD	PTFE	M05E0020	GVS	0.2	NA	218
[7]	VMD	PVDF	Durapore	Millipore	0.2	NA	125
[7]	VMD	PTFE	Flurupore	Millipore	0.22	NA	55
[7]	VMD	PTFE	Desal K150	Millipore	0.1	NA	34
[10]	VMD	PP	NA	Membrana	0.2	75	163
[8]	VMD	PP	NA	NA	0.2	75	163
[110]	VMD	PVDF	NA	NA	0.16	85	NA
[111]	AGMD	PVDF	NA	Millipore	0.45	75	110
[32]	AGMD	PTFE	Fluropore	Millipore	0.2	70	175
[32]	AGMD	PTFE	Fluropore	Millipore	0.5	85	175
[112]	AGMD	PTFE	NA	Millipore	1	85	150
[113]	AGMD	NA	NA	NA	0.45	50	96

2.2. Composite membranes

Presently, very few laboratory researchers are working on the fabrication and modification of membranes specifically for MD process. Some significant results have been achieved during last six years on the fabrication and modification of polymeric membranes for MD purposes leading to an increase in reliability for the MD process [23,35]. A good MD membrane should exhibit high permeability, low thermal conductivity, and high hydrophobicity. Design of the novel membranes fabricated especially for MD purposes has been recommended by MD investigators since commercially available membranes does not meet all the requirements listed above [4]. In the field of MD membrane engineering, detailed studies concerning the design of membranes for MD and systematic investigations of the effects of membrane parameters are still lacking. More must be done on fabrication of membranes and modules suitable for different MD configurations and applications with outstanding performance in order to attain a fully commercial status. Many researchers have been performed on new applications of MD but only few have ever tried to design and synthesize membranes for MD processes.

Table 2 covers most of the studies in which materials other than the typical hydrophobic polymers were used for the MD processes. Novel hydrophobic membranes for MD applications can be fabricated either by hydrophobic polymers or by surface modification of hydrophilic membranes. Various surface modification applications including surface segregation, impregnation and cross-linking, co-extrusion, coating, grafting, and plasma polymerization have been attempted until now. However, there is very limited number of studies on the design of MD membranes. Hence, new membrane required to develop for MD application.

The improved properties of the hydrophobic membrane allow reducing the rate of membrane wettability. Blending of PTFE particles into a spinning solution modified the PVDF membrane, and enhances the hydrophobicity of prepared membrane [36]. Also, the resistance to wetting can be improved by the preparation of membrane with uniform sponge-like structure [37].

One of the most promising attempts is the composite hydrophobic/hydrophilic membranes. In multilayered membrane, the hydrophobic thickness should be as thin as possible. The advantage of the composite hydrophobic/hydrophilic layered membrane is that a high mass transport is enabled by making the hydrophobic layer as thin as possible, while a low heat transfer is enabled by making the overall membrane thickness as thick as possible. The purpose of using the hydrophilic layer is to enhance the resistance for the conductive heat transfer resistance and make the membrane strong enough to prevent its deflection and rupture. But the hydrophilic layer should not increase the mass transfer resistance considerably [38]. Khayet et al. [39–41] were the initiator of the hydrophobic/hydrophilic composite membrane concept in MD where hydrophobic surface modifying macromolecules (SMM41) were synthesized and blended with the host hydrophilic polymer (PEI). Khayet et al. [42,43] proposed a new type of porous composite hydrophobic/hydrophilic flat sheet membranes for DCMD application. The membranes were prepared by the simple phase inversion method using fluorinated surface modifying macromolecules (SMMs). The hydrophobic side of the membrane was brought into

Table 2
Review on the modified new membrane materials used for MD

Ref.	Surface layer preparation method	Materials used in membrane preparation	
		Base materials	Surface-modifying material
[39]	Surface segregation	PEI (−M)	Fluoro hydrocarbone endcapped PU (+M)
[49]	Cross-linking	PVDF (+M)	PVA blended with PEG (−M)
[47]	Surface segregation	PES (−M)	Fluoro hydrocarbone endcapped PU- urea (+M)
[121]	Co-extrusion	PAN with hydrophilic NA + clay particles (−M)	PVDF with hydrophobic 15A clay particles (+M)
[122]	Plasma polymerization	PP (+M)	Silicon fluoropolymer (+M)
[16]	Coating	PPESK (−M)	Silicon rubber (+M) Polytrifluoropropyl-siloxane (+M)
[48]	Grafting	Alumina ceramic (−M)	TCS (+M) TMS (+M)
[123]	Cross-linking/dip-coating	PVDF (+M)	Chitosan (−M)
[124]	Impregnation and cross-linking	Stainless steel ASI 316 (−M)	PDMS (+M)

Note: (−M): hydrophilic material, (+M): hydrophobic material, PEI: polyetherimide, PU: polyurethane, PVA: polyvinyl alcohol, PES: polyethersulfone, PAN: polyacrylonitrile, PPESK: poly (phthalazinone ether sulfone ketone), TCS: trichloromethylsilane, TMS: trimethylchlorosilane, PDMS: polydimethylsiloxane.

contact with the hot feed solution, while the hydrophilic layer of the membrane was maintained in contact with cold water, which penetrates into the pores of the hydrophilic layer. The composite porous hydrophobic/hydrophilic membranes were found to be promising for desalination by DCMD as they combine the low resistance to mass flux. This is achieved by the diminution of the water vapor transport path through the hydrophobic thin top layer, and a low conductive heat loss through the membrane, obtained by using a thicker hydrophilic sublayer. The DCMD flux of one the SMM/PEI membranes prepared with 12 wt% PEI was found to be higher than those of the commercial PTFE membranes.

Huo et al. [44] prepared flat sheet PVDF-fabric composite membrane consisting of a fabric layer and a PVDF membrane layer. The fouling resistance of the composite membrane in MD desalination was investigated by AGMD, using simulated saline water and high concentration NaCl solution as the feed solutions, respectively. The experimental results showed that the water-and-oil repellent finishing of the fabric support had a significant effect on the bonding strength and the fouling resistance of the composite membrane. With the protection of the fabric layer for the PVDF membrane layer, the composite membrane exhibited better fouling resistance as its fabric surface was in contact with the feed solution in MD process, when the fabric support was finished with 2 g/L FK-501.

Last few years, polyethersulfone (PES) and polysulfone (PS) flat sheet membranes were further modified using different types of SMMs, different solvents, additives, and different membrane preparation conditions in order to optimize the MD performance of the composite hydrophobic/hydrophilic type of membranes [38,45–47]. Hendren et al. [48] also employed modified alumina anodisc membranes of different pore sizes (20 nm, 200 nm) by surface treatment using perfluorodecyltriethoxysilane, trimethylchlorosilane, or trichloromethylsilane. It was found that among the three components used, the perfluorodecyltriethoxysilane modified alumina membrane exhibited the highest DCMD permeate flux, which was also about 20% higher than that of the membrane TF200. Permeate fluxes below 18 L/m^2 h have been measured. However, the salt (NaCl) rejection factors of the modified alumina anodisc membranes were found to be between 93 and 99% proving the imperfections in the membrane structure, surface chemistry, and membrane modification procedure.

Peng et al. [49] prepared the composite hydrophilic/hydrophobic membranes and tested it for desalination by DCMD configuration using a 3.5 wt% NaCl aqueous solution. They used a dense hydrophilic polymer solution on porous PVDF membrane. The polymer solution was a blend of polyvinyl alcohol (PVA) and polyethylene glycol (PEG) cross-linked by aldehydes and sodium acetate. The behavior of the coated membranes was found similar to that of the uncoated PVDF membrane. A separation factor of more than 99% was achieved and the DCMD flux of the coated membrane was only 9% lower than that of the uncoated membrane, which was 23.7 kg/m^{2}h at 70℃ feed temperature and 22℃ permeate temperature. It was concluded that the hydrophilic layer could prevent wetting of the hydrophobic membrane pores means prevent the penetration of liquid solution into the pores. It minimizes the resistance to the mass transfer. Hydrophobic and hydrophilic layers would contribute to the overall resistance to heat transfer. Membrane can be fabricated from chemically resistance polymers to increases the membrane life.

Ohta et al. [50] prepared a partially hydrophilic dense fluoro-carbon composite membrane and tested it for seawater desalination. Authors used the term MD for both porous and dense membranes. DCMD configuration was used and the obtained fluxes (<6 kg/m^{2}h) were of magnitude similar to those achieved with porous hydrophobic membranes. The effects of the DCMD operation parameters were similar to those observed for a single porous hydrophobic layer. It was reported that the permeability and thermal efficiency of fluoro-carbon membrane were superior to those of silicon membranes.

Jain et al. [16] prepared a new hydrophobic poly (phthalazinone ether sulfone ketone) (PPESK) hollow fiber composite membrane coated with silicon rubber and with sol–gel polytrifluoropropylsiloxane by surface-coated modification method. The effects of coating time, coating temperature, and the concentration of silicon rubber solution on the VMD properties of silicon rubber coated membranes were investigated. It was reported that a high water permeate flux could be gotten in low temperature and low concentration of silicon rubber solution.

Recently, comparisons of hydrophobic zirconia (50 nm pore size) and titania (5 nm pore size) tubular ceramic membranes used in different MD configurations (VMD, DCMD, and AGMD) have been carried out [51]. The internal surface of the tubular membranes were chemically modified by grafting perfluoalkylsilane molecule, C_8F_{17} $(CH_2)_2Si(OC_2H_5)_3$ achieving coating layers of 10 µm for zirconia and 5 µm for titania. Salt rejection factors higher than 99% have been obtained for all tested MD configurations when using salt (NaCl) aqueous solutions of concentrations 0.5 and 1 M. The highest permeate fluxes obtained using zirconia modified membrane are 180, 95, and 113 L/m^{2}d in desalination by VMD, DCMD, and AGMD of a salt NaCl aqueous solution of 0.5 M, respectively. The corresponding permeates flux of titanium modified membrane are 146 L/m^{2}d for VMD, 20 L/m^{2}d for DCMD and AGMD.

2.3. Recent developments in membrane material

Recently, some of the researcher designed new promising techniques for generation of MD membranes using other polymers, solvents, and additives to improve the MD performance of nanofibrous membranes. Copolymers like polyvinylidenefluoride–hexafluoropropylene (PVDF–HFP) and polyvinylidenefluoride–tetrafluoroethylene (PVDF–TFE) are used to prepare MD membranes in flat sheet or hallow fiber using phase inversion method [52,53]. The effects of copolymer concentration on the morphological properties of the PVDF–HFP hallow fiber membranes were studied by microscopy technique and DCMD desalination experiments. Different copolymer concentrations, ranging from 17 to 24 wt%, were used. At high PVDF–HFP concentrations, the formed hallow fiber membranes exhibit a single sponge-like structure, whereas at low copolymer concentrations the cross-section of the prepared hallow fiber membranes has different layers of finger-like structure. The DCMD permeate flux decreased with the increase in the copolymer concentration in the spinning solution and the highest flux was obtained, 1.5 kg/m^{2}h [36,54]. Khayet et al. were experimental design to obtain an optimized membrane for DCMD desalination process. The membrane prepared under the determined optimum conditions such as 19.1 wt% PVDF–HFP, 4.99 wt% PEG, 35℃ coagulation temperature, and 102 s solvent evaporation time. The experimental result showed the highest salt separation factor of 99.95% with a permeate flux of 4.41 L/m^{2}h [55]. The low permeate flux observed for the PVDF–TFE membrane due to smaller pore size and porosity compared to those of PVDF membranes. However, the PVDF–TFE membranes exhibited excellent mechanical properties along with 100% separation factor [56].

Lately, attempts were made to use nanofiber membranes prepared by electrospinning method in AGMD desalination [57], carbon nanotube (CNT), and bucky-paper membranes in DCMD desalination [58]. In AGMD experiment, a permeate flux as high as 11.5 kg/m^{2}h with a NaCl rejection factor higher than 98.5% was obtained by using nanofiber membrane. Membranes with a high and controlled void volume would be achieved by designing nanostructured membranes based on nanofibers and microfibers [57].

A new architecture for the membrane distillation (MD) process which immobilizes CNTs in the membrane pores has been developed by Professor S. Mitra, chairman of the department of chemistry and environmental science of the New Jersey Institute of Technology, USA. The novel architecture not only increases vapor permeation but also prevents liquid water from clogging the membrane pores. For a salt concentration of 34,000 mg/L and at 80°C, the nanotube incorporation led to increases of 1.85 and 15 times in flux and salt reduction, respectively [59].

Ludovic Dumée et al. [60] designed CNT-based composite material membranes for DCMD. The composite CNT membranes were tested in a DCMD setup under different feed temperatures and test conditions. The permeability obtained was as high as 3.3×10^{-12} kg/(m.s.Pa) with an average salt rejection of 95%. No fouling was observed during 39 h of continuous testing of the membrane in DCMD setup.

Maryam et al. [61] prepared oxidized (using HNO_3 and H_2SO_4) CNT film. This was synthesized by a chemical vapor deposition of cyclohexanol and ferrocene in nitrogen atmosphere at 650°C. It was used for desalination process for the removal of NaCl from water. The results showed that temperature is the most influential factor on the oxidized CNTs membrane performance and its contribution percentage to be about 60%.

Mixed matrixes PVDF hallow fiber membrane for DCMD desalination were proposed by Wang et al. [62]. These membranes have been fabricated using the dry/wet spinning technique and water as an internal and external coagulants. The addition of Cloisite clay particles in the PVDF matrix enhanced the mechanical strength and long-term stability of the membrane. The permeate flux was obtained as high as 79.2 kg/m^2h with salt rejection of 100%. Also, no fouling was observed during 220 h continuous DCMD test.

2.4. Membrane module

Apart from the membrane properties, the MD performance depends on the module design. A proper MD module could provide better performance of the MD. The flux enhancements inferred from the membrane and module characteristics improvements depend on the nature and concentration of feed and the operating temperatures [63]. The different module configurations were used in the literature to conduct an experimental work of MD. Choice and arrangement of the membrane module in a MD application is based on economic considerations with the correct engineering parameters being employed. Plate and frame, spiral wound, tubular, capillary, and hallow fiber membrane modules are commonly used by MD researchers. In a module, membrane was inserted between two cylindrical compartments. In DCMD configuration, two compartments (hot feed solution compartment and cold water compartment) are separated by the membrane. While AGMD configuration, additionally an air gap and a cooling plate are used. The dimensions of all these compartments are different for each experimental study that are used such as cylinder with a length of 1.05 m and a diameter of 0.05 m [64], 0.115 and 0.019 m [20], 0.54 m and 0.017, 1.05, and 0.012 m [24], 0.6 and 0.007 m [65], 0.47 and 0.0018 m, 0.2 and 0.00033 m [66], 0.112 and 0.04 m, 0.19 and 0.032 m [67], 0.75 and 0.02 m [68]. From this scattered data of the module dimensions, used by various researchers in their work, it is needed to develop the new membrane module design specifically for MD application.

The flux enhancement is a consequence of film transfer coefficient improvement when a spacer is included in the module channels. Thus, the larger the improvement of the film transfer coefficient, the larger the enhancement of the flux, particularly in highly polarized system. Hence, if high fluxes are targeted, both membrane and module design must be adequate. If this is not so, the good characteristics of only one of them (membrane or module) would not produce the desired flux [63].

The flow channels are used in the membrane module for flat sheet membrane in MD process. The some of the investigators were used the different flow channels in their work such as length (L) 64 mm, width (W) 25 mm and height (H) 18 mm [69], $100 \times 40 \times 25\ mm^3 (L \times W \times H)$ [26], $100 \times 4 \times 1\ mm^3$ [70], $7 \times 4.5 \times 0.55\ mm^3$ [63], and $150 \times 90 \times 65\ mm^3$ [17]. The flow channel area is very important in MD process. The hydrophobic surface of membrane can be partially wetted due to very small nature of the flow channels in MD modules. Due to an increase in the pressure drop to levels, the hydrostatic pressure may exceed the liquid entry pressure of the feed or permeate solution into the membrane pores. The flow channel area may be reduced resulting high temperature polarization due to pressure drop across the membrane.

Even though, due to lack of the design of membranes and membrane modules more efforts must be done on the fabrication of membrane and module suitable for different MD configuration and application for outstanding performance and cost-effective membranes.

3. Effect of operating parameters

MD has higher rejection rate but relatively lower flux. The flux affecting factors are outlined as follows [8,10,71,72].

3.1. Feed temperature

Various researches shown in Table 3 have been carried out on the effect of the feed temperature on permeate flux in MD. Temperature is the main factor affecting on the permeate flux. For DCMD, enhancing the temperature difference between two sides could result in significant increase in water flux, but not in a linear relationship. There is an exponential increase of the MD flux with the increase of the feed temperature. As the driving force for MD is the difference in vapor pressure across the membrane, the increase in temperature increases the vapor pressure of the feed solution, thus results in an increase in the transmembrane vapor pressure difference. Temperature polarization effect also increases with the increase in feed temperature.

3.2. Feed concentration

With increase in feed concentration, water vapor flux decreases due to influence of feed concentration on activity coefficient of water. This phenomenon can be attributed to the reduction of the driving force due to decrease of the vapor pressure of the feed solution and exponential increase of viscosity of the feed with increasing concentration. The effect of contribution of concentration polarization effect is very small in comparison with temperature polarization effects.

3.3. Feed flow rate

Increasing feed flow rate, increases enhanced mixing of the flow channels. Due to this, the temperature polarization resistance, and heat and mass transfer boundary layer thickness decreases. Therefore, the temperature and concentration at the liquid–vapor interface becomes closer to the corresponding values at the bulk feed solution. Hence, the vapor transfer resistance through the membrane decreases and permeation flux increases.

3.4. Membrane material and structure

Hydrophobic microporous membrane was used in MD, and structure parameters such as pore size, porosity, and membrane thickness affects on water flux.

Several researchers have studied the effect of the operating parameters on the permeate flux and the results are listed in Table 3. As seen, the MD flux obtained in the range of 0.005–122 $\mathrm{kg/m^2\,h}$. There is an enormous difference found in permeate flux by using different commercial membranes. Additionally, different values of the permeate flux were found for the same membranes working under the same operating conditions. This may be depending on the membrane module used. The contributions of the factors such as temperature, feed flow rate, and feed concentration on permeate flux are almost the same and are lower than vacuum pressure in VMD. This means that vacuum pressure is the most important factor [10].

4. Membrane fouling

Membrane processes are used because of some unique applications such as high removals of constituents like dissolved solids, organic carbon, inorganic ions, as well as regulated and unregulated organic compounds. However, membrane fouling is a major obstacle for most of the applications in the drinking industry (water treatment and desalination), especially when high concentrations of natural organic matter and inorganic constituents occur. The fouling can be classified as inorganic, organic, and biofouling [73]. Despite its high potential in water treatment, certain limitations prohibit membrane process from large-scale and continuous operation [74].

Fouling and scaling are two important mechanisms that affect stability of the MD process and lead to reduce the overall efficiency. Fouling and scaling can cause pore clogging in MD membranes which lead to reduce the membrane area available for water vaporization and hence reduce the permeate flow rate. In addition, such build-up of fouling and scaling surfaces reduces the flow channel area which causes a pressure drop and lower flow rates, leading to higher temperature polarization effects and reduction in flux. Moreover, fouling and scaling may cause membrane partially wetting or sever membrane damage [75], but has only been observed with saturated process solutions. Particulate or colloidal species in the process liquids can lead to membrane fouling as well. These particles or collides tends to become trapped at the membrane–liquid interface by interfacial tension forces.

The membrane fouling caused by different inorganic salts, which reduces permeates flux, decreases product quality and ultimately shortens the membrane life. Consequently, membrane fouling increases the costs by increasing (1) energy consumption, (2)

Table 3
Review of operating conditions and flux obtained of NaCl solution in MD in various studies

Ref.	MD configuration	Membrane material	T_{bf} (°C)	Q_f L/h	V_f m/s	P_P kpa	C g/L	w_f NaCl	J kg/m^{2}h
[20]	DCMD	PP	85	NA	0.35	NA	1	NA	22.62
[101]	DCMD	Celgard	47.4	2.8	NA	NA	NA	0.01	0.122
[90]	DCMD	PP	60	NA	1.75	NA	0.6	NA	28
[90]	DCMD	PTFE	60	NA	1.75	NA	0.6	NA	82
[76]	DCMD	PVDF	70	NA	3	NA	NA	NA	61
[102]	DCMD	PVDF	80	0.1	NA	NA	NA	NA	27
[83]	DCMD	PVDF	70	NA	3.7	3	35	NA	56
[26]	DCMD	PVDF	70	NA	0.15	NA	NA	0.246	29.16
[103]	DCMD	PVDF	40	NA	0.7	NA	NA	0.3	0.5
[70]	DCMD	PTFE	41.6	NA	0.35	3	NA	0.003	16.2
[18]	DCMD	PP	60	75	NA	NA	35	NA	0.26
[63]	DCMD	PTFE	38	NA	0.55	NA	4	NA	7.2
[67]	SGMD	Silicon rubber	22	3	NA	NA	NA	NA	0.009
[67]	SGMD	PP	22	3	NA	NA	NA	NA	0.005
[27]	SGMD	PP	70	NA	0.8	NA	NA	NA	18.72
[82]	SGMD	PTFE	50	NA	0.15	NA	45	NA	5.94
[81]	VMD	PP	65	NA	0.6	4	NA	NA	27.72
[18]	VMD	PP	60	75	NA	8	35	NA	2.6
[19]	VMD	PP	55	75	NA	9.3	35	NA	5.4
[69]	VMD	PP	85	NA	NA	1	NA	0.01	71
[22]	VMD	PTFE	45	NA	2.65	NA	NA	0.01	52
[107]	VMD	PTFE	60	NA	0.38	3.2	NA	0.01	10.08
[85]	VMD	PTFE	77	60	NA	5.3	NA	0.01	78
[10]	VMD	PP	55	1.8	NA	4	100	NA	13.4
[10]	VMD	PP	55	1.8	NA	4	300	NA	9.1
[8]	VMD	PP	55	1.8	NA	3	50	NA	16.96
[8]	VMD	PP	45	0.9	NA	3	100	NA	5.674
[8]	VMD	PP	35	3.6	NA	3	150	NA	5.57
[94]	VMD	PVDF	75	NA	1	0.5	30	NA	122
[94]	VMD	PVDF	75	NA	1	0.5	300	NA	52
[9]	VMD	PVDF	25	NA	NA	1	60	NA	0.504
[9]	VMD	PVDF	25	NA	NA	1	300	NA	0.324
[101]	VMD	Celgard	45	NA	0.02	2	NA	0.01	0.86
[111]	AGMD	PVDF	90	0.08	NA	NA	NA	0.001	26
[34]	AGMD	PTFE	45	0.06	NA	NA	NA	0.03	5
[112]	AGMD	PTFE	75	0.06	NA	NA	NA	0.003	28

Note: Q_f: Feed flow rate, V_f: feed velocity, P_p: permeate pressure, C: salt concentration in feed, w_f: weight fraction of NaCl in feed.

system down time, (3) necessary membrane area, and (4) construction, labor, time, and material costs for backwashing and cleaning processes [26,30,64,74,76]. The membrane fouling due to inorganic salt is dependent on several factors, including but not limited to, membrane characteristics, module geometry, feed solution characteristics, and operating conditions [74].

It is very important to understanding the fouling phenomena in MD process. Very few literatures on the membrane fouling in MD and long-term performance are available. Most of the performed fouling studies so far examined fouling and scaling in seawater desalination or wastewater treatment application [26,30,64,76]. Theoretically, MD performance is not sensitive to high concentration of feed. However, the presence of these sparingly soluble salts may lead to membrane fouling at a moderate concentration. The scaling that occurred from seawater at moderate concentration appears to be readily removed from the membrane surface and benefits from operating at low temperature may be marginal [30].

The main techniques currently used to control fouling are the feed pretreatment and membrane cleaning. The membrane scaling can be effectively controlled by the use of the appropriate MD process conditions. An excessively advanced pretreatment system significantly increases the installation costs. Therefore, the development of simple and inexpensive method for module cleaning or fouling prevention is necessary in order to implement the MD on a commercial scale [24,64].

Permeate flux decline was mainly caused by an increase in the heat resistance of the fouling layer. The deposits were formed not only on the membrane surface, but also inside the pores. Salt crystallization in the membrane pores besides their wetting, also caused the mechanical damage of the membrane structure. The intensity of the fouling can be limited by the pretreatment of feed and selection of the operating conditions of MD [77].

A high concentration salt solution in DCMD experiments causes high membrane fouling [26]. The fouling in VMD is highly reversible and can be easily removed by simply water cleaning of the membrane surface. Indeed, permeability measurements before and after the experiments (after filtration and washing) show a variation less than 5% [7]. A lower reversible fouling could occur for longer experiment [14].

The fouling is fewer problems in MD than in other pressure-driven membrane separation processes. The premise is that the pores of MD are relatively large compared to the pores or diffusion pathways in RO or UF (both have pore sizes <2 nm, approximately three orders of magnitude smaller than those of MD membranes), which are not as easily clogged [71]. The lower operating pressure compared to RO must lead to reduced fouling. But RO obtained poorer permeate flux due to smaller pore size and lower operating pressure compared to MD operation.

A sharp decline of the permeate flux during MD process of tap water was observed by Gryta [24]. The precipitation of $CaCO_3$ on the membrane surface was the major reason of observed flux decline during the purification of tap water by MD process. The deposit layer changes the temperature polarization and creates an additional thermal resistance, thus decreasing the heat transfer coefficient from the feed bulk to the evaporation and condensation surface, and temperature polarization increases. The adherence of the deposit to the membrane is a critical factor for MD performance, as well as other membrane processes. The deposit of $CaCO_3$ on the membrane surface can easily be removed by rinsing the module with a 3 wt % solution of HCl, which allows to restore the initial permeate flux. After acid rinsing, the images of membrane surface were found to be similar to that observed for a new membrane [24]. Also, he found that the PP membrane was thermally stable, maintaining its morphology, and its good separation characteristics throughout three years of DCMD process. This process applied for production of the demineralized water. When using permeate of the RO system as DCMD feed solution, membrane pore wetting was not observed; and the DCMD flux was found to be similar to the initial permeate flux. However, a partial wetting of the membrane was found when tap water was used directly as feed. In this case, there was decrease in the permeate flux from 700 to 550 $L/m^2 d$ [78].

The brine obtained from RO plant (Total dissolved solid of 19,000 mg/L and Total organic carbon of 64 mg/L) was studied in DCMD, resulted with the initial flux of 21 $L/m^2 h$, which was rapidly lost under high temperature conditions until the membrane was totally covered with a recalcitrant foulent. Whereas a low temperature regime, with its initial lower flux of 16 $L/m^2 h$, appeared to form larger amounts with loosely packed precipitate, but was at able to distil the RO secondary reject to greater than 67% recovery [30].

It is a general conclusion that pretreatment has an important positive influence on MD. But the fouling is not a major problem encountered in a MD process as compared to other pressure-driven membrane processes because MD performance is not sensitive to high concentration of feed. However, the presence of these sparingly soluble salts may lead to membrane fouling at moderate concentration.

5. Heat and mass transfer phenomena

In MD processes, mass transport and heat transport are coupled. The driving force for mass transfer in MD systems is the difference in the partial pressure of water vapor across microporous hydrophobic membrane. The recognized transport mechanisms for mass transfer across the membrane are usually molecular diffusion and Knudsen diffusion, and, sometimes, viscous flow. Molecular diffusion has a partial pressure difference as driving force and nonidentical molecules that are in the way, these form the resistance to mass transfer. The driving force for Knudsen diffusion is also a partial pressure difference, but in this case molecules bounces into the membrane matrix, which form the resistance to mass transfer. Knudsen diffusion is thus important for small pores and/or low pressure. Finally, viscous flow has a total pressure difference as driving force, and the membrane matrix forms the resistance against it [79–83]. In a VMD configuration, the molecular diffusion is not adequate due to the very low value of the partial pressure of the air inside the pores. Consequently, the Knudsen and viscous flow diffusion should be a chosen as more appropriated [80,81,84,85].

The governing quantity which provides a guideline in determining the operative mechanism in a given membrane pore under a given experimental condition is Knudsen number (k_n) defined (Eq. (1)) as the ratio of mean free path, λ, and pore diameter, d_p.

$$K_n = \frac{\lambda}{d_\mathrm{p}} \tag{1}$$

The mean free path, λ, can be calculated by the following expression as:

$$\lambda = \frac{3.2\mu_\mathrm{v}}{P}\sqrt{\frac{RT}{2\pi M}} \tag{2}$$

where μ_v is viscosity of vapors at atmospheric temperature and ambient pressure, M is molecular weight, R is gas constant, T is temperature, and P is the mean pressure within the pores.

If k_n is less than 0.01, the mass transfer mechanism is considered as molecular diffusion and k_n values higher than 10, the mechanism is considered as Knudsen diffusion. If the value of k_n lies between 0.01 and 10, it is the transition zone and both the mechanism contributes to the mass transfer [80,81,84,85].

The membrane permeates flux, j, which is dependent on the membrane characteristics and the established driving force can be expressed as [6,64]

$$J_i = B_i \Delta p_i \tag{3}$$

where B is the MD coefficient of the membrane, Δp_i is the water vapor pressure difference between evaporating and condensing surface. The vapor pressure of the pure water component determined with the Antoine equation.

$$p_i = \exp\left[23.1964 - \frac{3816.44}{T - 46.13}\right] \tag{4}$$

The expression for steady state diffusion of water vapor through a stagnant film can be written as [85]:

$$B_i^\mathrm{D} = \frac{M_i}{RT}\frac{\varepsilon}{\tau\delta}\frac{PD}{p_\mathrm{a}} \tag{5}$$

where B^D is the mass transfer coefficient for molecular diffusion mechanism, p_a is the mean air pressure, δ is the membrane thickness, ε is the membrane porosity, τ is the pore tortuosity, D is the molecular diffusion coefficient, and P is the total pressure.

The membrane mass transfer coefficient of Knudsen diffusion mechanism (B_i^k) is calculated by Eq. (6) as:

$$B_i^k = \frac{2}{3}\frac{\varepsilon r}{\tau\delta}\left(\frac{8M_i}{\pi RT}\right)^{0.5} \tag{6}$$

where r is membrane pore radius.

The mass transfer coefficient of combined (Knudsen and molecular diffusion) mechanism (B_i^c) is calculated by Eq. (7) as:

$$B_i^\mathrm{c} = \left[\frac{3\tau\delta}{2\varepsilon r}\left(\frac{\pi RT}{8M_i}\right)^{1/2} + \frac{\tau\delta p_\mathrm{a}}{\varepsilon PD}\frac{RT}{M}\right]^{-1} \tag{7}$$

When a molecular mixture is brought to the membrane surface by the driving force action, some molecules would permeate through the membrane while others will be retained. This leads to an accumulation of the retained components and a depletion of the more permeating components in the boundary layer adjacent to the membrane surface. This phenomenon is referred as concentration polarization [34,86].

In MD process, there is a heat transfer occurs by two major mechanisms: (1) the latent heat transfer accompanying the transmembrane vapor flux and (2) heat transfer by conduction through the membrane matrix [79,83]. In VMD, the conductive heat transfer across the membrane is negligible because of the low pressure on the permeate side of the membrane [80,81]. Consequently, there is rather complex relationship between both heat and mass transfer. This is related and involved with the presence of an unstirred boundary layer that adjoins the membrane at the feed side. The temperature at the membrane surface is lower than the corresponding value at the bulk phase. This creates temperature gradients in the liquid film adjoining the membrane. This phenomenon is called temperature polarization [6,34,87,88].

The MD flux increases with the feed flow rate because of increased Re and decreased boundary layer resistances. At higher Re, high heat transfer from the bulk feed to the membrane surface approaches to the corresponding temperature in the bulk phases leading to greater MD flux and corresponding increase in the heat transfer coefficient [80,81,84,89]. This can be attributed to a reduction in the temperature polarization effect. As the heat transfer coefficient increases, the temperature at the membrane surface approaches to the bulk temperature and the vapor pressure driving force increases.

Attention would be better focused on designing MD module to provide high heat transfer coefficient practically. The MD process could be operated at low pressures with good membrane permeability in order to maximize the flux. Therefore, the process would be heat transfer limited [80]. So maximizing the heat transfer coefficient by a good module design maximizes the mass flux. The heat transfer coefficient (h_f) determined by the some researchers in their study for different membrane material and MD applications are reviewed in Table 4.

The effect of boundary layer heat transfer resistance relative to the total heat transfer resistance of the system is given by the Eq. (8) of temperature polarization coefficient, θ.

$$\theta = \frac{T_{m1} - T_{m2}}{T_\text{bf} - T_\text{bp}} \tag{8}$$

where T_{m1} and T_{m2} are the temperatures at feed side and permeate side membrane surface, respectively; T_bf and T_bp are the bulk temperatures of feed and permeate, respectively. The concept of the temperature polarization factor would be used as a tool for evaluating the effect of the input parameters on maximizing the mass flux. For well-designed MD modules, the θ approaches to unity. However, for MD modules with high thermal boundary layer resistances, θ values are very low; the MD process is heat transfer limited. Enhancements of θ are found with the increase of both the feed and permeate flow rates with a decrease of the temperature, especially the feed temperature, and it is strongly dependant on membrane characteristics [79–81,89].

6. Application of MD

Several researchers have applied the various MD configurations to produce fresh water from a salt solution. The characteristics of the membranes are listed in Table 1. Table 3 gives the flux obtained at operating parameters of various MD configurations for the production of fresh water from salt solution. In addition to producing water, the other applications of MD are listed in Table 5. It seems that the maximum work was reported on the treatment of salt water and a fewer work on removal of organic and inorganic matter removal from the wastewater by the MD process. Hence, the more detailed experimental work is needed for removal of organic and inorganic matter from the industrial wastewater by MD application; it is a more attractive and active research area.

The range of the flux obtained between 0.122 and 82 $\text{kg/m}^2\,\text{h}$ for DCMD; between 5 and 28 $\text{kg/m}^2\,\text{h}$ for AGMD; between 0.005 and 18.72 $\text{kg/m}^2\,\text{h}$ for SGMD; and between 0.324 and 122 $\text{kg/m}^2\,\text{h}$ for VMD. The wide variation of the permeate flux among researchers is may be due to use of different conditions in MD. It is imperative to know the maximum permeate flux of MD under optimal conditions so that the viability of the process can be assessed and compared with other desalination processes such as RO. More experimental work needs to be dedicated towards that objective.

The range of permeate fluxes in typical commercial RO processes is 12–15 $\text{kg/m}^2\,\text{h}$ for seawater and 18–26 $\text{kg/m}^2\,\text{h}$ for brackish water [8,71]. Since MD fluxes are not very sensitive to salinity, it is up to ninefold lower than the highest obtained in the reported MD experiments [10].

7. Assessment of energy

The MD process is an effectively operate at low temperature. Hence, it is possible to utilize low-grade waste heat. In MD, the cost of energy for heating the feedwater is negligible. Thus, other sources of energy such as renewable solar or geothermal energy could be utilized to heat the feedwater. As opposed to warm condenser water, use of renewable sources would involve higher capital investment. However, this investment may eventually be paid off by lower operating costs. Thus, the possibility of operating under very mild conditions enables MD to utilize various alternative energy sources, making it more promising for industrial application.

RO process operates on feed pressure and temperature, while MD operates on vapor pressure difference across the membrane. VMD process requires two pumps for operation, one for the feed,

Table 4
Review of heat transfer coefficients of membrane material obtained in various MD study

Ref.	Membrane material	T_{bf} ℃	B kg/m^2 s.pa	h_f W/m^2.K	Feed solution
[9]	PVDF	42	3.4×10^{-7}	160	Pure water
[9]	PVDF	26	3.4×10^{-7}	90	Pure water
[83]	PVDF	60	6.6×10^{-7}	14,018	35 g/L NaCl solution
[83]	PVDF	40	6.6×10^{-7}	12,839	Pure water
[83]	PVDF	40	6.6×10^{-7}	13,064	5 g/L NaCl solution
[89]	PVDF	30	NA	3,374	Aq. NaCl solution
[89]	PVDF	45	NA	3,612	Aq. NaCl solution
[89]	PVDF	60.1	NA	3,063	Aq. NaCl solution
[89]	PTFE	30	NA	3,524	Aq. NaCl solution
[89]	PTFE	50	NA	3,457	Aq. NaCl solution
[79]	PTFE	30	NA	705	Aq. NaCl solution
[79]	PTFE	37	NA	780	Aq. NaCl solution
[63]	PVDF	45	5.6×10^{-7}	16,150	Pure water
[63]	PVDF	45	5.6×10^{-7}	13,500	4 g/L NaCl solution
[63]	PVDF	45	5.6×10^{-7}	6,300	40% Sucrose solution
[84]	3 M	20	NA	6,800	Pure water
[67]	3 M	80	NA	11,200	Pure water
[114]	PTFE	35	8.2×10^{-7}	538.2	24% NaCl solution

and one for permeate. Low-pressure pumps are less expensive in both capital and operating costs. If the VMD configuration is employed, a vacuum permeate pump would be utilized, however, the operating cost is low due to the low-pressure gradient on the pump [2,90–93].

VMD performs better than the DCMD and the cross-flow module resulted to be the most effective design for obtaining high fluxes with moderate energy consumptions. The lower value of energy consumption/permeate flow rate ratios obtained were 3.55 kWh/kg (longitudinal—flow membrane module) and 1.1 kWh/kg (cross flow membrane module) for DCMD and VMD test, respectively [93]. Also, the energy requirement for RO process was 4 kWh/m^3 for 5–10 L/m^2 h flux at 20℃ feed inlet temperatures and for VMD process, it was 1.5 kWh/m^3 for 120 L/m^2 h permeate flux and 1.3 kWh/m^3 for 85 L/m^2 h at 25℃ feed temperature [94].

For a good performance of the MD unit, high fluxes have to be obtained with low-energy consumptions. This means that both the membrane properties and the module configurations have to be carefully optimized, in order to reduce temperature polarization phenomena as well as the temperature change of the solutions along the membrane module (reduction of the heating and cooling power costs). Several reports already appeared in the literature on the study of temperature polarization in MD. However, only few studies related to the calculation of the energetic requirements, mainly concerning lab-made modules, have been carried out until now [6,69,91,94].

MD could be convenient to utilize cheap heat sources such as solar energy, geothermal energy, and waste heat. Therefore, in combination with such cheap energy, MD is a process of phase transition, utilization of heat energy and could reduce due to latent heat of vaporization. The design of proper energy recovery facilities would be of great practical values in energy saving [72]. Further efforts need to be concentrated in this field, especially in utilization of waste energy or other alternative energy sources in the view of industrial implementation.

8. Heat Integration and Memstill technology

Heat integration is a critical point in the MD process. Meher et al. [95] presented the simple and maintenance free seawater desalination system, which uses MD process provided with heat and electricity generated by solar energy which has been developed in Tokyo. Heat to warm the seawater is provided by solar collector, and photovoltaic panels power the pumps so that the system can been installed at sites without an electricity supply. The distillation is performed at ambient pressure and at a maximum temperature of 80℃ (175℉). Operating costs are extremely low because the process can be driven by

Table 5
Review of MD applications other than desalination of sea water

Ref.	MD configuration	Membrane material	Feed solution	Application
[103]	DCMD	PVDF	30–60% glucose solution	Concentration of glucose solution
[63]	DCMD	PVDF and PTFE	45% sucrose & 4 g/L NaCl	Removal of organic and salt
[105]	VMD	PP	40–50% L-lysine HCl	Concentration of L-lysine HCl
[68]	VMD	PP	Water–ethanol–Ethyl 2,4-decadienoate	Removal of Ethyl 2,4-decadienoate
[106]	VMD	PTFE	Dilute solution of VOC	Removal of VOC
[17]	VMD	PP	20–60% ethylene glycol solution	Concentration of ethylene glycol
[22]	VMD	PTFE	Aqueous solution of ethanol	Concentration of ethanol
[5]	VMD	PS	Domestic wastewater	Water purification
[24]	DCMD	PP	Wastewater	Removal of dissolved matter
[20]	DCMD	PP	Thermally softened water	Removal of dissolved matter
[75]	MD	PP	Potable water	Water purification
[110]	VMD	PVDF	Cocking wastewater	Removal of organic matter
[64]	MD	PP	Effluents of regeneration of Ion exchange	Removal of iron oxide
[65]	DCMD	PP	Surface (lake) water	Removal of Ca, Mg, Na, Fe, Zn
[116]	DCMD	PP	Sugar cane	Concentration of sugar cane juice
[117]	DCMD	PVDF	Orange juice	Concentration of orange juice
[118]	DCMD	PP	Apple juice	Concentration of apple juice
[119]	AGMD	PTFE	Nitric acid/water mixture	Removal of water vapor
[120]	SGMD	PTFE	Wastewater	Removal of acetone and ethanol

low-temperature heat sources e.g. solar heat or waste heat from diesel engines. The MD system used spiral wound module with PTFE membrane having pore diameter between 0.051 and 0.2 m. In this process, the diffusion gap between evaporating and condensing surfaces is reduced to the thickness of the membrane that is only about 30 mm. With an actual pore fraction of 80%, high-specific evaporation rates are possible. The recovery of the heat of condensation is done by utilizing the heat of condensation to preheat the feedwater.

The module is of conventional design and construction, in that it incorporates membrane envelopes, within and between which are channels through which the feed and permeate streams flow. The feed and permeate channels are created by spacers on the feed and permeate sides of the membrane layers. Recovery of the heat of condensation is integrated in the module design. High heat transfer rates result in a 3–5 times higher distillate output compared to modules with integrated recovery of the heat of condensation.

An innovative membrane-based distillation technology for desalinating seawater called Memstill is holding great promise for the future. It is a combination of a two separation principles: distillation and membrane technology. Memstill uses residual heat, a source of energy that is widely available in industrialized countries. The process is driven by minor temperature differences, so little energy is required. Due to free residual heat Memstill puts ahead of the other-state-of-art techniques like RO, Multi-effect distillation (MED), and multistage flash distillation (MFD) [96–98].

Memstill process is designed in such a way that problems met so far in MD developments: high heat consumption and heat loss, low flux, expensive membranes, susceptibility to pore wetting, and fouling flow coincidence for the most part are solved [96]. This technology reveals important advantages in comparison with classical desalination techniques like MSF and MED, comprising—low-energy consumption, simple construction and minimal site work based on prefabricated modules, lower total cost price, potential of very high salt separation factors, limited corrosion and easy maintenance, and small footprint. [97].

Several limitations in conventional MD platforms dramatically reduce the viability of this water purification technology, namely low transmembrane fluxes, high thermal energy requirements, and low freshwater recovery rates. Keppel Seghers, through the logical application of system integration expertise, has succeeded in systematically removing these limitations during the development of Memstill technology. Memstill technology is a proprietary application of MD in an ideal counter-current flow configuration which allows for highly efficient recovery of heat within the desalination process. The recovery of heat within the Memstill process allows desalination to be driven with a minimal heat input. As such, Memstill desalination may be conducted using waste heat sources that would otherwise be rejected to the atmosphere. In addition, the efficient recovery of heat from the outlet stream of Memstill implies that it may be discharged at significantly lower temperatures than conventional thermal MD platforms [98].

The technology was first tested at bench scale and then with a $2\,m^3/d$ pilot plant testing at Senoko Refuse Incineration Plant from February 2006 to June 2007. This demonstrated the principle of Memstill on a pilot scale, and sustainable operation of the M26 type Memstill module. The upscaling of $3\,m^2$ (membrane area) bench scale to $600\,m^2$ proved that the integrity of membrane modules remained well and no severe leakage was observed. The distillate quality was superior throughout the pilot plant study period http://www.pub.gov.sg/research/Key_Projects/Pages/Membrane3.aspx.

The process has been tested for several thousands of hours in bench-scale tests and three pilot plants on both artificial seawater and real seawater. Studies at the three pilot plants and economic evaluations indicate that for large-scale applications, costs would lie between US$0.30 and $0.50/m^3$ approximately, if low-cost waste heat is available. The three pilot plants were tested under real-world conditions, with a nominal production capacity of $0.5–1\,m^3/h$. The first plant used seawater in Singapore; the other two plants used brackish water in and near the harbor of Rotterdam [100].

The Memstill Singapore pilot also pointed out certain areas for improvement to meet commercialization requirements. A second Memstill pilot in the Netherlands (E.ON pilot) was carried out with improved material and configurations, and was able to demonstrate up to 10× better results (e.g. flux, intake flow, distillate flow, energy efficiency, and heat input) than the Singapore pilot http://www.pub.gov.sg/research/Key_Projects/Pages/Membrane3.aspx.

Memstill can both be applied in small-scale as well as large-scale applications and is suitable for a number of applications such as production of drinking or ultrapure water from surface water, brackish water or seawater, concentration of brines, and treatment of waste streams. The Memstill technology can produce (drinking) water at a cost well below that of existing technologies like RO and distillation. With the Memstill technology, also anions like fluoride and arsenic are removed. It is expected that the Memstill technology would be developed for a small-scale applications using solar heat.

9. Conclusions and recommendations

The fields of MD desalination have grown rapidly over the past 50 years but did not attain commercial status for desalination process. It has a promising alternative to replace other membrane separation processes. In order to enhance the performance of MD flux, the effect of the operating parameters on MD configurations have been proposed by many researchers. The permeate fluxes can be significantly improved by increasing the hot feed temperature. The feed flow rate has a smaller effect than feed temperature. The concentration of the solute has a slight effect and it is negligible in VMD. The cold side conditions have a lower effect than the hot side. The vacuum pressure has the maximum contribution in improving the MD flux in VMD. The permeate fluxes are strongly affected by the boundary layer heat transfer coefficient, since lowering the temperature polarization coefficient is essential to enhance the process performance. In fouling test, the permeate flux was reduced with time that may be caused by some salt deposited on the membrane surface. However, this was easily removed by the water cleaning of the membrane. This shows a good sense for the application of MD in the field of high salinity brine and wastewater treatment.

MD has some significant advantages over the other processes, including lower operating temperature. Thus, this process uses energy sources such as renewable solar heat or waste heat. The low pressure pumps product quality and higher resistance to fouling comparable with other pressure-driven processes.

In MD process, the scarcity of experimental data and large scatter in the results indicate that a more intensive and focused research efforts in this field are needed, both in experimental and modeling. The issues are the high energy consumption in MD units, heat recovery, difficulties with long-term operations with risk of membrane pore wetting, and membrane fouling. Also, there is a lack of MD membranes and modules design, membrane materials selectivity, permeability, high economic costs, and constructions of pilot plants for scale-up studies. Heat integration is a critical issue in the MD operation. Hence, Memstill technology is one of the promising technology developed an economically for the application of desalination and wastewater treatment. Furthermore, there is need to improve the MD membranes properties and structure for improving the MD performance. More efforts must be done on fabrication of membrane and module suitable for MD configuration with outstanding performance. Also, the more efforts need especially utilization of waste energy or alternative energy in the view of industrial realization.

In addition, there is no commercial product available in the market, which is based on the MD process. The limited information on the removal of organic and multicomponent inorganic matter from MD process was found in the literature. Also, the research on the groundwater purification and removal of toxic inorganic constituents from groundwater by MD process was not studied in the literature. Moreover, there is no such information available to describe inorganic fouling on the membrane surface in a multi-component system. Hence, more detailed study of this field is needed to reveal the interactions.

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