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Fouling and Wetting in the Membrane Distillation Driven Wastewater Reclamation Process – A Review

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Abstract

Fouling and wetting of membranes are significant concerns that can impede widespread application of the membrane distillation (MD) process during high-salinity wastewater reclamation. Fouling, caused by the accumulation of undesirable materials on the membrane surface and pores, causes a decrease in permeate flux. Whereas membrane wetting, the direct permeation of the feed solution through the membrane pores, results in reduced contaminant rejection and overall process failure. Lately, the application of MD for water recovery from various types of wastewaters has gained increased attention among researchers. In this review, we discuss fouling and wetting phenomena observed during the MD process, along with the effects of various mitigation strategies. In addition, we examine the interactions between contaminants and different types of MD membranes and the influence of different operating conditions on the occurrence of fouling and wetting. We also report on previously investigated feed pre-treatment options before MD, application of integrated MD processes, the performance of fabricated/modified MD membranes, and strategies for MD membrane maintenance during water reclamation. We also discussed energy consumption and economic aspects of MD for wastewater recovery. Throughout the review, we engage in discussions highlighting research needs for furthering the development of MD: notably the incorporation of MD in the overall wastewater treatment and recovery scheme (including selection of appropriate membrane material, suitable pre-treatment or integrated processes, and membrane maintenance strategies), and the application of MD in long-term pilot-scale studies using real wastewater.

Keywords: Membrane distillation; fouling; wetting; wastewater; reclamation

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1. Introduction

The scarcity of clean water has become a significant challenge in today's world, which inevitably has led towards the need to develop novel technologies to help provide a dependable supply of fresh water [1–3]. As of late, Membrane Distillation (MD) has gained significant attention as a promising technology for the production of fresh water via the treatment of high-salinity wastewater. MD is a membrane-based, vapor-driven thermal desalination process, in which water molecules are transported in a vapor phase through a porous and hydrophobic membrane [4–8]. The porous, hydrophobic membrane is used to separate a hot, highly concentrated feed stream, and a cold distillate stream [4,8,9]. The temperature difference between the feed and distillate streams creates a partial vapor pressure difference that drives the water vapor through the membrane from the feed side to distillate side, where it condenses to pure water. The hydrophobic membrane prevents direct permeation of feed water, an essential feature for contaminant rejection. Due to reduced sensitivity to concentration polarization and the much high driving force resulting from a temperature difference, MD can operate at high salinities on the feed side [10]. MD demonstrates several distinct advantages such as: a 100% theoretical non-volatile salt rejection, a lower required operating temperature as compared to conventional thermal desalination processes, the ability to utilize low-grade thermal energy, a lower operating hydrostatic pressure, and less stringent mechanical property requirements for the membranes used when compared to conventional pressure-driven membrane processes such as reverse osmosis (RO) [8,9,19,11–18]. MD has the potential to provide sustainable water recovery when heat sources (low-grade or renewable) and waste-heat from industrial processes are readily available [20,21]. Despite these advantages, the extensive application of MD still faces uncertainty for its overall sustainability and effectiveness [6]. MD is not efficient in separating

volatile and semi-volatile compounds [22,23]. It is a highly energy intensive technology compared to pressure-driven (e.g., RO) desalination processes, which makes it unattractive unless very high-salinity brines (which cannot be treated effectively by RO) require treatment [24]. Though other thermal distillation processes like multi-effect distillation (MED) and multistage flash (MSF) can be used to treat highly saline brine at low temperature, the energetic performance of MD is reported to be superior to MED and MSF for small-scale systems ($<1000 \text{ m}^3 \text{ day}^{-1}$) [24]. A fundamental challenge involved in conventional MD revolves around heat management in the process. Single-pass recoveries are very low in MD [25], and the adoption of a multi-stage approach [18] through the involvement of many heat exchangers can enhance water productivity and energy efficiency [24]. The multi-stage approach moves away from the all-plastic system design and will increase the capital cost of the treatment system. Achieving higher fluxes and thermal efficiencies in the MD process can be reached through the optimization of operating conditions or system configuration. Novel options like self-heating membranes (membranes heated on the feed side by Joule heating or photo-thermal surface heating) have been adopted in MD, which reduces temperature polarization and yields higher single-pass recoveries than conventional MD membranes [20,26,27]. However, these advances have only been demonstrated at the laboratory scale, and further pilot-scale testing is necessary to assess their viability.

Wetting and fouling are two interrelated phenomena in MD, which influence each other and pose significant challenges in the application of MD. Membrane wetting is a unique challenge in MD, and it refers to the direct permeation of the feed solution through the membrane pores, resulting in reduced salt rejection and overall process failure [9,19,28,29]. Wetting has been associated as

a problem during the long-term operation of MD systems, provided appropriate operating conditions are maintained [30]. Wetting can also occur in short-term MD operations due to improper operating conditions (e.g., pore size, membrane hydrophobicity, LEP of the system, etc.) in the system. On the other hand, as in other membrane-based processes, membrane fouling is a significant drawback of MD, causing a decrease in permeate-flux due to the accumulation of undesirable material on the membrane surface and pores. Both fouling and wetting are time-dependent processes, and long-term effects cannot be easily predicted [31].

MD has been extensively studied for the removal of salts from brackish water, seawater, and high-salinity brines [16,32–36]. Numerous studies have investigated MD for the production of fresh water from seawater/brine water via desalination using different membranes and operating parameters. These studies have widely indicated the negative impacts of both membrane fouling and wetting on the overall performance of the MD process [14,34,37–41]. MD has also been studied for the recovery of heavy metals from water streams [42–44]. There are few review articles focused on membrane fouling and relevant control methods as encountered in different applications of MD [8,45]. A literature search for “membrane distillation”, in Web of Science, revealed more than 4,300 articles published from January 1991 to December 2018, with increasing growth in the number of articles published during the past decade (Figure 1). However, research concerning the application of MD in wastewater treatment and reclamation has gained attention recently. MD has found a niche application, in particular for recovery of hypersaline wastewater in emerging industries (e.g., shale-gas), which conventional membrane desalination such as RO cannot access [46–49]. MD has also received interest as a promising technology to produce high-quality freshwater from wastewater through utilization of available

waste-heat or low-grade solar or geothermal heat [50–53]. There is a continuous drive to improve energy and process efficiency of MD systems while recovering freshwater from wastewater, through improvement of MD system configuration, development of novel/modified membrane material, or integration of other processes with MD. It also provides good scalability due to its modular features. Though MD is primarily utilized for water recovery from highly saline/brine water, it showed potential for reclamation of high-strength wastewater in small-scale, decentralized systems with available waste/alternative heat sources.

This review discusses the fouling and wetting scenarios in MD as reported in the literature, along with contaminant-membrane interactions, influence of operational conditions, treatment performances, and the effects of different mitigation strategies employed during the recovery of various types of real wastewater. This article also discusses different MD membrane fabrication/modification, integrated MD processes, pre-treatment strategies for feed wastewater streams, and membrane cleaning strategies for wastewater reclamation. This review also contains, as a necessary background for readers, a brief discussion of classical and recent MD module configurations, MD membrane features as well as the mechanisms influencing membrane fouling and wetting. Different invasive and non-invasive membrane fouling and wetting monitoring techniques have also been discussed briefly in this article. The discussions also include future research directions pertaining to the application of MD in wastewater reclamation.

2. MD: process configurations and membranes

2.1 Process configurations in MD

Subject to the process of stimulating vapor pressure gradient across the membrane and gathering the transported vapors on the permeate side, there are four different classical configurations of MD [6,31]. The basic mechanisms of these classical configurations are briefly described in the following sections and illustrated in Figure 2.

Direct contact membrane distillation (DCMD): In DCMD, a hot solution (feed) and a cold solution are in direct contact with the hot feed side surface and the cold permeate side surface of the membrane, respectively. The vapor generated at the hot feed-side membrane surface flows through the membrane pores to the cold permeate-side due to the vapor pressure difference, resulting from the temperature difference, across the membrane. Warm pure water leaving the MD module preheats the feed in a separate external heat exchanger (not shown in Figure 2). The DCMD has been reported as the simplest of MD configurations and has been studied the most in literature for wastewater recovery, and concentration of aqueous solutions [Table 1]. The membrane remains as the only barricade between the recirculating hot feed and cold permeate solution streams. As a result, DCMD experiences the highest heat loss through conduction among the four standard configurations.

Air gap membrane distillation (AGMD): AGMD introduces a thin stagnant air gap between the membrane and a condensation surface on the permeate side, whereas the hot feed solution remains in direct contact with the membrane solution. The vapor passing through the membrane crosses the air gap and condenses on the cold condensation surface (usually a thin dense polymer

or metal layer) [54,55]. AGMD offers reduced heat loss through conduction. However, the enhanced resistance to mass transport, introduced by the air gap, results in a lower flux of AGMD than other MD configurations [56].

Vacuum membrane distillation (VMD): A pump is used on the permeate side to create a vacuum and provide driving force lower than the saturation pressure of volatile molecules in the feed water. Condensation may occur inside or outside of the membrane module [57–59]. Conducting heat loss is negligible in VMD [58,59].

Sweeping gas membrane distillation (SGMD): This configuration allows a sweeping flow of cold inert gas to collect vapor molecules from the membrane permeate surface and condense it outside the membrane module [31,60]. There is a moving gas barrier, which enhances mass transport efficiency compared to AGMD and also reduces conductive heat loss [31]. The SGMD requires external condenser to collect a small volume of permeate in a large volume of sweep gas [31,60].

Recent MD Configurations: Recent studies have revealed the development of some novel variations to the classical AGMD and VMD configurations to enhance the energy efficiency of the process and the water vapor flux through the membrane. The different novel configurations with modified gaps are the permeate gap MD (PGMD), the material gap MD (MGMD), and conductive gap MD (CGMD) [61–68]. PGMD, also known as water gap MD or liquid gap MD, is a hybrid of the AGMD and DCMD configurations where water or liquid is used to fill up the gap between the membrane and cold condensation surface [61–63,65,67]. The MGMD configuration uses additional material (such as sand) in the gap between the membrane and the

condensation plate [64]. Finally, the CGMD configuration employs a high thermal conductivity spacer (such as a metallic mesh) in the permeate gap to improve the conductance of the gap along the thickness direction [61–63]. Figure 3 provides a schematic of different gap MD systems.

In addition to these gap MD systems, another novel configuration introduced a flashed-feed VMD system where the feed stream was not allowed to touch the MD membrane [69]. The flashed-feed VMD configuration used a throttling valve in the feed line along with a vacuum pump (maintaining a vacuum in the flashing chamber) to regulate the feed flow rate to the flashing chamber (Figure 4). The novel flashed-feed VMD system eliminated the temperature polarization effect near the membrane (which can reduce the feed water temperature near the membrane relative to the bulk feed temperature) and provided up to 3.5 times higher flux than conventional VMD under similar operating conditions [69].

Efforts have been carried out to develop new MD process configurations and membrane modules with higher thermal efficiencies [70–78]. Fabrication of hollow fiber (single or multi-bore) membranes has been developed to enable the modular design of the MD systems [68,70,71,79,80]. Multi-stage and multi-effect MD (MEMD) configurations for gap MD and VMD systems have been proposed for seawater desalination with internal heat recovery and enhanced flux in the systems [74,76–78,81]. The concept of the MEMD systems involves placing the cold feed solution beneath the condensation surface, as a coolant, to gain some degree of pre-heating as the permeated vapor gets condensed [74,76–78,81]. The internal heat

recovery mechanism in the MEMD systems enable better thermal efficiency in the MD process [18,78,81].

The several recently developed MD configurations have been studied mostly in seawater desalination. The updated versions of traditional gap MD, VMD systems and the modular MEMD systems hold promising traits in terms of demonstrating enhanced flux and energy consumption performances than conventional MD systems during reclamation of high-salinity wastewater. However, high levels of organic contaminants in the wastewater, compared to seawater, might result in the occurrence of excessive organic fouling and biofouling in the updated systems. Similarly, module scale-up with efficient internal heat recovery and satisfactory flux in the MEMD systems will also pose challenges with altered membrane fouling and wetting scenarios. Hence these updated and modular MD systems should be studied for recovery of wastewater.

2.2 Features of MD membranes: MD membranes should have high porosity, high hydrophobicity, uniform pore size distribution, and low tortuosity [8]. To prevent heat loss across the membrane, microporous membranes employed in MD should possess low mass transfer resistance and low thermal conductivity [4]. Also, suitable thermal stability and resistance to chemicals (e.g., acids and bases), are essential characteristics of membranes used in MD [4]. Optimal membrane pore size must be balanced in terms of high permeate flux and effective pore wetting resistance. High porosity membranes with low mechanical strength tend to degrade under even mild operational pressures, resulting in a decline in membrane performance [82]. The porosity values for different MD membranes, used in high-strength wastewater

reclamation, are observed to be in the range between 70-85%. Usually, commercial hydrophobic MD membranes are made of polytetrafluoroethylene (PTFE), polypropylene (PP), or polyvinylidene fluoride (PVDF) active layers with optional support layer materials (e.g., PP, polyester) [4,8,83,84]. Another significant property of the MD system is “liquid entry pressure” (LEP), which is the pressure at which the liquid penetrates the membrane pores and causes wetting of the membrane. To prevent the penetration of feed solution through membrane pores, the applied pressure in MD should always be less than the LEP. LEP is an intrinsic property of the system involving the membrane and solution. The major parameters that influence the LEP are: surface tension of the solution, surface energy of membrane material (which controls the membrane hydrophobicity), membrane pore size and geometry, feed concentration, and the presence of organic solutes and surfactants [4,85]. LEP is described by the Laplace-Young equation [4]:

$$LEP = \frac{-4B_g \sigma \cos \theta}{d_{\max}}$$

Where, B_g = pore geometric factor, σ = surface tension of the solution, θ = contact angle between the solution and the membrane surface, and d_{\max} = diameter of the largest membrane pore size.

Apparently, the Laplace-Young equation might indicate that lower pore size is desirable to prevent the occurrence of membrane wetting. However, too much lowering of the membrane pore size will result in a decrease of trans-membrane flux and overall recovery performance. The membrane pore size thus should be selected in such a way that the trans-membrane flux must be enhanced without increasing the chance of membrane wetting. Fabrication of composite MD membranes with novel material and architecture, which involves different surface and inner

membrane conformation (discussed in a later section), demonstrated enhanced porosity and flux with low wetting potential.

3. Fouling and wetting phenomena in MD

3.1 Fouling mechanism in MD: Foulants (depositing compounds causing fouling) are usually of inorganic, organic, or biological nature and can interact with each other as well as membrane surfaces. Membrane fouling is affected by the following parameters [8]: i) foulant characteristics (e.g., concentration, molecular size, solubility, diffusivity, hydrophobicity, charge); ii) membrane properties (e.g., hydrophobicity, surface roughness, pore size and its uniformity distribution, membrane structure, surface charge, surface functional groups); iii) operational conditions (e.g., flux, solution temperature, flow velocity, pressure); and iv) feed water characteristics (e.g., pH, ionic strength, presence of organic/inorganic matters, microorganisms). Surface roughness influences the hydrophobicity of a membrane, which in turn impart antifouling and anti-wetting property. Higher surface roughness entraps more air fraction in the micro- and nano-sized pores of the membrane surface [86]. As a result, the membrane surface becomes more hydrophobic with increased solid-gas interface fraction in the overall mix of solid-liquid and solid-gas interfaces on the membrane surface. According to the extended DLVO model, three key interfacial interactions for particles in aqueous media are Lifshitz-van der Waals, Lewis acid-base, and electrostatic double layer interactions [87]. Fouling minimizes if the particle and surface have similar charges leading towards repulsion. Also, deposition of particulate matter forms on the membrane surface by agglomeration of particles in aqueous solutions. Higher aggregation occurs because of large attachment coefficients resulting from an extensive degree of collisions [88]. At high ionic strengths, the interaction between particles is

dominated by acid-base interactions as electrical double layer forces are weak in this condition [89,90]; whereas Van der Waals interactions are not susceptible to variations in pH and electrolyte concentrations. Studies have shown that increased ionic strength, in the presence of divalent cations, resulted in more fouling of humic substances on DCMD membranes [91–93]. At high ionic strength, the charges of the membrane surface and humic macromolecules are significantly reduced, which leads to a decrease in the electrostatic repulsion between the membrane surface and humic macromolecules. As a result, the humic macromolecules, which become coiled and spherical in shape, forms a more compact fouling layer [93]. The presence of a foulant layer causes additional thermal and hydraulic resistance based on the characteristics (porosity, thickness, etc.) of the fouling layers [11,92]. Feed water foulants can attach to the hydrophobic membrane surface, and block membrane pores leading to a decline in permeate flux [85]. Fouling is severe when the feed contains ample hydrophobic contaminants (oil, hydrophobic organics, etc.) as hydrophobic-hydrophobic attraction results in strong bonding between the membrane surface and the contaminants [45,94].

Fouling in MD has been broadly classified into the following groups: (a) inorganic fouling, (b) organic fouling, and (c) biological fouling [10,31,95,96]. Figure 5 schematically represents these fouling mechanisms and their combined effect on MD, leading to partial or complete pore blocking and surface fouling. Inorganic fouling mainly refers to scaling that is comprised of the precipitation of hard salts such as calcium carbonate, calcium sulfate, silicate, sodium chloride, or calcium phosphate. Water evaporation and temperature changes create supersaturation on the feed side that lead to nucleation and crystallization in the feed and on the membrane surface, resulting in inorganic fouling [85]. Colloidal organic matter, (e.g., humic substances, proteins,

extracellular polymeric substances (EPS), etc.) are responsible for organic fouling in the MD process [8,97]. Finally, biological fouling or biofouling refers to the accumulation and evolution of microorganisms on the membrane surface that cause permeate flux decline [8]. Dynamic biofouling experiments (with *Anoxybacillus* sp. as a model bacterium) were carried out to indicate the impact of increasing feed water temperatures on biofilm growth and MD performance [98]. The *Anoxybacillus* sp. has been identified as a major bacterial genus in MD bioreactor suspended sludge [99]. Biofouling situations in PVDF MD membranes were studied in the feed side at temperatures of 47°C (temperature below the optimum temperature for thermophilic bacterial growth), 55°C (optimum temperature for thermophilic bacterial growth) and 65°C (temperature above the optimum temperature for thermophilic bacterial growth) [98]. Extensive bio cell growth was observed on the feed side at 55°C when compared to the same at 47°C. As a result, the water flux decline was more (78%) at 55°C compared to the water flux decline at 47°C (30%) after three days of operation. Increasing temperature to 55°C also enhanced biofouling induced membrane wetting and allowed bacterial cells and endospores through the membrane to the permeate side. Bacterial growth was impaired when feed water temperature was increased to 65°C. However, excessive production of extracellular polymeric substances (EPS) at 65°C caused severe pore wetting and hampered MD function [98]. Bacterial EPS, protein and polysaccharides were observed on the fouling layers of flat-sheet PVDF and PTFE membranes in a submerged MD bioreactor [100]. The polysaccharide concentration on the fouling layer and total amount of fouling on PVDF membranes were more than that observed on PTFE membranes. The polysaccharide concentration and fouling amount indicated that the polysaccharides play a vital role in the initial attachment and subsequent formation of fouling layer [100]. Thus, the interaction between membrane material and specific fouling component

can enhance overall fouling in the system [100]. It has been suggested that thermophilic bacteria may also survive in the high feed temperature by forming spores, which later settle and accumulate on the membrane surface at a lower temperature zone [101,102]. Small colonies of *S. faecalis* bacteria was observed on the membrane surface on the distillate side in the vicinity of large membrane pores while recovery of wastewater generated from processing animal intestines [101]. The growth of the *S. faecalis* bacteria was restricted due to the scarcity of nutrients and organic matters on the distillate side [101]. The biofouling conditions reported across different publications varied in extent due to the various feed water conditions, operational conditions, and duration of the experiments. Dynamic biofouling experiments at different temperatures, with specific microorganism (*Anoxybacillus* sp.) dosed on the feed side, have generated a better understanding of the biofouling mechanisms [98]. Experiments with other major microorganism groups may indicate how different microorganisms interact with each other as biofouling takes place on MD membranes. Also, the impact of water quality (e.g., change in nutrient content) and operational conditions should also be assessed in similar dynamic biofouling experiments to achieve a better understanding of MD membrane biofouling process.

3.2 Wetting mechanism in MD: Wetting refers to the permeation of water through membrane pores, which degrades permeate quality, especially during long-term MD operation [30]. Membrane wetting is stimulated in MD by the presence of inorganic fouling/scaling, amphiphilic molecules (e.g., surfactants and protein), low surface tension liquids (e.g., alcohol), the use of antiscalants, and chemical degradation of the membrane [8,45]. Wetting can also occur when the pressure on the feed side exceeds the LEP of the membrane [45]. Often, fouling by salt deposition on the membrane surface, as well as in the membrane pores (inorganic fouling),

provides hydrophilicity to the membrane, resulting in wetting [45]. Low surface tension contaminants and surfactants, which are commonly found in wastewater streams, can lead to the wetting of conventional hydrophobic membranes in MD [46,103,104]. These contaminants, which have a hydrophobic tail moiety, tend to adsorb on the surface and pore walls of MD membranes through hydrophobic-hydrophobic interactions and can make the membrane surface and pores more hydrophilic. The wettability of membranes have been classified as (a) non-wetted (with maximum vapor transport through the pores, which obtain the highest flux and maximum salt rejection), (b) surface-wetted (gap for vapor transport reduced, but no permeation of feed water towards the permeate), (c) partially-wetted (feed water permeates through some pores, while vapor transport gap decreases in other pores), and (d) fully-wetted (all membrane pores allow permeation of feed water, which remarkably deteriorates permeate quality due to contaminants' penetration) [28,105–107]. Some studies have also referred to different stages of MD membrane wetting as (a) non-wetted (refers to the state where maximum vapor pressure exists through the pores to achieve the highest flux and maximum salt rejection), (b) surface/partial-wetted (refers to the transition state, where partial penetration of the feed solution occurs, which decreases the average distance between the two liquid-air interfaces, or the thickness of the air gap within the pores), and (c) pore-wetted/wetted (refers to the state where some membrane pores are fully penetrated, and the salt in the feed stream can freely move through the wetted pores to the permeate side) membranes [104,108–110]. Studies have observed that operational parameters in MD, (e.g., pressure, temperature and flow rate) can affect membrane wettability and salt rejection rates [29,77,78,111].

3.3 Fouling and wetting monitoring techniques in MD: The conventional fouling and wetting monitoring techniques in different types of MD processes involves observing the change in flux through the membrane to the permeate side and measuring the conductivity on the permeate side, respectively. The occurrence of fouling on the feed side of the membrane results in a low trans-membrane flux while wetting of the MD membrane effects in an increase in conductivity on the permeate side. Although measurement of trans-membrane flux and permeate conductivity provides information on the occurrence of fouling and wetting in MD, respectively, they do not necessarily provide much insight on the mechanism and kinetics of fouling and wetting occurrences. Many analytical techniques both invasive and non-invasive have been developed to study fouling and wetting in the MD process. These are briefly discussed in the following subsections:

Invasive analytical techniques: The invasive fouling and wetting monitoring methods in MD involve conducting the MD experiments repeatedly over different periods under different operational conditions and then analyzing the membrane after disassembling it outside the MD module. These invasive techniques of membrane surface analysis help in understanding the fouling and wetting characteristics, mechanism and extent on the membranes. The most commonly reported invasive procedures for fouling and wetting assessment involves using direct visualization and/or SEM (scanning electron microscopy) to evaluate the surface morphology of the membrane surface as it is altered by the deposition of inorganic, organic, and biological foulants. SEM and/or optical laser techniques are also employed to measure the membrane thickness.

Additionally, analytical techniques like EDX (energy dispersive x-ray spectroscopy) and/or XPS (x-ray photoelectron spectroscopy) have been used along with SEM to gather elemental composition of the membrane surfaces [5,19,47,104,112–115]. Techniques like AFM (atomic force microscopy) and XRD (x-ray diffraction) have been employed to characterize the surface structure, roughness of the membranes [5,113,116–119] and the crystal composition of the scales formed on the membrane surface, respectively [91,118,120–122]. FTIR (Fourier transform infrared spectrometer) has been used to assess chemical composition of foulants (like functional groups, biopolymers, polysaccharides or humic acids), which helps in understanding the interaction and bonding between the foulants and the membrane surface [95,121,123–126]. Also, the contact angle (Table 1) and the zeta potential [123,127] are measured on the membrane surface to evaluate the change in surface hydrophobicity and charge due to fouling and wetting, respectively. Apart from these primary analytical techniques, many water quality analysis experiments are also carried out in both feed and permeate water to gain an understanding of the feed water constituents influencing the mechanism of fouling and wetting.

Non-invasive analytical techniques: Recent studies have reported novel non-invasive methods, which enable membrane fouling and wetting monitoring while the membrane is held during operation within the MD module. Optical coherence tomography (OCT) has been reported to study in-situ fouling (inorganic fouling, organic fouling, and biofouling) in DCMD systems [98,112,123,128,129]. The OCT device is placed next to the DCMD set up to monitor the feed half, using a special viewing window on the MD module. The cross-sectional image of the foulant on the membrane surface is then captured as a function of time while the MD operation ensues. Recent studies have successfully employed OCD based fouling visualization methods

and validated the monitoring method using conventional invasive techniques [98,112,123,129]. Bauer et al. (2019) presented an innovative methodology using OCT, which enables 3D dataset analysis allowing for quantification of scaling on the membrane surface in a DCMD. The generated data from OCT were not only used to describe the structural development of scaling in the MD system, but the data was further processed to formulate and calculate quantitative fouling parameters based on layer volume and coverage, which can allow for process control. The developed methodology was able to assess the fouling condition independent from the flux decrease, and hence it can be used for an early prediction of process efficiency loss due to fouling [128].

An electrochemical impedance-based method has been reported recently to in-situ monitor membrane pore wetting in a DCMD setup [108]. The study provided an impedance-measuring arrangement in a DCMD configuration. Membrane wetting was observed using both single-frequency cross-membrane impedance measurements and distillate conductivity measurements. The noteworthy response of single-frequency impedance to partial pore wetting before any change in distillate conductivity suggest that the in-situ impedance measurement method can provide early detection of imminent membrane wetting [108].

The novel in-situ fouling and wetting monitoring techniques offer the advantage of linking real-time fouling and wetting mechanisms and kinetics to operating conditions and water quality. As the number of studies concerning the application of MD for wastewater reclamation is increasing in the research community, implementation of these novel-monitoring techniques will provide a better perception on the dynamics of fouling and wetting in the system. However, for the

fundamental understanding of the fouling and wetting scenario involving different contaminant groups in the feed stream, the non-invasive methods will be critical.

4. Factors affecting the occurrences of fouling and wetting in MD

Several studies have reported operational parameters (Table 1) and performance (Table 2) of MD process when it is applied either individually or integrated into a more extensive treatment system for the treatment and recovery of different types of wastewater. The following sections review critical observations concerning the influence of wastewater composition and process operating condition on fouling and wetting in MD.

4.1 Impact of wastewater composition: Most studies involving the use of MD for wastewater recovery use synthetic wastewater with model contaminants to assess scaling and fouling performance [118,124,130]. Reports describing MD with real wastewater indicates that system performance varies significantly from studies conducted with synthetic wastewater [131,132]. Several studies have observed the occurrence of fouling and wetting in direct contact membrane distillation (DCMD) [118,124,132,133] and vacuum membrane distillation (VMD) [130] of synthetic solutions prepared using dyes specifically found in textile/dyeing wastewater. VMD demonstrated complete rejection of five different dyes in a bench-scale setup during short duration (less than 2 hours) experiments [130]. Fouling performance of treatment via DCMD for four different dyes (methylene blue, crystal violet, acid red 18, and acid yellow 36) reported dye-dye interactions and membrane-dye interfacial interactions [124]. Negatively charged PVDF/PTFE membrane surfaces performed well in the treatment of acid and azo dyes of the same charge and showed higher fluxes [124].

Similarly, the charge of contaminants in pharmaceutical wastewaters influenced the interaction among the contaminants and the membrane yielding fouling and wetting of MD membranes during treatment/reclamation of pharmaceutical wastewaters [123]. A total of 12 selected antibiotics were mixed with feed solution and treated in DCMD process with a PVDF membrane. The antibiotics were chosen on the basis of the charges in them (i.e., positive, negative or neutral). Eight antibiotics with negative charge (Cefazolin, Cefotaxime, Amoxicillin trihydrate, Cephalothin, Ceftazidime hydrate, Piperacillin, Cloxacillin monohydrate, Antimony (III) isopropoxide), two antibiotics with positive charge (Gentamicin sulfate, Tobramycin), and two antibiotics with neutral charge (Ciprofloxacin, Enrofloxacin) were dosed in the range of 1-200 mg/L in DI feed water to produce pharmaceutical wastewater. For a negatively charged PVDF membrane, a significant decline in water flux and wetting was observed during reclamation of pharmaceutical wastewaters containing a positively charged antibiotic, while water flux remained stable in the case of negatively charged and neutral antibiotics with 100% rejection [123]. Rejection of positively charged antibiotics: Gentamicin sulfate and Tobramycin were 86% and 78%, respectively [123]. Air gap membrane distillation (AGMD) pilot trials in pharmaceutical wastewaters recovery witnessed greater removal efficiencies than most other technologies (activated sludge, membrane bioreactors, membrane bioreactors with flocculation and sedimentation, forward osmosis) and comparable removal performances as nanofiltration and RO [134]. A total of nineteen pharmaceutical residues were detected in the effluent from a municipal wastewater treatment plant [134]. Table 3 outlines the removal efficiencies (%) for different pharmaceutical residues observed by AGMD, DCMD, and other technologies. A study evaluated rejection of 25 pharmaceutical compounds (Table 3) by DCMD process using a PTFE

membrane and observed more than 99% rejection for all the pharmaceutical compounds (even in the presence of humic acid) [135]. DCMD experiments were carried out with and without humic acid (0, 20, 40, 60, and 80 mg/L) in DI feed solution, which contains pharmaceuticals (each compound having a concentration of 1 $\mu\text{g/L}$). It was observed that the retention of pharmaceutical compounds predominantly occurred by membrane rejection (which is mainly governed by volatility and, to a lesser extent by hydrophobia) [135].

DCMD was also employed successfully to treat low-level radioactive wastewater using PVDF hollow fiber membranes [136] and spiral wound PTFE membranes [137]. In the study involving treatment of simulated radioactive solutions containing caesium (Cs^+), strontium (Sr^{2+}), cobalt (Co^{2+}) in a PVDF hollow fiber membrane module, two solutions were prepared with concentrations of 20 mg/L and 100 mg/L for all the cations. DCMD achieved complete rejection of the cations as no detectable concentrations were observed for Cs^+ , Sr^{2+} , and Co^{2+} in the permeate solution, which reflected an infinite decontamination factor [136]. A synthetic solution, prepared using inorganic salts (non-active) and radioactive elements, was treated using a spiral wound PTFE membrane module [137]. The non-active inorganic ions in solution were Na^+ (1060.6 mg/L), NH_4^+ (207.1 mg/L), K^+ (21 mg/L), Mg^{2+} (33.7 mg/L), Ca^{2+} (87.2 mg/L), F^- (5.7 mg/L), Cl^- (744.2 mg/L), NO_3^- (1832.9 mg/L), SO_4^{2-} (37.6 mg/L) and the radioisotopes were ^{140}La ($<6.53 \times 10^{-1}$ Bq/L), ^{133}Ba (2.99×10^3 Bq/L), ^{170}Tm (5.26×10^2 Bq/L), $^{114\text{m}}\text{In}$ (86.2 Bq/L), ^{192}Ir (37.3 Bq/L), $^{110\text{m}}\text{Ag}$ (10.4 Bq/L), ^{65}Zn (3.39×10^3 Bq/L), ^{134}Cs (7.84 Bq/L), ^{137}Cs (29.5 Bq/L), and ^{60}Co (4.51×10^3 Bq/L) [137]. All the radioisotopes, except ^{137}Cs and ^{60}Co , displayed infinite decontamination factor, and the decontamination factor of ^{137}Cs and ^{60}Co were 43.8 and 4336.5, respectively [137]. Jia et al. reported treatment of a synthetic feed solution containing 10

mg/L SrCl_2 or $\text{Co}(\text{NO}_3)_2$ in a VMD using a PP hollow fiber membrane and reported very high rejection of Co^{2+} (99.67% – 99.82%) and Sr^{2+} (99.60% – 99.74%) in the membrane [138,139]. Decontamination factors (DF) observed for low- and medium-level radioactive wastewater in other treatment processes, like evaporation, ion exchange (organic), ion exchange (inorganic), chemical precipitation, bioaccumulation, biosorption, and reverse osmosis are 10^3 - 10^6 , 10 - 10^3 , 10 - 10^4 , 10 - 10^3 , more than 10^3 , less than 10^3 , and 10 - 10^3 , respectively [136,140]. Membrane distillation with its high DFs (almost infinite with many radioisotopes) is a competitive method in the treatment and recovery of radioactive wastewater. However, it has to be mentioned that these high-decontamination factors are achieved from low-volatile solute after adequate pre-treatment [140].

Fermentation wastewater, having high organic content, resulted in a 50.5% reduction in flux after 12-hour DCMD treatment with PP membranes without any pre-treatment of feed water [141]. The fermentation wastewater samples were collected from a yeast factory with initial chemical oxygen demand (COD), total organic carbon (TOC) and protein concentrations as 54,900 mg/L, 20,900 mg/L, and 1,765 mg/L, respectively [141]. Gas chromatography-mass spectrometry analysis revealed 14 major organic compounds including isoamyl; 2-methyl butyric acid; 2,3,5-trimethyl pyrazine; 2-acetyl pyrrole; 2-pyrrolidinone; phenethyl alcohol; benzoic acid; phenylacetic acid; 4-ethenyl-2-methoxyphenol; o-hydroxybenzoic acid; p-hydroxyphenyl ethanol; p-hydroxyphenylcyanide; 4-hydroxy-3-methoxyphenethyl alcohol; and butyl phthalate in the fermentation wastewater [141]. Among the dominant organics present in fermentation wastewater, volatile organic compounds (trimethyl pyrazine, 2-acetyl pyrrole, phenethyl alcohol and phenylacetic acid) and a non-volatile (dibutyl phthalate) transferred through the membranes

and were detected in permeate water due to membrane wetting, which resulted in 95.3% and 95.7% rejection for COD and TOC, respectively [141]. After 5 hours of DCMD operation, 2,3,5-trimethyl pyrazine, 2-acetyl pyrrole, and phenethyl alcohol were detected in the permeate stream [141]. While after 10 hours another organic compound phenylacetic acid was detected in the permeate stream, whose late occurrence was attributed to its complex nature. Finally, dibutyl phthalate, which is not a volatile compound, was observed in the permeate stream after 12 hours due to membrane wetting [141]. The deposited foulants were mostly organic components combined with inorganics, which were hard to remove by only water rinsing (for 60 minutes), while most of them were removed in a sequential wash of water, acid ((HCl solution 0.5 mol/L), base (NaOH solution 0.5 mol/L), and water for 10, 20, 20, and 10 minutes, respectively [141]. Transfer of organic matter to the distillate solution through the membrane has also been associated with an adsorption-desorption mechanism [91,142]. Organic humic acid, which initially adsorbs on the membrane surface, forms a hydrogen bond with water vapor (between the carboxylic group in the humic acid and the oxygen molecule in water vapor) and moves through the membrane pore space. The hydrogen bond weakens as the water vapor moves through the membrane pore space and re-adsorption of humic acid takes place in the downstream membrane pore location [142]. This adsorption-desorption process ensues recurrently until the humic acid reaches and disperse into the permeate [142]. Ammonia ($\text{NH}_4\text{-N}$) rejection in MD has been reported to be poor in different types of organic wastewater treatment and reclamation in comparison to other kinds of contaminants [143,144]. Low $\text{NH}_4\text{-N}$ rejection may be attributed to the preferential generation of volatile ammonia gas and its permeation through membrane pores during the heating process [144]. Recovery of water from raw and biologically pre-treated municipal wastewater by DCMD using PTFE and PVDF membranes was calculated to yield

high (about 87-99% for PTFE and 63-97% for PVDF) rejection of the conductivity, COD, alkalinity, hardness and low rejection (about 50-60% for PTFE and 35-50% for PVDF) of $\text{NH}_4\text{-N}$ [143]. The experimental operating conditions and rejections of these water quality parameters by PVDF and PTFE membranes are separately mentioned in Table 1 and Table 2, respectively. Increased wetting of the PVDF membrane with raw municipal wastewater when compared to PTFE membrane, resulted in reduced $\text{NH}_4\text{-N}$ rejection efficiency in PVDF membranes [143]. Also, the increase in feed stream temperature resulted in a higher temperature gradient across the membrane, which favored volatilization of ammonia gas and its permeation through the membrane pores [143]. DCMD of raw landfill leachates using PTFE and PVDF membranes (operational conditions in Table 1) demonstrated high rejection efficiencies for most of the water quality parameters (conductivity, alkalinity, hardness, COD, sulfate) but a low rejection of $\text{NH}_4\text{-N}$ (Table 2) [144]. The presence of organic biomass in wastewater resulted in an observable decrease in vapor pressure (due to the non-volatile fraction of biomass) in feed water and reduced the permeate flux in DCMD system to more than 50% and 70% of initial flux value ($2.09 \text{ L/m}^2/\text{h}$) for 6 and 12 g/L biomass, respectively after 72 hours of operation [145].

Oily wastewater recovery using PVDF membrane in DCMD showed that presence of only oil, with salt or surfactant, caused a gradual decline in flux and increase in permeate conductivity, while the presence of oil and surfactants together, with salt, severely affected MD performance [86]. In general, the presence of surfactants promotes wetting, while the presence of oil enhances fouling through hydrophobic-hydrophobic interaction with membrane surface and pores. Presence of only oil in feed water eventually led to higher fouling and pronounced flux decline, due to the higher affinity between the hydrophobic species (i.e., oil) to the hydrophobic MD

membrane [86]. Only oily feed water, with 100 ppm oil concentration, did not show any increase in permeate conductivity for 15 hours of operation [86]. The permeate conductivity started to increase after 5 hours when feed stream oil concentration was 200 ppm but was less than 5 $\mu\text{S}/\text{cm}$ even after 15 hours of operation [86]. So a gradual increase in permeate conductivity was also observed with increasing oil concentration in the feed water, possibly through volatilization of hydrocarbons in the oil from the feed stream (operated at elevated temperature) to the permeate stream. Presence of surfactants with oil stabilized the oil emulsion, which reduced membrane fouling but increased permeate conductivity (indicating an increased tendency to membrane wetting) [86]. The combined presence of both surfactants and oil, along with salt, thus creates a severe situation in which both wetting and fouling contributes to MD performance deterioration. As a result, the membrane flux reduced quickly to 50% (due to membrane fouling) and the permeate conductivity dramatically increased (due to membrane wetting) [86]. The PVDF and PTFE membranes have demonstrated different wicking phenomenon to nonpolar materials such as oil, which may be attributed to the differences in hydrophobicity and surface roughness of the two membranes. The in-air oil contact angle of PVDF membrane was not observable as the oil droplet was adsorbed entirely on the membrane surface through hydrophobic-hydrophobic interaction [146], while the in-air contact angle of PTFE membrane with mineral oil was dynamic [147]. The mineral oil droplet initially beaded up upon the more hydrophobic PTFE membrane as drops with measurable contact angles but then penetrated into the porous membrane and propagated along the membrane surface with observable wetting fronts in about 6 minutes [147]. PTFE membranes showed higher surface roughness than PVDF membranes [124], which might be responsible for the dynamic wetting nature of PTFE. The higher surface roughness of PTFE membranes might have caused the formation of initial mineral

oil droplets on the PTFE surface, which eventually adsorbed on the porous membrane due to hydrophobic-hydrophobic interaction. It should be kept in mind that for wastewater containing oil, MD is not a favorable option due to its inclination to higher fouling. If a high-strength wastewater contains oil, its recovery using MD will depend on how well the membrane can resist fouling due to oil in the feed water. Many novel membrane modifications/fabrications have been made to enhance the performance of MD in oily wastewater recovery (discussed in a following section). Some pre-treatment is necessary to lower oil, surfactant, or salt concentration before recovery of oily wastewater using MD [86]. For DCMD of oily wastewater, no oil concentration was detected in the permeate of a feed with up to 1000 ppm oil [148]. This observation might be influenced by the high molecular weight of the crude oil derivative compounds in the feed. For oily wastewater consisting of low molecular weight hydrocarbons, the low molecular weight hydrocarbons will readily volatilize into the distillate.

The different studies carried out using synthetic/simulated wastewater facilitate a basic understanding of the interaction between specific types of contaminants and the membrane surface. However, for real wastewater (containing a combination of different dissolved charged contaminants, surfactants, salts, biomass, etc.) the interactions between different constituents and the membranes led to a multidimensional fouling and wetting scenario [86,141]. In almost all cases, MD systems were found to be unsuitable for direct treatment of raw wastewater as both fouling and wetting of membranes occurred soon after the process commenced [86,131,132,141]. There is no data in the literature related to the contribution to different types of fouling (inorganic, organic, and biofouling) that occur in MD during the recovery of real wastewater. This provides an impetus for conducting a systematic study of different types of wastewater to

evaluate their association to different types of fouling, which, in turn, will help in the development of effective and optimized mitigation measures in MD. Also, further investigation of different MD configurations for reclamation of different types of pre-treated wastewater should be carried out.

4.2 Influence of operating condition: Operating conditions such as feed and permeate streams temperatures, feed stream flow rate, membrane pore size, and membrane material have demonstrated considerable influence on the performance of different MD processes (i.e., DCMD, AGMD, VMD). The degrees of permeate vacuum also exhibited a remarkable impact on the overall performance of the VMD process. The following sections discuss the influence of these parameters on the performances of different MD processes.

Effect of feed/permeate temperatures: Antoine equation, which expresses the relationship between the vapor pressure (as a driving force for MD process) and feed temperature, demonstrates that the vapor pressure increases exponentially with the temperature following the relation [84]:

$$p_i^0(T) = \exp\left(a - \frac{b}{g + T}\right)$$

where p_i^0 is in Pa, T is the absolute temperature in K, and a , b , and g are constants that are readily available (for water, these constants are 23.1964, 3816.44, and -46.13, respectively).

Hence, the permeate flux of the membrane distillation process is enhanced due to increased feed temperature [85]. While treating 18.5 mg/L methylene blue dye containing wastewater with PP

membrane via VMD with a feed flow rate of 14 mL/s and a 5 mm Hg pressure with varying temperature (40° – 70°C), the temperature increase resulted in an increase in the permeate flux (4.25, 4.8, 5.6, and 6.3 kg/m²/h in the first hour for 40°C, 50°C, 60°C, and 70°C respectively) due to the exponential relation between the vapor pressure difference and the temperature [57]. The VMD experiment at vacuum pressure of 10 mbar and Reynolds number (Re) of 4341.6 with PP membrane using 50 ppm RBBR (Remazol Brilliant Blue R) dye from Sigma Aldrich showed an 27.3% increase in flux at 50°C from 27.5 kg/m²/h flux at 40°C and 62.9% increase in 60° from the 35 kg/m²/h flux of 50°C [130]. A similar finding was observed in another VMD experiment with saline water where temperature variation of 25°C, 40°C, and 55°C showed flux enhancement with increased temperature [149]. Another study conducted with three different (unmodified, plasma modified, and chemically modified) hydrophobic PVDF hollow fiber membranes at varying feed temperatures of 40°C, 50°C, 60°C, and 70°C and a permeate temperature of 25°C with synthetic seawater of 3.5 wt% NaCl solution in a DCMD set-up (with feed and permeate flow rates of 2.5 L/m and 0.4 L/m, respectively) [12], observed exponential increase of trans-membrane flux with increase in temperature for all three membranes. At low feed temperatures, all three membranes had similar permeate flux. However, temperature increase showed significant variation in the permeate flux of the three membranes, with unmodified membrane having the highest permeate flux and around 20% flux drop of modified membranes at 70°C feed temperature due to membrane modification that resulted in partial pore closure, loss of large pores as well as overall decrease in porosity [12]. Hollow fiber VMD process with commercial PP membrane was implemented to study the separation efficiency of Co²⁺ ion from a synthetic solution simulating radioactive wastewater with a varying feed temperature of 30-70°C with 41.8 L/h feed flow rate, and 0.98 atm permeate vacuum degree

[138]. Highest permeate flux was observed at 70°C temperature with an exponential increase of the flux with an increase in temperature ($R^2=0.9845$) due to the change in the saturated vapor pressure of the solution. Another study on a full-scale spiral wound module with PTFE membrane with a PP support in a PGMD set up with an evaporator inlet temperature of 80°C, and saline water (0-105 g/kg) as feed at a feed flow rate 500 kg/h varied the a condenser inlet temperature (20°C-40°C) to observe the condenser inlet temperature variation effects on the permeate flux [77]. The result demonstrated a decrease of output rate with an increase in the condenser inlet temperature rate ranging in between 9 to 25 kg/h for 0-105 g/kg of salinity [77]. The highest flow rates of 25, 24, 22, 20, 17.5, and 15 kg/h were observed for the salinity 0, 13, 35, 50, 75, and 105 g/kg, respectively, when the condenser inlet temperature was the lowest, 20°C. The flow rates observed for the same salinity values were 20.5, 18.2, 16.5, 14.5, 12, and 9 kg/h, respectively, when the condenser inlet temperature was 40°C [77]. Another study conducted with FO draw solute as feed on DCMD operation observed 250% enhancement in permeate flux (from 10 kg/m²/h to 35 kg/m²/h with a cold permeate temperature of 15°C) while increasing feed temperature from 40°C to 70°C [150]. The same study observed enhanced permeate flux through lowering the permeate temperature from 30°C to 15°C with different feed temperatures of 40°C (about 100% permeate flux increased from 5 kg/m²/h to 10 kg/m²/h) and 70°C (about 25% permeate flux increased from 28 kg/m²/h to 35 kg/m²/h) [150].

Studies also revealed that temperature gradient enhancement between the membrane surfaces positively influence the diffusion resulting in enhanced permeate flux [151,152]. Similarly, increased feed temperatures led towards reduced temperature polarization and hence improved the mass transfer across the membrane [150,153]. Also, enhancing the feed temperature

demonstrated a significant increase in permeate flux compared to reducing the permeate temperature due to low alteration in vapor pressure [37,150]. Table 4 summarizes the effect of feed/permeate temperature on the permeate flux performance of various MD configurations (DCMD, VMD, AGMD, etc.).

Effect of feed cross flow rate: The boundary layer resistance minimization at an increased flow rate leads towards enhanced mass transfer by increasing the heat transfer coefficient [154]. The enhancement in flow rate results in high permeate flux due to the reduced thermal boundary layer thickness and consequently decreased temperature polarization effects [151]. An elevated flux of 9.22 kg/m²/h was observed as the boundary layer resistance decreased to 1.74×10^6 m²s Pa/kg with an increase in cross flow velocity of 0.014 m/s (from 0.005 m/s) at a fixed feed temperature of 70°C [145]. An approximate three times increase in cross-flow velocity (from 0.005 m/s to 0.014 m/s) decreased the boundary layer and increased the flux by 1.27 times (from 7.22 L/m²/h to 9.22 L/m²/h) [145]. The effect of varying feed flow rate (14, 17, 30, 42, and 57 mL/s) was investigated for 18.5 ppm methylene blue dye containing wastewater by vacuum membrane distillation using a PP membrane at 50°C feed temperature [57]. At Reynolds number < 5000, significant flux increase was observed with the increase in the flow rate, mainly due to the prevention of the pore blocking by the dye molecules as well as reduced temperature and concentration polarization effect due to enhanced heat and mass transfer [57]. A study with a VMD configuration having 19.1, 26, 34.9, and 41 L/h flow rates with a feed temperature of 50°C and vacuum pressure of 10 mbar for 50 ppm RBBR (Remazol Brilliant Blue R) dye solution observed permeate fluxes of 23.5, 26, 26.5, and 28.5 kg/m²/h, respectively over a 100 minutes operation period [130]. High flow rate resulted in a high heat transfer coefficient leading towards

higher permeate flux of the VMD system [130]. Flow rate increase from 15 mL/s to 30 mL/s in a VMD experiment using a PP membrane with saline (NaCl) water reduces both the temperature and concentration boundary layer thicknesses near the membrane interface due to higher turbulence flow leading towards enhanced VMD performance [149]. Flow rate variation along with module size variation also significantly affects the hydrodynamic conditions in the hollow fiber DCMD process [12]. Flow variation from 2 to 7.5 L/m kept the MD flux unchanged in a smaller 9.5-mm housing module as the feed stream reached turbulence within this range. However, for a bigger 19-mm housing module, initial increase of permeate flux was observed with an increase in flow rate and eventually, an asymptotic value was reached at feed side Reynolds number (Re_f) > 2500 [12]. However, the maximum permeate flux was lower in the big module under same operating conditions due to the similar permeate flow rate in both modules that resulted in lower permeate side Reynolds number (Re_p) as well as the larger fiber length of the big module. This study revealed that moderate feed flow rate could be adequate if satisfactory permeate flux is achieved, as enhanced flow rate has no additional advantages once the turbulence is reached [12]. The study also demonstrated that lumen side (permeate side) flow rate also has an impact on permeate flux as increasing the permeate flow rate can result in improved heat transfer and reduction of temperature polarization effect on the permeate side that can enhance the driving force. However, increasing permeate flow rate resulted in an enhanced permeate flux mostly in the low permeate side Reynolds number ($Re_p < 300$) [12]. At Reynolds number higher than 300 the permeate flux reached a steady asymptotic value, which might have resulted from the enhanced transverse vapor flux causing higher mixing on the membrane surface by breaking down the laminar boundary layer that aided the permeate side heat transfer.

This study concluded with the recommendation of using a reasonably low permeate circulation flow rate to optimize the MD performance with relatively low energy consumption [12].

Feed flow velocity variation of 10.5 to 41.8 L/h was conducted with a feed temperature of 70°C and permeate vacuum degree of 0.98 atm to elucidate the effect of flow velocity while removing cobalt ions from simulated radioactive wastewater [138]. Linear correlation ($R=0.9912$) was observed between the permeate flux and the feed flow velocity because of the variation in the thickness of the boundary layer formed between the membrane and the bulk solution due to the accumulation of the retained Co(II). The study also observed that permeate flux was more affected by the permeate vacuum and the feed temperature than the feed flow velocity [138]. Full-scale spiral wound module with PTFE membrane (having a PP support) was studied in a PGMD set up, with a condenser inlet temperature of 25°C, an evaporator inlet temperature of 80°C, and the feed flow rates varied to 200, 300, 400, and 500 kg/h [77]. The result demonstrated an increase of output rate with an increase in the feed flow rate ranging in between 2.5 to 25 kg/h for 0 – 105 g/kg salinity. The high flow rates resulted in enhanced flux with the same salinity, and parallel curves were detected for different salinity feed [77]. AGMD study with simulated seawater using a 0.45 μm PVDF membrane was carried out at 60°C feed temperature and 20°C cold stream temperature with varying feed flow rate (1 – 5.7 L/m) as well as varying cold stream flow rate (1 – 4.5 L/m) [37]. The hot feed flow rate variation caused a permeate flux increase from 2.7 to 3.4 $\text{kg/m}^2/\text{h}$ whereas the cold stream flow rate variation resulted in similar permeate flux (around 3.4 $\text{kg/m}^2/\text{h}$) with a feed flow rate of 5.5 L/min without any significant influence [37]. The negligible effect of cold stream flow rate on permeate flux in AGMD can be explained by the overall heat transfer coefficient, which includes the hot side, the

air-gap, and the cold side heat transfer coefficients. As the heat transfer coefficient in the air-gap is much smaller than the hot and the cold side heat transfer coefficients, it will dominate the overall heat transfer coefficient. Hence the change in the cold stream flow rate will have little effect on permeate flow rate. It should be pointed out here that the heat transfer coefficients of the hot side and cold side are dependent on the geometry of the membrane module and the characteristics of the fluid flow [37]. Table 5 summarizes the findings from studies evaluating the impact of different feed flow rates on permeate flux.

Effect of membrane pore size: Highly hydrophobic, thermally stable, and chemically resistant commercial PTFE membranes of different pore sizes (1 μm , 0.45 μm , and 0.2 μm) with a feed flow rate of 1.5 L/m and feed temperature of 50°C were investigated in terms of permeate flux, salt rejection, and energy consumption by AGMD module with a varying range of concentrations of different salts, NaCl (5,844 – 180,000 mg/L), MgCl_2 (4,760 – 95,210 mg/L), Na_2SO_4 (4,260 – 142,000 mg/L), and Na_2CO_3 (5,300 – 106,000 mg/L) [36]. Permeate flux of the pure water increased with the increase of the membrane pore size irrespective of the salt types due to enhanced mass transfer in the pores, with the highest increase with NaCl (39.6% and 56.9% increase for 0.45 μm and 1 μm from 0.2 μm) at 180,000 ppm; and lowest increase with Na_2SO_4 (10.9% and 23.22% increase for 0.45 μm and 1 μm from 0.2 μm) at 142,040 ppm. Also, the study observed co-relation among concentration, pore size, and permeate flux. With increasing pore size, the high concentration caused a decrease in the rejection, whereas, at 0.2 μm pore size (the lowest pore used in this study), the effect of concentration was insignificant. This results from the decrease in the LEP with an increase in the pore size under higher concentrations [36]. Moreover, high concentration and high pore size result in fouling enhancement. Scale and

foulant layers on the membrane surface results in reduced membrane hydrophobicity [155]. The scale formation, initiated with the largest pores on the membrane surfaces, leads towards membrane wetting. The difference in pore sizes did not have a significant influence on the energy consumption of the AGMD process, and a slight decrease in the energy consumption was observed with the highest pore sizes due to enhanced mass transfer [36]. Investigating dyeing wastewater treatment efficiency through commercially available PVDF membranes (pore size 0.45 μm and 0.22 μm) exhibited high flux with 0.45 μm membrane compared to 0.22 μm membrane, however, better permeate quality by the high rejection of dye was attained through the smaller pore size [124]. The high rejection of dyes with a smaller pore size in the PVDF membrane could be attributed to lower partial wetting of the 0.22 μm membrane pores compared to 0.45 μm membrane pores [124].

Effect of membrane material: PVDF (0.22 μm) and PTFE (0.2 μm) membranes were implemented to study a simulated dyeing wastewater treatment via a DCMD application. It was revealed that the PTFE membrane demonstrated a 63% higher flux when compared to PVDF membrane [124]. Two possible reasons were attributed for the efficient color rejection by PTFE membranes. It was postulated that the dye molecules could not enter the membrane pores due to the formation of the dye-dye flake-type foulant (foulant-foulant) on the membrane surface, and this loosely bound dye foulant and the high fraction of water had a repulsion effect to the hydrophobic PTFE membrane surface. As a result, the PTFE membrane did not suffer from membrane wetting, and its properties could be recovered through water flushing [124].

Effect of permeate vacuum pressure for VMD: Permeate side vacuum degree (pressure difference between the vacuum and feed side) was varied from 0.1 to 0.98 atm (~10 – 100 kPa) with 70°C feed temperature and 41.8 L/h feed flow rate while removing Cobalt ions in a hollow fiber VMD system [138]. No permeate flux was observed until the permeate side vacuum degree was more than 0.6 atm as a positive pressure difference was reached beyond this point. An increase in the permeate side vacuum degree above 0.6 atm resulted in an enhanced permeate flux with a steady value of around 6 L/m²/h at a vacuum degree above 0.9 atm [138]. Another notable observation was that the permeate side pressure was not homogenous all through the shell side and there was a pressure build up in the shell side opposite to the vacuum chamber as it was not stripped away in time resulting in accumulation and reduced driving force. The study suggested that instead of having a permeate side vacuum degree as high as possible; it should be optimized so that the pressure buildup can be avoided. For this specific study, the optimized value for the permeate side vacuum degree was 0.9 atm [138]. Another study using VMD configuration with a PP membrane with sodium chloride as feed to simulate highly saline water observed reduced VMD performance (i.e., decreased permeate flux) with increasing vacuum side pressure from 40, 60, 80, 100 to 120 mbar [149]. Increasing pressure on the vacuum side lowers the pressure difference between the feed and permeate side of the membrane and hence decreases the driving force for passage of water vapor through the membrane pores. The study found that vacuum pressure is the most significant contributing factor in VMD performance compared to the temperature, flow rate, and feed concentration [149]. Another study investigated the variations in vacuum side pressure from 5.05 kPa to 90.9 kPa at 70°C feed temperature and with a lumen side flow rate of 41.8 L/h in a hollow fiber VMD setup to observe the efficiency of Caesium removal from feed water and had similar findings where nearly zero permeate flux was observed for 40.4

kPa or more vacuum side pressure [156]. For vacuum side pressures less than 40.4 kPa, a gradual increase in permeate flux was observed. Decreasing vacuum side pressure from 40.4 kPa to 5.05 kPa resulted in enhanced permeate flux from 0.5 L/m²/h to 7 L/m²/h [156].

The influence of different operating conditions on the permeate flux and contaminant rejection performance in different MD configurations is equally important as the feed water composition. While a number of studies have demonstrated the impact of operational parameters on MD performance while recovering selected types of wastewaters (hypersaline wastewater, radioactive wastewater, organic wastewater, etc.), there are scopes to comprehensively observe effect of these operational parameters for other challenging wastewater categories (e.g., oily wastewater, textile wastewater, pharmaceutical wastewater, etc.) in different MD configurations. It should be mentioned that the extent of fouling and wetting would change with varying operational conditions when MD is employed for recovery of wastewater. Hence there are great prospects in studying the performance of different MD configurations (both traditional and emerging), in terms of permeate flux and contaminant rejection, under different operating conditions. A better understanding of how membrane fouling and wetting is influenced by wastewater compositions and operational states in an MD configuration will enable effective selection of mitigation approaches for enhanced treatment and recovery in the MD process.

5. Mitigation of fouling and wetting in MD

5.1 Pre-treatment of feed wastewater: Conventional treatment approaches, such as physicochemical (coagulation-flocculation) and/or biological treatment, have been applied as pre-treatment options for textile/dyeing wastewater [131,132], municipal wastewater [143], and

olive mill wastewater [157] prior to MD. Reduction of organic content through biological treatment and particulates through physicochemical (coagulation-flocculation) treatment reduced the fouling potential of different complex wastewaters. In the case of textile dyeing wastewater, pre-treatment using physicochemical and biological (anaerobic + aerobic) processes resulted in lower fouling and wetting in PTFE membranes. Over a period of 48 hours the pre-treated wastewater showed only 14% drop in flux compared to more than 97% drop for the same with raw wastewater and the conductivity observed in the permeate stream for pre-treated wastewater, after 48 hours, was also only about 2.8% of that found with raw wastewater (Table 2) [132]. These pre-treatments yielded stable performance with no significant change in flux during extended bench-scale DCMD operation using PTFE membrane [131,132]. In addition to enhanced flux, the COD, color, and conductivity rejections of pre-treated textile/dyeing wastewater were enhanced when compared to raw wastewater [132]. Active surface substances were removed from textile/dyeing wastewater using a simple foam fractionation process, which slightly reduced the membrane flux and kept the permeate quality within acceptable levels [131]. The foam-fractionation process is an adsorptive separation technique in which air is sparged to produce bubbles in a separator liquid column, and as the air bubbles travel through the continuous phase, surfactant adsorbs at the air-liquid interface [158]. Once emerged from the liquid, the air bubbles form a honeycomb-structured cell in the foam matrix with a surfactant-stabilized thin liquid film between the air bubbles. After separation, the collapsed foamate solution offers a highly concentrated solution of surfactants separated from the initial solution [158]. Dow et al. (2017) reported a 60% drop in trans-membrane flux in 2.5 hours and immediate occurrence of membrane wetting when raw textile wastewater was used as feed water in a bench-scale DCMD system with PTFE membrane [131]. While a pilot-scale study carried out with

continuous foam fractionation of conventionally (physicochemical-biological) treated textile/dyeing wastewater produced no wetting of membranes over a 3-month trial [131]. The mass transfer coefficient (flux per unit trans-membrane pressure) of the module declined to 40% of its initial value after more than 65 days, and caustic cleaning efficiently restored it to 79% of the original value [131]. In the case of municipal wastewater, biological pre-treatment enhanced DCMD performance for both PTFE and PVDF membranes [143].

Performance of the DCMD process for the reclamation of raw and pre-treated (coagulation/flocculation or microfiltration) olive mill wastewater were carried out using PTFE and PVDF membranes [157,159]. PTFE membranes showed better separation coefficients and olive mill wastewater concentration factors, but permeate flux decreased rapidly in the first 30 hours of treatment for raw olive mill wastewater [157]. Microfiltration pre-treatment was more efficient than coagulation/flocculation in removing total organic carbon (TOC) and total solids from olive mill wastewater. Therefore, of the two pre-treatment processes, the integrated microfiltration-DCMD method was found to be more useful for obtaining clean water from olive mill wastewater [157]. Application of membrane bio-reactor (anoxic, aerobic and ultrafiltration) as a pre-treatment for the landfill leachates demonstrated better effluent quality and higher flux in MD due to reduced organic contaminants in feed water [144].

Other pre-treatment options reported in the literature include thermal pre-treatment of acid rock drainage, granular activated carbon adsorption (GAC) for RO concentrate, and coagulation-precipitation-filtration-acidification-degassing for recirculating cooling water. High variability in membrane scaling and flux of raw acid rock drainage through the membrane has been linked to

precipitate formation in this system [120]. 85% water recovery with only a 13-15% decline in flux and a 99% ion rejection were achieved. The high organic content of RO concentrate caused a significant reduction in membrane hydrophobicity and attributed to adhesion of low molecular weight organics onto the membrane. GAC pre-treatment helped reduce the organic content of RO concentrate by 46-50% and adsorbed a range of hydrophobic and hydrophilic micro-pollutants, ensuring high-quality water production in the associated MD [127]. About 15-18% improvement in batch recovery was achieved, in a vacuum-enhanced DCMD, by dosing an RO brine feed water with a calcium sulfate scale inhibitor (Pretreat Plus 0400, dosing range 2 – 8 ppm) [160]. With dosing of scale inhibitor in the feed water, the flux declined rapidly at first and was partially recovered afterward. The unusual flux behavior was attributed to the formation of amorphous silica and silicates, which precipitate in a series of steps generating soft and hard gels [160]. The initial rapid flux decline was attributed to the formation of soft silica gels that form on the membrane surface, and further reaction of this silica resulted in hard gels, which were scoured off of the membrane surface [160]. Recirculating cooling water operating at several cycles of differing concentration have high levels of contaminants, and chemicals were added for corrosion, scaling and bio-fouling management of cooling system water [161–164]. Reclamation of recirculating cooling water from a coal-fired power plant (with 2-3 cycles of concentration) by MD requires a series of pre-treatment steps such as coagulation, precipitation, filtration, acidification, and degassing [165]. Incorporation of coagulation at the beginning of the pre-treatment scheme demonstrated a 23% improvement MD flux after 30 days when compared to a pre-treatment scenario with no coagulation. Coagulation removed most of the natural organic matter and chemical additives in recirculating cooling water, resulting in the formation of bigger magnesium-calcite crystal deposits on the membrane surface. The larger sized deposits could not

enter the membrane pores and only cause partial wetting of the membrane and hence enhanced trans-membrane flux [165]. pH adjustment of feed water has been studied as an option for prevention and management of silica scaling in MD while recovering cooling tower makeup water of a geothermal power plant [166]. Silica polymerization and scaling risk in MD was reduced at feed water pH of below 5, or above 10 [166]. Consideration of cost (for pH adjustment to 5.0 using HCl or 11.0 using NaOH) and scaling tendencies of the cooling water indicated that feed water pH adjustment with HCl might provide a viable pre-treatment strategy for recovery of studied power plant cooling water [166]. For each particular type of wastewater, pre-treatment options should be selected to remove target contaminants responsible for fouling and wetting in MD. The pre-treatment options should be chosen to remove potential foulants in the wastewater such as particulates, colloids, inorganic salts, organic contaminants, and microorganisms. Application of microfiltration, ultrafiltration, or nanofiltration can effectively remove particulates, colloids, and microorganisms [8,157]. Since MD employs hydrophobic membranes to treat and recover fresh water, feed water with high hydrophobic contaminants (e.g., oil, hydrophobic organic material) can cause serious fouling due to the strong hydrophobic-hydrophobic interaction [45,167,168]. On the other hand contaminants such as low surface tension and water-miscible liquids (e.g., alcohols), amphiphilic molecules (e.g., surfactants), or other natural surface active agents can induce wetting in hydrophobic membranes [142,147,169]. Table 1 and 2 highlights different pre-treatment options used in the studies involving the treatment and recovery of different wastewater. While the pre-treatment options like coagulation/flocculation, biological (anaerobic-aerobic) treatment, membrane-based (ultrafiltration, microfiltration) processes offer removal of different range of contaminants; some pre-treatment options have been employed at removal of specific contaminants (e.g. foam

fractionation used for removal of surfactants, granular activated carbon or ultraviolet treatment for removal of organic contaminants, etc.).

5.2 Application of integrated MD processes: MD has been incorporated with other separation technologies to enhance the overall water recovery performance in a treatment scheme. It can be integrated easily and inexpensively (as it is not a pressure driven system) to a hybrid system and is one of the most preferred membrane processes for inclusion in a hybrid separation technologies [170]. Having an integrated separation process improves the fouling and wetting scenarios in MD operation, and the hybrid system can generate consistent flux over the long term. A number of studies have reported hybrid systems incorporating MD to recover high-strength wastewater.

Integration of MD into other desalination processes like RO, NF, and MED units have been reported to reduce brine discharge, enhance overall freshwater production and energy efficiency [171–176]. The MD receives the reject water from the desalination processes as feed and further improves the water recovery performance of the entire process. The scaling of inorganic salt crystals is the primary concern when MD is integrated into RO [174,176]. Use of integrated RO-MD system has also been reported for reclamation of wastewater [127,175]. With RO concentrate originating from wastewater recovery, fouling scenario deteriorates as organic fouling adds to the inorganic scaling [10,127].

Application of an integrated FO-MD process, with or without additional pre-treatment processes, has been reported to offer successful treatment and reclamation of different types of wastewater.

The FO process offers the advantage of higher rejection while using a dense membrane at ambient pressure, and less fouling propensity as compared to other membrane-based separation processes (e.g., microfiltration or ultrafiltration) [177–179]. As a result, FO requires less scouring and less frequent backwashing than microfiltration or ultrafiltration [180]. MD can be considered as an economical option for recovery of FO draw solution in wastewater treatment and produce fresh water from the initial wastewater feed, provided that waste or low-quality heat source is available [181,182]. In comparison to RO, MD does not require high electrical energy input to recover FO draw solution by application of high hydraulic pressures [183,184]. In an integrated FO-MD process, the FO carries out the initial wastewater treatment as water gets separated from dissolved solutes and passes through a semi-permeable FO membrane towards the highly concentrated (relative to feed solution) draw solution. This diluted draw solution then acts as a feed to the MD process, which continuously regenerates the FO draw-solute. Use of a cellulose-triacetate FO membrane and PVDF hollow fiber MD membrane in an integrated FO-MD setup for real domestic wastewater treatment (with 35 g/L NaCl as draw solution and real domestic wastewater as feed solution for FO) yielded less fouling in the MD membrane as compared to the FO membrane, over 120-hours of continuous experiment [185]. The FO membrane being the first barrier in contact with the feed water showed more fouling than MD. Water quality analysis indicated that the FO membrane removed a significant percentage of the contaminants and the integrated FO-MD process removed more than 90% contaminants [185]. Husnain et al. (2015) introduced secondary treated municipal wastewater effluent as the FO feed in an integrated FO-MD system for treatment, with 1 M NaCl solution used as the FO draw/MD feed, and purified water used as the permeate [150,186]. While the FO membrane showed a gradual flux decline over time, for MD, most of the flux declined in the initial 4-6 hour and

remained consistent throughout the 50-hour long experiment. For PP membranes, cleaning with tap water after 48 hours yielded no flux recovery, indicating significant irreversible fouling and wetting due to adsorption of organic foulants on the hydrophobic membrane surface. Long-term (ten day) tests indicated reduced hydrophobicity of the PP membranes due to adsorption of organic foulants, which caused wetting problems and allowed contaminants to pass through after only six days of operation [186]. Reported results from the literature indicate better trans-membrane flux performance of PVDF membranes than PP membranes in the treatment of municipal wastewater in an integrated FO-MD system. The results from two studies (both used similar commercial cellulose triacetate FO membranes, and similar temperatures for feed, draw and permeate sections) showed that the flux through a PVDF hollow fiber membrane (average pore size 0.073 μm , thickness $186 \pm 5 \mu\text{m}$) was 17.6 $\text{L}/\text{m}^2/\text{h}$ over a 120-hour operation period [185] and the same through a PP membrane (average pore size 0.22 μm , thickness $150 \pm 20 \mu\text{m}$) was 14.4 $\text{L}/\text{m}^2/\text{h}$ over a 20-hour operation period [150]. Despite lower average pore size, the higher flux in PVDF hollow fiber membranes might have resulted from variations in other operational parameters (like lower draw solution concentration, higher flow rate in hot side stream compared to cold side stream, etc.). Incorporation of a third treatment scheme (e.g., GAC treatment or ultraviolet oxidation) to prevent contaminant accumulation in the draw solution has offered further performance enhancement of the integrated FO-MD process in treating raw sewage [187]. Other FO-MD studied processes used seawater [188] or oily wastewater [189] as draw solution and municipal wastewater as FO feed water. An integrated ultrafiltration-FO-MD (UF-FO-MD) process has been reported for the treatment of real oily wastewater and sewage through the utilization of the osmotic and thermal energy of the oily wastewater [189]. Following UF, the highly saline and heated oily wastewater (mixed with FO permeate of sewage) was

simultaneously used as FO draw and MD feed. The FO-MD performance was mostly affected by oil content, while temperature and salt content of the oily wastewater had little influence on the system performance [189]. Use of the integrated FO-MD process also indicated enhanced treatment performance of highly saline landfill leachates than that individual FO or MD could offer [190]. The enhancement of landfill leachate treatment performance depends on the salinity of the feed solution. At a total salt concentration of 25,000 mg/L (calculated as NaCl), the total organic carbon, total nitrogen, ammonia nitrogen, mercury, antimony, and arsenic removal performances of FO were 91%, 94%, 97%, 48%, 99%, and 88%, respectively (over 250 minute operation). While the same for the integrated FO-MD process were >98%, >98%, ~100%, ~100%, ~100%, respectively [190]. Also, the integrated FO-MD process was able to completely remove ammonia nitrogen, which is poorly removed by MD alone due to its volatilization and permeation through MD membrane pores (as discussed in a previous section).

MD has also been integrated with different forms of bioreactors to form integrated membrane bioreactors (MDBR) for the treatment and recovery of wastewater. An integrated aerobic-anaerobic osmotic membrane bioreactor (OMBR, comprising of a bioreactor and a FO subsystem) with MD was studied for the production of potable water from a synthetic wastewater feed solution designed to stimulate high-strength domestic wastewater [183]. The feed solution was prepared from sucrose and ammonium bicarbonate to achieve a strength of 1350 mg/L COD and 160 mg/L NH_4^+ -N. The bioreactor was inoculated with a combination of return activated sludge and biomass from a trickling nitrification filter, and the bioreactor was kept at continuous mixing with a submersible pump maintaining a solid retention time of 30 days [183]. The draw solution concentration and draw solution circulation flow, in the FO subsystem

using cellulose triacetate membrane, were 35 g/L NaCl and 100 ml/min. A cross-flow DCMD module was integrated with the OMBR system. Flat sheet PTFE membranes were used in the DCMD process with counter-current flow between the feed and distillate streams. The MD feed and permeate stream temperatures were maintained around 80°C and 10°C, respectively [183]. The MD productivity had an early decrease due to membrane fouling, which caused the average, steady-state MD water flux between hours 15 and 48 to become 0.8 L/m²/h. The low flux performance in the large-scale MD system was attributed to the reduced driving force in the system resulting from heat transfer from the feed side to the distillate side of the membrane [183]. The FO productivity also declined slightly over 48 hours and the average FO water flux was 5.1 L/m²/h. The slight decline in FO flux was due to membrane fouling and to some extent, reduction in osmotic pressure driving force due to an increase in bioreactor salinity from reverse salt flux. The integrated system performance in the treatment of wastewater was evaluated by the average NH₄⁺-N and COD concentrations in the bioreactor, and MD permeate solution. NH₄⁺-N concentration in the permeate solution was 24.6 ± 6.2 mg/L (corresponding to 84.6% removal from OMBR feed solution). The average COD concentration in the permeate was 21.6 ± 2.8 mg/L (corresponding to 98.4% removal from the OMBR feed solution) [183]. The NH₄⁺-N concentration in the bioreactor (229-275 mg/L) was higher than the feed solution during the 48-hour test period, which is indicative of slower acclimation of ammonia-oxidizing bacteria compared to other bacteria in the freshly seeded inoculum. Hence, the system performance is expected to improve over a longer duration, as the amount of NH₄⁺-N in the bioreactor will decrease with time [183]. The lower rejection of NH₄⁺-N can be attributed to a number of factors: (a) biological treatment with aerobic/anoxic cycling (where low dissolved oxygen concentration can lead to higher NH₄⁺-N concentration compared to continuously aerobic

bioreactors that do not incorporate denitrification process) [191], and (b) high MD feed temperature (80°C) used in the current study may have caused higher amount of volatile NH_3 to form and pass through the MD membranes [60,192]. Jacob et al. (2015) placed a DCMD module in series following a two-stage thermophilic anaerobic membrane bioreactor [145]. The two-stage thermophilic anaerobic membrane bioreactor used a monolithic tubular ceramic membrane (55 channels, 2.5 mm diameter in each channel, 30 mm diameter, 450 mm length, 0.18 m² surface area; NGK Insulators, Japan) with a nominal pore size of 0.1 μm [145]. The treated anaerobic effluent was used as feed to the DCMD module with and without the addition of biomass. The COD rejection efficiencies were 97.2%-99.5% and 98.4%-99.9% due to the absence and presence of biomass, respectively. Presence of biomass significantly reduced the flux due to organic fouling [145]. A hybrid process was also reported with MD placed in a submerged membrane bioreactor operated at elevated temperature [100]. Both flat sheet and tubular membrane modules were submerged in the bioreactors and tested for the recovery of synthetic wastewater [100]. Incorporation of an air sparging mechanism on the sides of the tubular membrane bundles provided more consistent permeate flux performance (approximately 5 L/m²/h) for over two weeks of operation at a bioreactor temperature of 56°C [100]. The system also demonstrated consistent TOC rejection and kept the permeate TOC concentrations lower than 0.7 mg/L [100]. DCMD has been integrated with photocatalysis processes for degradation and removal of azo dyes (Acid Red 18, Acid Yellow 36, and Direct Green 99) in aqueous solution [193]. TiO_2 Aeroxide® P25 (Degussa, Germany) was used as photocatalyst on the DCMD feed tank and irradiated with an UV-lamp (Philips Cleo, irradiation intensity was 146 W/m² on the feed tank). Acid Yellow 36 was most difficult to photo-decompose, among the three azo dyes used in the study, and this has been postulated to its less adsorption capacity to the

photocatalyst surface [193]. In general, MD was able to reject the photocatalyst particles at different applied concentrations without major changes in permeate flux over a 5-hour operation period. The MD distillate quality varied with the type of azo dyes rejected, with the highest concentrations of TOC (1.2 mg/L), conductivity (2.2 μ S/cm), and TDS (1.4 mg/L) content in distillate observed with Direct Green 99 [193].

Among different reported hybrid systems involving MD, the FO-MD process has been studied most comprehensively concerning occurrences of fouling and wetting. Integration of FO with MD provides the advantage of auto-regenerating the FO draw solution on the feed side of MD, and it has been successfully applied to recover high-strength wastewater. The RO-MD, or other desalination processes integrated with MD, as a whole, offers an approach to enhance water recovery efficiency of the entire system. In such hybrid systems, the MD receives the concentrate from the RO process (or other desalination processes like NF or MED), and this creates severe fouling and wetting condition for the MD membrane. Incorporation of MD with different bioreactors or photocatalytic reactors has shown promising results for treatment and recovery of wastewater. However, membrane fouling and wetting in such MD integrated bioreactor or photocatalytic reactors for synthetic and real wastewater merit further research.

5.3 Membrane maintenance: Long-term MD performance has been associated with changes in membrane surface properties (like hydrophobicity, roughness) and the membrane lifetime depends on the recoverability of these surface properties [119]. Most of the literature concerning long-term real wastewater treatment and reclamation using MD reported the use of PTFE and PVDF commercial MD membranes. The higher hydrophobicity of PTFE membrane

surfaces reduced wettability and fouling while reclaiming pre-treated municipal wastewater [143] and landfill leachates [144], and also enabled flux recovery by water flushing in textile/dyeing wastewater recovery over a more extended operational period [124] compared to PVDF membranes. A pilot scale system treating textile/dyeing wastewater with PTFE membranes demonstrated complete recovery of original flux and about 79% recovery of membrane mass transfer coefficient (expressed in $\text{L}/\text{m}^2/\text{h}/\text{bar}$) through a series of cleaning steps after an operation period of 65 days [131]. This study operated a pilot-scale DCMD system for 65 days using a PTFE membrane and real treated textile wastewater as feed water. The performances of different cleaning options were evaluated from membrane flux ($\text{L}/\text{m}^2/\text{h}$) and membrane mass transfer coefficient ($\text{L}/\text{m}^2/\text{h}/\text{bar}$). The membrane flux and membrane mass transfer coefficient reduced to 72% and 53% of the original clean brine values after 65 days of pilot-scale operation. The study performed three different cleaning operations in series and used a clean brine solution as feed to assess the cleaning effectiveness after cleaning operation. The cleaning methods used were: (a) warm caustic clean (1.5% NaOH at 55°C for about 45 minutes), (b) ambient chlorine cleaning (0.1 wt% NaOCl as free chlorine at ambient temperature for 30 minutes), and (c) DI water cleaning (DI water was pumped through the MD module channels until the electrical conductivity stopped to increase and the DI water was left to soak the membrane overnight) [131]. Among the three different cleaning mechanisms employed, the caustic cleaning was successful in recovering membrane flux and membrane mass transfer coefficient. The hypochlorite cleaning did not enhance the mass transfer coefficient. This was linked to the attachment of the fouling materials on the PTFE membranes or the nature of the textile processing material and their resistance to chlorine degradation. DI water cleaning, which is popularly employed to remove inorganic fouling, did not show any improvement in the

membrane performance as most of the fouling was organic in nature [131]. Due to the effectiveness of the first caustic cleaning (which achieved membrane flux and membrane mass transfer coefficient enhanced to 77% and 61% of the original clean brine values), a second caustic cleaning was employed over 60 minutes time period. After the second caustic cleaning, the membrane flux was recovered completely, and the mass transfer coefficient was 79% of the initial value [131]. There is a scope for optimization of the caustic cleaning for a particular type of wastewater in terms of caustic concentration, temperature, and time. Also, the cleaning frequency should be selected appropriately, as the fouling rate increased significantly after the cleaning operation [131]. Hydrophobicity of PTFE membranes was mostly recovered by chemical cleaning (0.1% citric acid) during reclamation of pre-treated wastewater (combination of stormwater and biologically treated sewage effluent) RO concentrate in DCMD [127]. The wastewater RO concentrate was pre-treated by batch adsorption using 5 g/L GAC (Coal based GAC, MDW4050CB, James Cumming & Sons Pty. Ltd., particle size range: 425-600 μm , average pore diameter 30 \AA , and 1000 m^2/g , respectively) [127]. Whereas, significantly faster loss of hydrophobicity with the PTFE membrane was observed when raw RO concentrate was used as feed water (mainly due to the combined adhesion of hydrophilic organics and inorganic CaCO_3 on the membrane), which did not improve through water or acid washing [127]. Although after cleaning, the membrane flux was recovered close to its initial value, the membrane flux dropped more rapidly with enhanced wetting [127]. Chemical rinsing, using an acid (2% w/w HCl solution) and a base (2% w/w NaOH solution) solution, for 30 min each, enabled recovery of the hydrophobic characteristics of the PVDF hollow-fiber membrane during recovery of recirculating cooling water [165]. A NaOH solution was recirculated (at 60°C feed and 20°C permeate temperatures, with periodic addition of NaOH to maintain a pH above 11 in

the feed side) for cleaning a PP membrane, following DI water rinse, between DCMD of a synthetic feed water containing a target concentration of silica (~225 mg/L) [194]. The cleaning with NaOH solution achieved recovery of permeate flux to 23 L/m²/h when testing with new solution began for the second cycle, which is lower than the initial clean membrane flux of 28 L/m²/h [194]. The flux decline in the second cycle (i.e., after cleaning) was rapid when compared to the first cycle [194]. Membrane flux recovery scenarios investigated using synthetic water do not necessarily reflect the complexity of real wastewater and usually provide better flux recovery performances. A membrane distillation bioreactor (MDBR) with 6 and 12 g/L MLVSS biomass added to a feed solution from an anaerobic reactor treating high-strength simulated wastewater exhibited permeate flux decreases of 50% and 70%, respectively after 72 hours of operation using a PTFE membrane, most of which were removable fouling [145]. 71–77.5% of the fouling of the membrane surface was observed to be removable (after washing with de-ionized water), while 21.2–25.6% of fouling was reversible (after caustic cleaning) [145]. The PTFE membrane recovered 96% of the initial flux after combined water and caustic cleaning [145]. There is a need to perform a more organized study of membrane flux recovery using a number of different membrane cleaning processes (i.e., water flushing, caustic cleaning, acid cleaning, etc.) for different real wastewaters. For wastewater causing organic fouling in the membranes, caustic cleaning showed better performance to recover membrane performance in several studies. However, the fouling rates were enhanced post cleaning operation of the system, which can be associated with the change in membrane characteristics due to the cleaning operation. As a result, there is a need for optimization of the cleaning processes (in terms of chemical concentration, cleaning duration, frequency or cleaning) for particular types of wastewaters, which can cause inorganic fouling, organic fouling or biofouling. Such analyses will enhance the

understanding of the membrane-foulant interaction, and help in the design of the operational protocol for MD systems when applied in wastewater recovery.

Recovery of wetted membranes has mostly been studied with saline water but holds practical significance in the application of MD for wastewater reclamation. Dewetting techniques of MD membranes reported in literature involves (a) chemical/water rinsing and/or drying, and (b) backwashing [106,195]. To eliminate wetting, membranes must be dried and cleaned to remove the water and solutes deposited in the membrane pores, which usually takes several hours leading to process downtime and potential membrane degradation [116]. Reducing the hydrostatic pressure on the membrane to less than LEP will not achieve recovery of wetted membrane pores to its un-wetted form after wetting initiates after reaching LEP [6]. The decrease of pressure below LEP at this point only reduces the flux linearly [6]. Just drying of a wetted MD membrane does not mitigate the wetting issue completely as the salt deposits inside the membrane pores make an irreversible structural change inside the pores [122,196]. Rinsing of MD membranes with distilled water and solvents to remove scalants have shown some improvements in abating wetting in MD systems; however, the membrane gradually loses its resistance to wetting with time in feed solutions with common foulants, as the cleaning poorly restores performance [197]. Membrane recovery by rinsing with concentrated HCl solution was performed to remove iron dioxide precipitates from the surface and pores of a PP membrane [95]. The membrane flux increased after partial dissolution of deposit from the membrane surface, but partial wetting of membrane took place when all the deposits dissolved (also including that precipitated in the pores), and the permeate flux reduced gradually with time after cleaning [95]. Another approach for recovery of the wetted membrane is backwashing. Air

backwashing (with an air pressure higher than the liquid entry pressure) of a wetted membrane containing the liquid can force wetting liquid out and prevents the solutes from precipitating inside the pores [195,198,199]. On the other hand, air backwashing to dried membrane has been reported to be useful only for removal of deposits on the pore mouth [200]. Dewetting of wetted MD membranes has also been achieved with high-temperature air backwashing [201,202]. The optimum temperature and time of exposure for dewetting a wetted membrane in VMD were reported to be 60-70°C and 8-12.5 min., respectively [202]. A study was carried out to evaluate the relative effectiveness of a pressurized air backwashing technique to the membrane dry out process in reversing membrane wetting in MD [195]. The pressurized air backwashing system restored the LEP to 75% of the pristine membrane in ~10 s treatment time (for lower salinity feeds) by removing the saline solution from the membrane using a cold air stream and hence did not involve a dry out step or evaporation [195]. Compared to the dry out method, which only evaporates the water from membrane pores and leaves behind trapped crystalline solutes within the membrane to promote rewetting, the pressurized air backwashing system removes saline solution (both water and salts) from the membrane without any vaporization [195]. Analysis of SEM image showed possible superficial tears of the membrane in the pressurized air backwashing technique [195]. The risk of partial membrane wettability can also be limited by reducing the period between cleaning process to maintain a thin scaling layer on the membrane surface [203]. Removal of scaling from the membrane surface in quick intervals limits the degree of oversaturation inside the wetted pores, which reduces internal scaling [203]. The dissolution of pore deposits can initiate wetting as a result of internal scaling [204][205]. As stated before, the recovery techniques of wetted membranes have been studied mostly for saline water. There is a scope to assess the suitability of these techniques in the reclamation of different types of

wastewater using MD. The complex composition of different kinds of wastewater might offer a completely different scenario to these recovery options, which might warrant modification or enhancement of recovery techniques for wetted membranes. Nevertheless, the reported wetted membrane recovery techniques will offer fundamental approaches to researchers for the development of novel wetting recovery methods for membranes when MD is applied for wastewater recovery.

5.4 Membrane modification/fabrication: Many studies have reported enhanced MD performance during wastewater recovery by using fabricated novel membranes or modified commercial membranes. Wetting resistance of MD membranes has been improved through the construction of superhydrophobic and omniphobic surfaces. Self-cleaning membranes have also been developed to reduce fouling in MD, whereas modifications of membrane matrix and surface composition have also been carried out to achieve better fouling and wetting performance during the recovery of wastewater. The following sections briefly discuss different modified/novel MD membranes.

Superhydrophobic membrane: Superhydrophobic MD membranes are essentially formed by roughening of hydrophobic surfaces, by using inorganic nanoparticle (e.g., silica, titanium oxide, fluorographite) [15,113,206] or micro-particle [118] coating, which inherently lowers the membrane surface energy. A superhydrophobic polydimethylsiloxane (PDMS)/PVDF hybrid electrospun membrane showed 50% higher flux than that of commercial PVDF membranes without any observable fouling or wetting while treating textile/dyeing wastewater [118]. The superhydrophobic membrane containing PDMS microspheres prevented dye particles from

entering into the membrane pores and permitted the formation of a loose fouling layer on the membrane surface. As a result, the hybrid PDMS/PVDF membrane showed excellent flux recovery through intermittent water flushing [118]. A tri-bore PVDF hollow fiber membrane with superhydrophobic Teflon AF2400 coating (optimized to a concentration of 0.025 wt% Teflon AF 2400 for 30 sec.) demonstrated enhanced anti-wetting properties (LEP increased by 109%, membrane surface contact angle 151°) and membrane performance in long-term DCMD experiments with synthetic feed water [207]. The superior anti-wetting properties of the coated membranes could be explained due to the lower surface tension and smaller maximum pore size of the coated surface, which makes it more difficult for the liquid to penetrate the pores and due to the low-surface-energy of the surface, which reduces possibility of surface nucleation and further scaling [207]. Superhydrophobic MD membranes can offer long-term wetting resistance to water into membrane pores when compared to hydrophobic membranes. However, the presence of low surface tension contaminants (e.g., alcohol) and surface-active reagents (e.g., surfactants) in feed water poses a critical challenge to the reclamation of wastewater using superhydrophobic membranes. Wastewater containing amphiphilic-surfactants or low surface tension contaminants may cause wetting in long-term operation of superhydrophobic membranes.

Omniphobic membranes: Omniphobic membranes, which repel both water and oil, provide enhanced resistance to wetting resulting from low surface tension contaminants. The modification of membrane surface chemistry and morphology to have low surface energy materials and single/multi-level re-entrant structures, respectively on the membrane surface enables development of omniphobic membranes [49,103,104,115,147,208]. The incorporation of

single/multi-level re-entrant structures to the membrane surface and attainment of low surface energy provides added wetting resistance to omniphobic membranes than the superhydrophobic membranes. The re-entrant structure provides a local energy barrier even to the low surface energy contaminants from transitioning from the meta-stable Cassie-Baxter state (in which microscopic air pockets remain trapped below the liquid and membrane pores) to the Wenzel state (in which the solid-liquid interface is maximized) and enable propagation of the liquid-air interface within the membrane pore [49,103,209]. An omniphobic membrane was fabricated by grafting negatively-charged silica nanoparticles in a positively-charged nanofiber mat prepared by electrospinning a polymer-surfactant solution of PVDF-hexafluoropropylene (HFP) and cationic surfactant (benzyltriethylammonium) [103]. DCMD experiments were carried out using a synthetic feed solution containing low surface tension substances, prepared to mimic industrial wastewater generated from shale gas production [103]. To demonstrate the DCMD performance in recovering high salinity and low surface tension water mimicking shale gas wastewater, a 1 M NaCl solution with varying (0.1, 0.2, and 0.3 mM) concentrations of sodium dodecyl sulfate (SDS, an anionic surfactant) was introduced as feed water [103]. While the control PVDF-HFP nanofiber membrane failed in freshwater reclamation due to low wetting resistance, the fabricated omniphobic membrane exhibited successful freshwater production and stable performance over 8 hours of operation [103]. A number of studies have reported grafting of silica nanoparticle (SiNPs) on MD membranes to achieve single/multi-level re-entrant structures on the membrane surface and functionalization of fiber substrate with fluoroalkylsilane (FAS) to achieve lower surface energy of the membrane while fabricating an omniphobic membrane [104,210]. These studies utilized a synthetic recipe similar as given above [104], or a recipe for an emulsion prepared by ultrahigh-speed mixing of SDS: hexadecane: NaCl at a concentration

ratio of 240: 2400 :10000 (mg/L) in water [210], and used as the feed solution to simulate oily waste water. One study reported, modification of a PVDF membrane to produce an omniphobic membrane by coating the PVDF membrane with SiNPs (following NaOH alkaline treatment and (3-Aminopropyl)- triethoxysilane grafting) and lowering the surface energy of the coated membrane using perfluorodecyltrichlorosilane (FDTS) via vapor- phase silanization [49]. The study observed the flux and salt rejection performance on the omniphobic PVDF membrane and compared it to the control PVDF membrane. Synthetic solutions were prepared as feed water with 1 M NaCl and progressively varying SDS concentration (0.05, 0.1, 0.2 mM) or mineral oil concentration (8, 40, 80 mg/L) after every 2 hours [49]. Four-hour long DCMD experiments demonstrated almost complete rejection of salts in the omniphobic PVDF membrane, while the flux showed a minimal gradual decline over the four hours. The control PVDF membrane was completely wetted with increasing SDS concentration (>0.1 mM) [49]. Whereas, in case of mineral oil in feed (8 mg/L) the flux rate started to decline due to fouling, and eventually the membrane wetted as the mineral oil concentration was raised above 40 mg/L, and was evident through the rapid increase of flux and decrease of salt rejection [49]. The same study reported DCMD experiments with real shale gas brine (pre-filtered using 16 μ m filter, water quality: total dissolved solid 101,000 mg/L, surfactant 3.2 mg/L, oil and grease 2.0 mg/L, total volatile organics <0.14 mg/L, total suspended solids 41 mg/L) as feed water with the modified omniphobic PVDF membrane and control PVDF membrane until 500 mL permeate volume was gathered. The flux decline in the control PVDF and omniphobic PVDF membranes were 50% and 86%, respectively, and the permeate conductivity in case of the control PVDF membrane was about four times of that of the omniphobic membrane [49]. The Performance of omniphobic membrane surpasses that of the superhydrophobic membrane in repelling low surface tension

contaminants [104]. Another fabrication methods for omniphobic membranes involve layer-by-layer assembly of negatively charged silica aerogel and perfluorodecyltriethoxysilane on PVDF membrane and interconnecting them with positively charged poly(diallyldimethyl ammonium chloride) via electro-static interaction [115]. The fabricated omniphobic membrane, demonstrated good wetting resistance in an AGMD with feed water from reverse osmosis brine of coal seam gas produced water (from Gloucester Basin located along the lower north coast of New South Wales, Australia, conductivity ~ 22.6 mS/cm), which contained externally added surfactants (SDS at an increasing concentration of 0.1, 0.3, and 0.5 mM) [115]. Chung et al. reported fabrication of an omniphobic PVDF hollow-fiber membrane via silica nanoparticle deposition (causing surface roughness and re-entrant structure) followed by a Teflon AF 2400 coating (causing surface energy lowering), which demonstrated good repellency toward different liquids with varying surface tensions and used it successfully in a VMD with synthetic water containing sodium dodecyl sulfate surfactant (at varying concentrations of 0.2, 0.4, and 0.6 mM in a 3.5 wt% NaCl solution) [208]. Observations from different studies indicate that omniphobic membranes demonstrate superior wetting resistance to water, low surface tension contaminants (e.g., alcohol), and surfactants. So, the omniphobic membranes can be used in place of superhydrophobic membranes to prevent wetting in MD. In this sense, the omniphobic membranes can be regarded as a superior version of the superhydrophobic membranes. However, for other types of water (i.e., water without low surface tension contaminants or surfactants) superhydrophobic membranes can be used with enhanced wetting resistant performance than usual hydrophobic membranes.

Hydrophobic membrane with hydrophilic skin layer: Recent research works demonstrated fabrication of an in-air hydrophilic (or underwater oleophobic) coating layer on hydrophobic membranes to prevent adsorption of non-polar contaminants on membranes [114,211]. Lin et al. compared wettabilities of a PVDF hydrophobic membrane, a composite PVDF membrane with superhydrophilic skin layer, and an omniphobic membrane [146]. The superhydrophilic skin was developed by spray coating a perfluorooctanoate/chitosan/silica nanoparticle (PFO/CTS/SiNP) nanoparticle-polymer composite onto a PVDF membrane. Both hydrophobic PVDF membrane and omniphobic membranes were in-air hydrophobic, while the superhydrophilic coated surface of the composite membrane was in-air hydrophilic. The composite membrane underwent an oleophilic-to-superoleophilic transition with complete adsorption of an in-air oil droplet on the surface in 10 min. The reconfiguration of surface functional groups on the membrane has been suggested to be a possible mechanism for dynamic wetting by an oil droplet. It was assumed that the oil was initially in contact with the low-surface-energy perfluoroalkyl chains in the PFO and after extended contact with the PFO/CTS/SiNP surface coating layer, the interaction between oil and CTS became dominant, and thus membrane wetting was promoted [146]. Dynamic wetting of membranes has also been reported with commercial PTFE membranes contacting different low-surface-tension liquids where the time required to thoroughly wet the surface varied and depended on the contacting liquids [147]. Both the hydrophobic PVDF membrane and composite membranes were wicked by oil droplet in air, while the omniphobic membrane was not wicked by oil in air due to its combined reentrant surface morphology and low-surface-energy of materials. The underwater oil contact angles were very low for PVDF membrane due to the strong hydrophobic-hydrophobic interaction of membrane surfaces with oil droplet. The composite membrane was highly oleophobic under water due to strong repulsive hydration force

experienced by the oil droplet when it endeavored to wet the superhydrophilic PFO/CTS/SiNP surface. The omniphobic membrane also demonstrated oleophobic character under water. However, when compared to the in-water oleophobicity of the composite membrane, the omniphobic membranes were relatively less oleophobic underwater due to the hydrophobic-hydrophobic interaction between oil and the low-surface-energy membrane materials [146]. Nonetheless, omniphobic membranes have demonstrated larger contact angles towards hydrophobic and low-surface tension liquids, when compared to hydrophobic membranes [49,103,104,115,147,208].

Fouling and reusability of three different MD membranes were evaluated to study the effect of membrane surface wettability modification on reclamation of shale oil and gas produced water [47]. The concentrations of total dissolved solids, total organic carbon, oil and grease, and total volatile petroleum hydrocarbon in the shale oil and gas produced waters used in this study was 39,650-40,370 mg/L, 700-1,400 mg/L, 6.2-9.2 mg/L, 4.8-4.82 mg/L, respectively [47]. The three membranes were (a) PVDF hydrophobic membrane, (b) superhydrophobic PVDF membrane (with low surface energy material FAS and a re-entrant structure attained by grafting with silica nanoparticle), and (c) composite PVDF membrane with hydrophilic PVA coating (Janus membrane, the PVDF-PVA membrane was in air hydrophilic and underwater oleophobic) [47,212]. The superhydrophobic membrane fabricated in this study featured both low surface energy material and a re-entrant structure, which makes it equivalent to an omniphobic membrane as referred by other researchers. The relation between membrane surface wettability and fouling potential was influenced by feed water composition. The membrane fouling was reversible by physical membrane cleaning in all the membranes studied in the reclamation of

shale oil and gas produced water [47]. However, the superhydrophobic (equivalent to an omniphobic) membrane exhibited better reusability among the three studied membranes, at the expense of water productivity, in three successive treatment cycles [47].

Self-cleaning membrane: Self-cleaning properties of membranes against inorganic/organic scaling have been reported in several literatures [117,213]. An electrically conducting composite PP membrane with a carbon nanotube-poly(vinyl alcohol) layer demonstrated enhanced cleaning capacity of silicate scaling that developed during MD operation through the generation of hydroxide ion by water electrolysis [117]. Incorporation of TiO₂ nanoparticles in a PVDF membrane showed decomposition of gallic acid foulants in the membrane under irradiation of UV light due to photocatalytic activity of TiO₂ nanoparticles blended in the membrane [213].

Other novel composite/surface modified membranes: Apart from the variations mentioned above, many studies have reported the modification of membrane matrix/surface layer property to enhance flux and alleviate fouling-wetting scenarios in MD. A carbon nanotube incorporated PVDF-PP membrane for the MD of pharmaceutical wastewaters demonstrated higher rejection for four active pharmaceutical ingredients (ibuprofen, dibucaine, acetaminophen, diphenhydramine) and improved permeate flux due to the integration of immobilized carbon nanotubes in the membrane matrix [214]. CNTs are highly hydrophobic and are known to have rapid sorption-desorption capacity: as a result, it has been postulated that water vapor molecules hop from one site to another by interaction with the CNT surfaces and increase overall vapor transport [214]. The CNTs also provided alternate routes for mass transport via diffusion along their smooth surface and directly through their inner tubes, which enhanced vapor transport

[214]. Khayet (2013) developed composite hydrophobic/hydrophilic membranes via the phase inversion method using a blend of fluorinated surface modifying macromolecules and host polymers (polysulfone and polyethersulfone), and successfully employed them in DCMD of low-level and medium-level radioactive wastewater with higher LEP of water values, lower permeate fluxes, higher rejection factors, and lower radioactive adsorption to the membrane surface [215]. Some researchers reported fabrication/modification of membranes to enhance wetting resistance at the expense of permeate flux. A fabricated PVDF-Cloisite 15A nanocomposite membrane was able to improve the permeate quality significantly while treating textile/dyeing wastewater in DCMD, but the membrane flux rapidly declined to 50% within the first few hours of a 40-hour operation [125]. Lin et al. (2015) modified the surface of a hydrophobic porous PTFE membrane by applying a thin layer of agarose hydrogel for textile/dyeing wastewater reclamation [216]. The modified PTFE membrane exhibited no wetting and about 71% of the flux of the bare PTFE membrane while treating textile/dyeing wastewater [216].

Despite the increasing interest in fabrication/modification of MD membranes for enhanced flux and reduced fouling/wetting propensity, most novel studies report short-time performance of the membranes in bench-scale systems using synthetic/simulated wastewater. To assess the full potential of the fabricated/modified membranes, long-term pilot-scale performances of these membranes must be evaluated using real wastewaters.

6. Energy consumption and economic aspects of MD for wastewater recovery

Many studies have looked into energy consumption in MD processes, using thermodynamic modeling or pilot-scale operations, while it is applied for desalination of seawater, brackish

water [25,53,62,63,78,196]. Thiel et al. (2015) reported energy consumption scenarios in the reclamation of shale gas produced water for several desalination technologies through the modeling of produced water properties (i.e., high salinities and diverse compositions commonly encountered in produced water from shale formations) using Pitzer's equation [217]. This study emphasized on how the produced water qualities create differences in system thermodynamics at salinities significantly above the oceanic range. Efficiency models were developed for mechanical vapor compression (MVC), multi-effect distillation (MED), forward osmosis (FO), humidification-dehumidification (HDH), permeate gap membrane distillation (PGMD), and reverse osmosis (single- and double-stage RO) systems [217]. Thermal and electrical energy consumptions (in kWh/m³ of recovered water) were evaluated for the processes mentioned above with a feed stream and brine stream salinity of 15% and 26%, respectively. Total energy consumption of RO and MVC was lower among all the processes. However, all of the energy consumption for RO and MVC was electrical energy. For the feed and brine salinity conditions considered, the total energy consumption in single-effect MVC, dual-effect MVC, single-stage RO, and dual-stage RO processes were 26 kWh/m³, 19 kWh/m³, 14 kWh/m³, and 10 kWh/m³, respectively. The total energy consumption in tri-effect MED, zero-extraction HDH, PGMD, and FO processes were ~200 kWh/m³, ~360 kWh/m³, ~510 kWh/m³, and ~600 kWh/m³, respectively [217]. Majority of the energy consumption in the MED and FO and almost all of the energy consumption in HDH and PGMD processes were thermal energy. Shihong Lin et al. (2014) also demonstrated an energy requirement of 27.6 kJ/kg of seawater for recovery of seawater using DCMD at a working temperature of 60°C, which regardless of the mass transfer kinetics will not be able to achieve a single-pass feed water recovery rate higher than 6.4% [25]. When compared to typical seawater desalination using RO process the energy requirement is about 3.18 kJ/kg of

seawater (for a typical recovery of 50%) [25]. Fouling comparison study conducted among DCMD, RO, and FO under similar hydrodynamic conditions, observed superior MD performance (with a 14% flux reduction) over RO and FO (with around 48% and 46% flux reductions, respectively) for organic (alginate) fouling after 18 hours application [218]. The rise of the diffusion coefficient of the organic foulants due to high feed temperature of MD resulted in the transport away of contaminants from the membrane surface; hence flux enhancement occurs when compare to RO and FO. Also, hydraulic resistance of the membrane-fouling layer in MD has insignificant influence on permeate flux [218]. When inorganic (calcium sulfate) feed solution was used, all three (RO, FO, and MD) systems operated under somewhat supersaturated condition for 36 h without scaling. FO exhibited the greatest scaling resistance against a feed of 33 ± 2 mM calcium sulfate without significant flux decline. Scaling began to occur at significantly higher concentrations at the membrane, and the concentrations were 46-58 mM for FO membrane (cellulose triacetate membrane), 35-38 mM for RO membrane (polyamide thin film composite membranes), and 33-38 mM for MD membrane (PVDF membrane) [218]. The superior inorganic scaling resistance in FO could be explained by the low surface energy of the FO cellulose triacetate membranes and due to enhanced crystallization kinetics of inorganic salt at high temperatures in the MD systems. The flux decline in MD was faster than that of FO and RO after gypsum scaling triggered. So MD systems should be used with appropriate membrane management schemes when the feed water source contains both organic and inorganic foulants (e.g., municipal wastewater). Furthermore, MD feed stream temperature should also be selected in a way that the solubility of inorganic contaminants does not decline drastically to cause severe fouling and flux decline [218].

The gained output ratio (GOR), which is defined by the ratio between the useful heat (i.e., the heat associated with water vapor transfer) and the total heat input of the system, is used to evaluate the thermal efficiency of MD processes [25,53,217]. For PGMD, the GOR ranges from about 1 to 2 depending on the system size, feed and brine salinity [217]. The low GOR value, due to a single-pass application, can be improved by recirculating the brine for high recovery ratio. Also, multi-stage MD configurations can be adopted for better heat recovery in the system and improve GOR. GOR and flux performance of common single stage MD configurations (DCMD, AGMD, CGMD, PGMD) were modeled up to high feed salinity levels (salinity up to 260 g/kg), and AGMD was observed to be more resistant to higher feed salinity levels and can achieve high GOR values than other configurations due to lower heat loss across the low thermal conductivity air gap [62]. The GOR values for a feed salinity of 250 g/kg and a flux of 2 L/m²/h was observed to be ~ 2.75 (AGMD), ~ 2.1 (for CGMD, thick membrane of 1.2 mm thickness), ~ 1.6 (for CGMD), and ~ 1 (for PGMD) [62]. AGMD systems should be operated without any partial or complete flooding of the air-gap. Any flooding of the air gap will lower the performance of AGMD towards that of PGMD. On the other hand, CGMD and DCMD with a thick membrane (thickness equal to the sum of the membrane and air gap thickness of AGMD) are also resistant to high salinity without having any gap flooding concerns during operation. However, the performance of an AGMD system, without gap flooding, is better than that of a CGMD with a thick membrane, mainly due to the higher permeability coefficient of the open air-gap, and the likely lower thermal conductivity of the air gap than that of the membrane [62].

In the presence of an alternative waste-heat or low-grade heat source, the MD process can compete with different desalination processes. Application of DCMD, coupled with a salt-

gradient solar pond (SGSP), for reclamation of terminal lake water demonstrated the use of low-grade heat from the lower convective zone of the salt-gradient solar pond [50,52]. The coupled system constructed an SGSP inside a lake for reclamation of terminal lake water and utilized approximately 20 kW/m^2 and 60 kW/m^2 of energy from the solar pond to drive thermal distillation, for two different feed temperatures (33.9°C and 53.9°C , respectively) [50]. Water production was on the order of $1.6 \times 10^{-3} \text{ m}^3/\text{d}/\text{m}^2$ of SGSP, with membrane areas ranging from 1.0 to $1.3 \times 10^{-3} \text{ m}^2/\text{m}^2$ of SGSP [50]. Approximately 75-80% of the extracted energy was used to transport water across the membrane (the enthalpy flow), and the remainder was lost by conduction in the membrane [50]. Therefore, improvement of DCMD membranes and modules to reduce conductive heat losses would yield higher water fluxes. The use of an alternative renewable thermal energy source compensated the high thermal energy requirement of MD, and only little electrical energy is required to operate the MD process [50,52]. Noel Dow et al. (2017) demonstrated the use of DCMD in recovering textile wastewater and reported an average specific thermal energy consumption of $1,600 \text{ kWh/m}^3$ until the total permeated water volume was $2 \text{ m}^3/\text{m}^2$ of membrane surface area [131]. With increasing fouling in the membranes, the specific thermal energy consumption rose sharply to $4,180 \text{ kWh/m}^3$ before the system was stopped for cleaning [131]. The substantial rise in thermal energy consumption leads to less water treated for the same thermal energy input and justified membrane cleaning. Assessment of waste-heat (generated in the textile plant) integration observed that MD could be applied to the particular textile plant when other treatment strategies (like reverse osmosis or nanofiltration) are introduced for saline-wastewater isolation and pre-concentration of the feed stream to reduce waste volume [131].

Woldemariam et al. (2016) reported AGMD pilot plant trials with pharmaceutical residues and relevant energy demand analysis with economic evaluations of large scale water recovery systems [134]. The low-temperature district heating return line feasibly supplied the thermal energy required for the MD process. Specific heat demands for the AGMD ranged from 692 to 875 kWh/m³ without heat recovery and as low as 105 kWh/m³ when heat recovery is possible [134]. The economic evaluation was performed for three cases: (i) Case 1: specific thermal energy input of 692 kWh/m³ with no heat recovery and employing 1176 MD modules, (ii) Case 2: specific thermal energy input of 735 kWh/m³ with no heat recovery and employing 644 MD modules, and (iii) Case 3: specific thermal energy input of 875 kWh/m³ with recovery of 770 kWh/m³ (i.e. with a demand of 105 kW/m³) and employing 1212 MD modules [134]. The capital cost of water treatment was estimated based on five years lifetime for membranes and a twenty-year operational span of other MD equipment in the system (having 10 m³/h treatment capacity). Case 2 configurations have the least specific capital expenditure (CAPEX) due to the higher permeate flux and so smaller number of modules requirement. Cases 1 and 3 have nearly overlapping specific CAPEX values due to the very close permeate flux, and so closer number of MD modules is required for particular production capacity. Hence, case 2 specific CAPEX showed a reduction from \$50,000 to \$20,000 per (m³/h) when the plant capacity increases from 10 to 100 in m³/h [134]. For a plant capacity of 8000 m³/h, specific CAPEX will be as low as \$9,800 and \$16,000 per (m³/h) for Cases 2 and 1, respectively. The annual operational and maintenance expenditure (OPMEX) were also evaluated for the three scenarios. Heat demand had the highest contribution (about 94%) in the total expenditure for the systems followed by CAPEX (3.4%), service and maintenance (1.2%), and costs of the membrane (0.7%). Case 3 and Case 2 registered the lowest and highest cost of heat, which was mostly due to heat recovery in

Case 3 and larger heat demand for Case 2. The total unit cost of water was $\$5.4/\text{m}^3$ for an MD plant having $8,000 \text{ m}^3/\text{h}$ treatment capacity, and heat requires an amount of $\$5.1/\text{m}^3$ of water [134]. Heat recovery (Case 3) enabled achievement of the lowest unit cost of water treatment, but this scenario also generates least permeate flux (so it will require large membrane area and higher initial investment) [134].

Energy consumption and economic concerns are essential for the considerations of any technology. MD, which requires very high thermal energy input compared to many desalination processes, shows great potential and competitive energy consumption scenarios to other desalination technologies when an alternative (waste-heat or low-grade heat) energy sources are available to heat the feed stream. Pre-treatment of wastewater before MD becomes necessary to reduce fouling and wetting concerns, which otherwise will increase energy consumption and decrease efficiency in the treatment and recovery process. The contribution of pre-treatment strategies to the overall expenditure of water recovery is an important factor. While many studies have looked into the incorporation of different pre-treatment and integrated processes with MD, it is important to evaluate the overall increase in capital, operational, and maintenance expenditure due to the inclusion of varying pre-treatment strategies.

7. Outlook on MD for wastewater reclamation

MD for wastewater reclamation differs from saline water desalination mostly due to differences in feed water quality and the interaction between contaminants and the membrane surface. It should be mentioned here that the different fouling and wetting mechanisms in MD remain the same in both these applications. It is evident that fouling and wetting scenarios (i.e., occurrence

rate, extent, etc.) will significantly vary in MD when used for wastewater reclamation, compared to desalination of saline water. Applicability of MD in desalination has been limited to high-salinity brines due to its high-energy requirement compared to pressure-driven RO process. It should be kept in mind that, while various pre-treatments are provided to wastewater to control fouling (inorganic, organic and biofouling) and wetting in MD, the justification of employing MD over RO, in recovering pre-treated wastewater, is seldom studied in detail. Nevertheless, MD has been highlighted as an economical option for recovery of highly saline pre-treated wastewater provided waste/alternative heat sources are available [183]. Pre-treated wastewater with low/moderate salinity and organic content might still pose significant organic fouling and biofouling problems in RO membranes due to low operational temperature. Such wastewater might necessitate a higher degree of pre-treatment before RO or make MD a better option for reclamation. While some studies have compared between RO and MD based on feed salinity and energy requirement, there is a scope for investigating the impact of organic and microbial quality of feed wastewater in the selection of recovery process for a given volume of wastewater.

Successful application of MD for wastewater reclamation will require a comprehensive understanding of membrane fouling and wetting mechanisms and relevant mitigation strategies. As interest grows for wastewater reclamation using MD, the following issues should be kept in mind:

- The interaction between the membrane and wastewater constituents complexly affects MD performance, influencing permeate flux, permeate quality, membrane fouling and wetting.
- Pre-treatment of wastewater is essential to achieve a consistent performance of MD in wastewater reclamation. For industries with an existing wastewater treatment facility, the use

of MD for wastewater reclamation often becomes feasible due to the availability of pre-treated wastewater and waste-heat in close proximity. There is a scope to study different pre-treatment processes integrated with MD for wastewater reclamation.

- Limited systematic research has been conducted into different membrane maintenance procedures. There is a significant lack of organized information on cleaning approaches for flux recovery in long-term operation of MD with real wastewater.
- Several novel/modified MD membranes (superhydrophobic, omniphobic, hydrophobic membrane with hydrophilic skin layer, etc.) have been reported in the literature. In most cases, these novel/modified membranes have been studied using synthetic wastewater. Only a few of these membranes were examined for reclamation of real wastewater. It is important to select a membrane type considering the type of contaminants in the feed stream.

Results from the literature indicate that MD is a promising wastewater reclamation process and it can be effectively used when paired with suitable pre-treatment options and low-grade/waste-heat sources. However, systematic, long-term, pilot-scale evaluation of different MD module configurations are required to ensure robust operational processes in industrial-scale wastewater treatment and reclamation. On top of this, combined energy and cost analyses are imperative to compare the applicability of MD with other wastewater recovery processes to further optimize and enhance the economic performance of MD.

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Author Contribution

M.R.C. and N.A. contributed equally to this work.

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Figure Captions:

Figure 1. The growth in research activity related to MD and application of MD for wastewater reclamation from 1991 to 2018 (Source: Web of Science). Numbers in the stacked columns indicate the number of published papers in each category.

Figure 2. Schematic diagrams showing configurations of classical single-stage MD systems: (a) Direct Contact Membrane Distillation (DCMD), (b) Air Gap Membrane Distillation (AGMD), (c) Vacuum Membrane Distillation (VMD), (d) Sweeping Gas Membrane Distillation (SGMD).

Figure 3. Schematic diagrams showing variations in configurations of different types of gap MD systems: Air gap membrane distillation (AGMD), Permeate gap membrane distillation (PGMD), Conductive gap membrane distillation (CGMD), and Material gap membrane distillation (MGMD).

Figure 4. Schematic diagram showing configuration of Flashed-feed Vacuum Membrane Distillation. (Redrawn following [69])

Figure 5. Combined effect of different fouling mechanisms (i.e. inorganic fouling, organic fouling, and biological fouling) leading to partial or complete pore blocking (internal fouling) and surface fouling (external fouling) in membrane distillation process

Table 1. Operational parameters in MD processes applied to different types of wastewater treatment and reclamation.

MD setup	Feed type	Pre-treatment	Membrane Properties					Temperature (°C)		Flow Rate/Velocity		Re f.
			Membrane type (Module: Material)	Mean pore size (µm)	Porosity (%)	Thickness (µm)	In-air contact angle (°)	Feed	Permeate	Feed	Permeate	
DCMD	TDW	Foam fractionation, Conventional (flocculation-biological) treatment	Flat sheet: PTFE	0.5	---	---	---	60	20	0.8 L m ⁻¹ 45–47 L m ⁻¹	0.8 L m ⁻¹ 45–47 L m ⁻¹	[131]
DCMD	TDW	NP, physicochemical-biological (anaerobic-aerobic) treatment	Flat sheet: PTFE	0.22	85.1	180	133.7	50	20	0.35 L m ⁻¹	0.25 L m ⁻¹	[132]
DCMD	TDW	NP	Hollow fiber: PVDF-Cloisite 15A composite	0.088	83.70 ± 0.67	---	97.7	90±1	25±2	0.023 m s ⁻¹	0.002 m s ⁻¹	[125]
DCMD	TDW	NP	Flat sheet: PTFE on PET support with Agarose	0.2	85%	130	127	60	21	2 L m ⁻¹	2 L m ⁻¹	[216]
DCMD	OMW	NP	Flat sheet: PTFE, PVDF	0.199 0.283	---	55 ± 6 118 ± 4	---	30 - 60	20	---	---	[159]
DCMD	OMW	NP, Coagulation/flocculation, MF	Flat sheet: PTFE	0.2	80%	178	---	40	20	---	---	[157]
DCMD	MW	NP, advanced biological treatment	Flat sheet: PTFE, PVDF	0.45, 0.45	---	---	124.9, 123.6	40 - 60	10	---	---	[143]
FO-DCMD	FO feed: sanitary wastewater; DCMD feed: OW+FO permeate	Ultrafiltration for OW	Flat sheet: PTFE	0.45	---	---	120	45.5	25	---	---	[189]
FO-DCMD	FO feed: secondary MW, DCMD feed: 1M NaCl+FO permeate	FO for secondary MW effluent	Flat sheet: PP	0.22	---	130-170	---	50	20	0.4 L m ⁻¹	0.4 L m ⁻¹	[186]
FO-DCMD	FO feed: secondary MW, DCMD feed: 1M NaCl+FO permeate	FO for secondary MW effluent	Flat sheet: PP	0.22	---	130-170	---	50	20	0.4 L m ⁻¹	0.4 L m ⁻¹	[150]
FO-DCMD	FO Feed: domestic wastewater, DCMD feed: 35 g/L NaCl+FO permeate	FO for domestic wastewater	Hollow fiber: PVDF	0.073	---	186±5	---	53	20	0.5 m s ⁻¹	0.15 m s ⁻¹	[185]
FO-DCMD	FO feed: raw sewage, DCMD feed: 1.5M NaCl+FO	FO for raw sewage, MD feed solution was pre-treated using GAC or UV	Flat sheet: PTFE	0.3	---	---	135±15	40	20	1.0 L m ⁻¹	1.0 L m ⁻¹	[188]

MD setup	Feed type	Pre-treatment	Membrane Properties					Temperature (°C)		Flow Rate/Velocity		Re f.
			Membrane type (Module: Material)	Mean pore size (µm)	Porosity (%)	Thickness (µm)	In-air contact angle (°)	Feed	Permeate	Feed	Permeate	
	permeate											
DCMD	RCW	Coagulation-sedimentation, filtration, acidification and degasification	Flat sheet: PVDF	0.18	82	---	---	50	20	0.5 m s ⁻¹	0.2 m s ⁻¹	[165]
DCMD	OW: oil, sodium dodecyl sulfonate and sodium chloride	NP	Flat sheet: PVDF	0.22	75	125	111	55	15	0.8 L m ⁻¹	0.8 L m ⁻¹	[86]
DCMD	OW: 1 wt% NaCl solution with oil	NP	Capillary: PP	0.2	73	---	---	40-80	20	---	---	[148]
DCMD	OW: shale oil and gas produced water	Filtration through 8-µm filter	Flat sheet: PVDF, PVDF-PVA, PVDF-SiO ₂ -FAS	0.45 (PVDF)	---	125 (PVDF)	119±4, 50±2, 159±2	60	20	0.4 L m ⁻¹	0.35 L m ⁻¹	[47]
DCMD	LLRW	NP	Hollow fiber: PVDF	0.15	80	---	---	47.5±0.5	27.0±0.5	0.303 m s ⁻¹	0.075 m s ⁻¹	[136]
DCMD	LLRW	NP	Spiral wound: PTFE	0.2	80	---	---	35-80	5-30	16 L m ⁻¹	16 L m ⁻¹	[137]
DCMD	LLRW/MLRW	NP	Flat sheet: PS, PES, PTFE	---	---	138.80 - 146.56	92.45 - 113.99	55	21.5	0.0023 L m ⁻¹	0.0014 L m ⁻¹	[215]
DCMD	ROC	NP, GAC	Flat sheet: PTFE	0.2	70-80	179	139.4 ±1.5	55	25	0.06 m s ⁻¹	0.06 m s ⁻¹	[127]
DCMD	ARD	NP, thermal precipitation	Flat sheet: PVDF	---	---	---	122.7 ±7.7	57.1±1.7	22.5±1.1	3.5 L m ⁻¹	3.5 L m ⁻¹	[120]
DCMD	PW	NP	Flat sheet: PVDF	0.22	---	104	124.9	60±2	20 ± 2	0.5 L m ⁻¹	0.5 L m ⁻¹	[123]
AGMD	PW	Pre-filtration	Flat sheet: PTFE with PP	0.2	80	200	---	55-90	15-50	20 L m ⁻¹	20 L m ⁻¹	[134]
Modified DCMD	LL	NP, MBR (anoxic+aerobic+UF)	Flat sheet: PTFE, PVDF	0.22, 0.45	---	170-240, 120-180	127.61, 124.91; 128.99, 123.59	40 - 60	10	3.5 L m ⁻¹	3.5 L m ⁻¹	[144]
FO-DCMD	FO feed: LL, DCMD feed: 4.82 M NaCl and FO permeate	FO	Flat sheet: PTFE-PVDF composite with PET	0.45	---	---	---	72.5±0.5 62.5±0.5	15±0.5	0.31 L m ⁻¹	0.31 L m ⁻¹	[190]
DCMD	FW	NP	Hollow fiber PP	0.46	80	250	---	55-60	30	2 L m ⁻¹	2 L m ⁻¹	[141]

Note: TDW = textile/dyeing wastewater, OMW = olive mill wastewater, MW = municipal wastewater, RCW = recirculating cooling water, OW = oily wastewater/oil-water emulsion, RW = radioactive wastewater, LLRW = low-level RW, MLRW = mid-level RW, ROC = wastewater reverse osmosis concentrate, ARD = acid rock drainage water, PW = pharmaceutical wastewater, LL = landfill leachate, FW = fermentation wastewater, NP = no pre-treatment, MF = microfiltration, FO = forward osmosis, MBR = membrane bioreactor, DCMD = direct contact membrane distillation (MD), VMD = vacuum MD, AGMD = air gap MD, PP = Polypropylene, PTFE = polytetrafluoroethylene, PVDF = polyvinylidene fluoride, PET = polyester, PS = polysulfone, PES = polyethersulfone, PVA = polyvinyl alcohol, FAS = Heptadecafluoro-1,1,2,2-tetrahydrodecyl triethoxysilane, GAC = granular activated carbon adsorption.

Table 2. Performances of treatment processes involving MD applied to different types of wastewater treatment and reclamation.

MD setup	Feed type	Pre-treatment	MD performance		Ref.
			Mean permeate flux, L m ⁻² h ⁻¹ (Time)	Reported rejections, water recovery	
DCMD	TDW	Foam fractionation, Conventional (flocculation-biological) treatment	~5 (0-40 days) ~2 (66 days) ~ 4 (after caustic cleaning)	Sulphate (>99.9%) Water recovery (91.6%)	[131]
DCMD	TDW	NP, physicochemical-biological (anaerobic-aerobic) treatment	NP: 19.8 (~6 hours); <1 (48 hours) P: ~21 (~6 hours); ~18 (48 hours)	NP: Color (94%); Conductivity (98.78%); COD (90%) P: Color (100%); Conductivity (99.95%); COD (96%)	[132]
DCMD	TDW	NP	37.8 (150 minutes) 13-15 (40 hours)	Rejection in 150-minute experiment: Color (95.3%); Conductivity (93.7%); Turbidity (93.0%); TDS (93.6%); COD (89.6%); BOD ₅ (90.8%)	[125]
DCMD	TDW	NP	Bare PTFE (salt solution): 32 (24 hours) Bare PTFE (wastewater): 8 (24 hours) Protected PTFE (wastewater): 20 (24 hours)	---	[216]
DCMD	OMW	NP	PTFE: 7.68 ± 0.22 (9 hours) PVDF: 4.95 ± 0.14 (9 hours)	Phenolic Compound separation factor: PTFE 99%, PVDF 89% (9 hours)	[159]
DCMD	OMW	NP, Coagulation/flocculation, MF	NP: 5.6, Coagulation/flocculation: 6.9, MicrofiltrationL 7.7 (initial); NP: 3.5, Coagulation/flocculation: 5.5, MicrofiltrationL 7.1 (3 hours); NP: 1.44 L m ⁻² h ⁻¹ (76 hours)	Phenolic Compound separation factor >99% (8 hours)	[157]
DCMD	MW	NP, advanced biological treatment	NP: PTFE 4.1 – 13.5, PVDF 2.9 – 8.6 (1.5 hours) P: PTFE 6 – 16.4, PVDF 2.2 – 8.16 (1.5 hours) (Maximum and minimum variations in flux results from temperature differences of 30°C and 50°C, respectively, between the feed and permeate side)	PTFE: NP (conductivity 93-96%, COD >98.5%, alkalinity 94%, hardness 98%, ammonia-nitrogen 45-50%); P (conductivity 96-98%, COD 89%, alkalinity 87%, hardness 98.7-99.1%, ammonia-nitrogen 50-60%) PVDF: NP (conductivity 74-76%, COD 97%, alkalinity 53-63%, hardness 66-83%, ammonia-nitrogen 31-50%); P (conductivity 79-81%, COD 89%, alkalinity 65-78%, hardness 76-82%, ammonia-nitrogen 35-40%)	[143]
FO-DCMD	FO feed: sanitary wastewater; DCMD feed: OW+FO permeate	Ultrafiltration for OW	6-8.5 (salt content = 0.1-0.75 mol/L)	High rejection (~99%) achieved for different organic, nutrient and ionic parameters due to complimentary ultrafiltration and FO pre-treatment.	[189]
FO-DCMD	FO feed: secondary MW, DCMD feed: 1M NaCl+FO permeate	FO for secondary MW effluent	Initial: 14.4 (DCMD), 12.24 (FO) Aftr 48 hours: 6.84 (Both FO-DCMD)	Conductivity rejection >97% in first 6 days, then deteriorated rapidly due to the presence of organic materials in the feed solution.	[186]
FO-DCMD	FO feed: secondary MW, DCMD feed: 1M NaCl+FO permeate	FO for secondary MW effluent	---	Overall 99.9% rejection of combined solutes in the system after 48 hours	[150]
FO-DCMD	FO Feed: domestic wastewater, DCMD feed: 35 g/L NaCl+FO permeate	FO for domestic wastewater	FO-DCMD: 17.60 (120 hours)	FO: TOC>95%, NH ₃ -N>73%, TN>65%, TP>95%, NO ₃ ⁻ >70%, SO ₄ ²⁻ >95%, PO ₄ ³⁻ >90% FO-DCMD: TOC>98%, NH ₃ -N>90%, TN>90%, TP>98%, Cl ⁻ >95%, NO ₃ ⁻	[185]

MD setup	Feed type	Pre-treatment	MD performance		Ref.
			Mean permeate flux, L m ⁻² h ⁻¹ (Time)	Reported rejections, water recovery	
				>95%, SO ₄ ²⁻ >98%, PO ₄ ³⁻ >97%	
FO-DCMD	FO feed: raw sewage, DCMD feed: 1.5M NaCl+FO permeate	FO for raw sewage, MD feed solution was pre-treated using GAC or UV	7 (FO-DCMD) 4.5 (DCMD alone) (Cumulative permeate volume of 4000 mL)	>98% for TOC, TN, and UV ₂₅₄ absorbance, >83% for conductivity, >90% for trace organic contaminants. 99.5% trace organic contaminants in FO-MD hybrid system coupled with GAC adsorption or UV oxidation.	[188]
DCMD	RCW	Coagulation-sedimentation, filtration, acidification and degasification	RCW with filtration, acidification, and degassing: normalized flux reduced from 0.964 to 0.664 (30 days) RCW with coagulation-sedimentation, filtration, acidification, and degassing: normalized flux reduced from 0.966 to 0.876 (30 days)	---	[165]
DCMD	OW: oil, sodium dodecyl sulfonate and sodium chloride	NP	Normalized flux reduced to 0.4 (600 min)	TOC rejection 49.1 ± 20.3 %	[86]
DCMD	OW: 1 wt% NaCl solution with oil	NP	For 1000 ppm oil: 4.93 (ΔT = 60°C); 0.55 (ΔT = 40°C)	Oil rejection: 99.996% and 99.969% (for oil concentration of 1000 ppm and 2000 ppm, respectively)	[148]
DCMD	OW: shale oil and gas produced water	Filtration through 8-μm filter	PVDF: 30.9, 29.4 (initial), 17.3, 23.52 (after 800 ml permeate collection in 16.4 and 14.9 hrs, respectively); PVDF-PVA: 30.3, 31.5 (initial), 23.3, 24.3 (after 800 ml permeate collection in 14.6 and 14.3 hrs, respectively); PVDF-SiO ₂ -FAS: 23.4, 26.2 (initial), 15.7, 20.2 (after 800 ml permeate collection in 21.1 and 18.1 hrs, respectively)	Salt removal efficiencies >99.9%, distillate conductivity increased by less than 75 μS/cm (corresponds to an increase in salinity of less than 35 mg/L NaCl). Water recovery achieved 53.33%	[47]
DCMD	LLRW	NP	7.85 (120 min)	100% rejections for Cs ⁺ , Sr ²⁺ , and Co ²⁺	[136]
DCMD	LLRW	NP	6.75 (20 hours)	High rejection (>90%) for major anions and cations Most radioisotopes were undetectable in permeate. Only Co-60 and Cs-137 were detected in permeate with high rejection values (97.7% and 99.9%, respectively)	[137]
DCMD	LLRW/MLRW	NP	Thickness normalized permeate flux J _w , (kg m ⁻¹ h ⁻¹): SMM1/PES: 0.143, SMM2/PES: 0.16, SMM1/PS: 0.07, SMM2/PS: 0.08, PTFE: 0.155	Almost 100% rejection of non-radioactive ions (Co ²⁺ , Cs ⁺ , Sr ²⁺); and radioisotopes (⁶⁰ Co, ¹³⁷ Cs, ⁸⁵ Sr)	[215]
DCMD	ROC	NP, GAC	NP: 16 (initial), 11 (at 85% water recovery) P: 16 (initial), 12.3 (at 85% water recovery)	99% ion rejection, more than 90% rejection of all (with GAC) and majority (with NP) micro-pollutants. For NP condition low rejections of propylparaben (50%), salicylic acid (86%), benzophenone (62%), triclosan (83%), bisphenol A (84%), atrazine (88%)	[127]
DCMD	ARD	NP, thermal precipitation	NP: 38.4 (Initial), 36.4~32.7 (after 13 hours) Thermal precipitation pre-treated ARD: 38.4	Salt rejection: 99.88 – 99.93% (NP), 99.96% (thermal precipitation pre-treated ARD)	[120]

MD setup	Feed type	Pre-treatment	MD performance		Ref.
			Mean permeate flux, L m ⁻² h ⁻¹ (Time)	Reported rejections, water recovery	
			(Initial), 36.28~36.25 (after 13 hours)		
DCMD	PW	NP	Cefotaxime: 20.6 (initial), ~18.5 (24 hour) Ciprofloxacin: 20.6 (initial), ~19 (24 hour) Tobramycin: 20.6 (initial), ~16 (24 hour)	100% (for neutral and negatively charged antibiotics) 86% (for positively charged Gentamicin sulfate) 78% (for positively charged Tobramycin)	[123]
AGMD	PW	Pre-filtration	2–6.8 (one week)	Diclofenac 99%, Atenolol 99%, Carbamazepine 99-100%, Ciprofloxacin 37-99%, Estradiol 70-98%, Estriol 76-87%, Estrone 66-86%, Ethinylestradiol 72-90%, Hydrochlorothiazide 99-100%, Ibuprofen 95-98%, Ketoprofen 92-98%, Metoprolol 100%, Naproxen 62-95%, Norfloxacin 60-98%, Progesterone 67-83%, Propranolol 96-100%, Ranitidine 89-100%, Sulfamethoxazole 92-99%, Trimetoprim 80-99%	[134]
Modified DCMD	LL	NP, MBR (anoxic+aerobic+UF)	NP: PTFE (0.45 µm) 4.56-9.87, PVDF (0.45 µm) 4.7-8.1 PTFE (0.22 µm) 4.1-6.1, PVDF (0.22 µm) 3.7-7.9 (2 hours) P: PTFE (0.45 µm) 6.5-15.54, PVDF (0.45 µm) 2.5-7.5 PTFE (0.22 µm) 6.0-13.8, PVDF (0.22 µm) 2.4-4.6 (2 hours)	NP (% Rejection range for PTFE, PVDF): Conductivity (75-85%, 77-84%), COD (99-99.5%, 97.8-99.5%), SO ₄ (92-95.5%, 91-95.5%), alkalinity (82-91%, 79-87%), hardness (97-99%, 95-97%), NH ₄ -N (43-73%, 30-62%) P (% Rejection range for PTFE, PVDF): Conductivity (98-99%, 98-99%), COD (97.5-98.5%, 97-97.5%), SO ₄ (90-96%, 90-96%), alkalinity (79-93%, 82-87%), hardness (97-98.5%, 97-98.5%), NH ₄ -N (85-95%, 90-93%)	[144]
FO-DCMD	FO feed: LL, DCMD feed: 4.82 M NaCl and FO permeate	FO	4.75 – 6.29 (250 minutes)	Salt: 96.70%-98.99%, TOC >98%, TN >98%, NH ₄ ⁺ -N 100%, Hg 100%, As 100%, Sb 100% (250 min)	[190]
DCMD	FW	NP	8.7 (initial), 4.3 (12 hours), 7.6 (after cleaning by pure water)	COD 95.3%, TOC 95.7%, Protein 98.9%	[141]

Note: TDW = textile/dyeing wastewater, OMW = olive mill wastewater, MW = municipal wastewater, RCW = recirculating cooling water, OW = oily wastewater/oil-water emulsion, RW = radioactive wastewater, LLRW = low-level RW, MLRW = mid-level RW, ROC = wastewater reverse osmosis concentrate, ARD = acid rock drainage water, PW = pharmaceutical wastewater, LL = landfill leachate, FW = fermentation wastewater, NP/P = no pre-treatment/pre-treatment, MF = microfiltration, FO = forward osmosis, MBR = membrane bioreactor, DCMD = direct contact membrane distillation (MD), VMD = vacuum MD, AGMD = air gap MD, PP = Polypropylene, PTFE = polytetrafluoroethylene, PVDF = polyvinylidene fluoride, PET = polyester, PS = polysulfone, PES = polyethersulfone, PVA= polyvinyl alcohol, SMM = surface modifying macromolecule, FAS = Heptadecafluoro-1,1,2,2-tetrahydrodecyl triethoxysilane, GAC = granular activated carbon adsorption, TDS = total dissolved solids, COD = chemical oxygen demand, BOD₅ = biochemical oxygen demand, TOC = total organic carbon, NH₃-N/NH₄⁺-N = ammonia/ammonium-nitrogen, TN = total nitrogen, TP = total phosphate, NO₃/NO₃⁻ = nitrate, SO₄/SO₄²⁻ = sulfate, PO₄/PO₄³⁻ = phosphate, Hg = mercury, As = arsenic, Sb = antimony, Co = cobalt, Cs = caesium, Sr = strontium.

Table 3. Removal efficiencies (%) of selected pharmaceutical residues in pharmaceutical wastewater using different treatment technologies. (*Values obtained from graphs.)

Pharmaceutic al Compound	Activat ed Sludge	Membra ne Bioreact or	Bioreactors with flocculation and sedimentati on	Forwa rd osmosi s	Nanofiltrati on	Revers e Osmos is	Air Gap Membra ne Distillati on	Direct Contact Membra ne Distillati on
Diclofenac	-143 – 80	-8 – 87.4	-370	92 – 100*, 92.9 - 96	55 – 101*, 94 – 98.5*	98 – 101*	99	
Atenolol	0 – 97	65.5 – 76.7			48 – 96*		99	93.4 – 99.4
Carbamazepine	-122 – 58	-22 – 23		95 – 98*, 84.7 –	64 – 98*	75 – 100*	99 – 100	

Pharmaceutic al Compound	Activat ed Sludge	Membra ne Bioreact or	Bioreactors with flocculation and sedimentati on	Forwa rd osmosi s	Nanofiltrati on	Revers e Osmos is	Air Gap Membra ne Distillati on	Direct Contact Membra ne Distillati on
				94.4				
Ciprofloxacin			90.9	98.7 – 99			37 – 99	
Estradiol			>82.6				70 – 98	
Estriol							76 – 87	
Estrone			-343.9				66 – 86	
Ethinylestradiol							72 – 90	
Hydrochlorothia zide	0 – 76.3	0 – 66.3					99 – 100	
Ibuprofen	52 – 99.7	89 – 99.8	98.9	82 – 97*	47 – 100*, 92 – 98*	96 – 102*, 90 – 100*	95 – 98	
Ketoprofen	9 – 91.1	43.9 – 97					92 – 98	
Metoprolol	-1 – 77	29.5 – 58.7		98.1 – 98.7			100	
Naproxen	-2 – 98	71 – 99.3	92.1	64 – 97*, 90.2 – 97.9	53 – 103*		62 – 95	
Norfloxacin				99.7			60 – 98	94.5 – 99.9
Progesterone							67 – 83	
Propranolol	59	65.5 – 77.6		95 – 97.8			96 – 100	
Ranitidine	24.7 – 42.2	29.5 – 95		98.8 – 99.3			89 – 100	99.6
Sulfamethoxazol e	-138 – 99	57 – 90		88.2 – 93.9	45 – 100*	90 – 100*	92 – 99	
Trimetoprim	-40 – 40.4	47.5 – 66.7			42 – 101*		80 – 99	99.5
Loratadine	15	0 – 33.5						99.6
Paroxetine	91	90						99
Omeprazole								98.5 – 99.1
Cimetidine								99.5 – 99.6
Fenofibrate								95.4 – 99.6
Phenylbutazone								95.8 – 99.9
Phenazone								87.7 – 99.8
Betamethasone								92.4 – 97.6
Prednisone								98.6 – 99.6
Scopolamine								99.9
Metformin								92 – 95.6
Enrofloxacin								92.7 – 95.8
Enoxacin								91.6 – 99.5
Danofloxacin								100
Caffeine					32 – 88*	86 – 101*		89.8 – 93.3
Atorvastatin								93 – 99.3
Ampicillin				~ 100				99.9
Amoxicillin								99.9
Erythromycin				99.5 – 99.8				94.7 – 99.6
Clarithromycin								95 – 96.4
Fluconazole								95.6 – 99.9
Reference	[219]	[219]	[220]	[221], [222]	[223], [224], [225]	[225], [226]	[134]	[135]

Table 4. Effects of feed/permeate stream temperatures on permeate flux for different MD configurations. (*Values obtained from graphs.)

MD	Membran	Pore	Major	Concentra	Feed	Pressu	Feed Temperature	Permeat	Ref
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Configura tion	e/ Module	size/ Mean pore diameter (μm)	Feed Constitu ent	tion	flow rate/ veloci ty	re (for VMD)	(T_f), Permeate/cold side Temperature (T_p)	e Flux	.
VMD	PP/ Flat Sheet	0.2	Methyle ne blue dye	18.5 mg/L	14 mL/s	5 mm Hg	$T_f = 40^\circ\text{C}, 50^\circ\text{C},$ $60^\circ\text{C}, 70^\circ\text{C}$	4.25, 4.8, 5.6, 6.3 $\text{kg}/\text{m}^2/\text{h}$	[57]
VMD	PP/ Flat Sheet	0.2	Remazol Brilliant Blue R (RBBR) dye	50 mg/L	0.78 – 1.67 m/s	10 mbar	$T_f = 40^\circ\text{C}, 50^\circ\text{C},$ 60°C	27.5, 35, 57 $\text{kg}/\text{m}^2/\text{h}$	[13 0]
VMD	PP/ Flat Sheet	0.2	NaCl	100,200,30 0 g/L	15 mL/s, 30 mL/s	40 – 120 mbar	$T_f = 25^\circ\text{C}, 40^\circ\text{C},$ 55°C	~1.8 – 15 $\text{kg}/\text{m}^2/\text{h} *$	[14 9]
DCMD	PTFE/ Flat Sheet	0.1	Tapioca starch based synthetic wastewat er	COD (1240 \pm 360 mg/L), $\text{NH}_3\text{-N}$ (512 \pm 70 mg/L), VFA (512 \pm 112 mg/L), TS (2918 \pm 236 mg/L), TDS (3008 \pm 172 mg/L)	250 – 1000 mL/m in (0.00 5 – 0.014 m/s)	-	$T_f = 40^\circ\text{C}, 50^\circ\text{C},$ $60^\circ\text{C}, 70^\circ\text{C}$ $T_p = 10^\circ\text{C}$	1.41, 2.66, 4.51, 7.22 $\text{L}/\text{m}^2/\text{h}$ (for 250 mL/min) 1.67, 2.94, 4.97, 7.35 $\text{L}/\text{m}^2/\text{h}$ (for 500 mL/min) 1.80, 3.09, 5.38, 7.71 $\text{L}/\text{m}^2/\text{h}$ (for 600 mL/min) 1.82, 3.34, 6.4, 8.98 $\text{L}/\text{m}^2/\text{h}$ (for 800 mL/min) 2.09, 3.44, 6.62, 9.22 $\text{L}/\text{m}^2/\text{h}$ (for 800 mL/min)	[14 5]
DCMD	PVDF/ Hollow Fiber (unmodifi ed, plasma modified, chemically modified)	0.421 (unmodifi ed) 0.191 (plasma modified) 0.189 (chemical ly modified)	NaCl	3.5 wt%	2.5 L/min	-	$T_f = 40^\circ\text{C}, 50^\circ\text{C},$ $60^\circ\text{C}, 70^\circ\text{C}$ $T_p = 25^\circ\text{C}$	~6 – 65 $\text{kg}/\text{m}^2/\text{h} *$	[12]
VMD	PP/ Hollow Fiber	0.18	$\text{Co}(\text{NO}_3)_2$	10 mg/L	41.8 L/h	0.98 atm	$T_f = 30^\circ\text{C} - 70^\circ\text{C}$	~0.65 – 6.1 $\text{L}/\text{m}^2/\text{h} *$	[13 8]
PGMD	PTFE/ Spiral wound	0.2	Salinity	0-105 g/kg	500 kg/h	-	$T_f = 80^\circ\text{C}$ (Evaporator inlet) $T_p = 20^\circ\text{C} - 40^\circ\text{C}$ (Condenser inlet)	~9 – 25 $\text{kg}/\text{h} *$	[77]
DCMD (in an integrated FO-MD setup)	PP/ Flat Sheet	0.22	NaCl (FO Draw Solution)	0.25 – 2 M	0.4 L/min	-	$T_f = 40^\circ\text{C}, 50^\circ\text{C},$ $60^\circ\text{C}, 70^\circ\text{C}$ $T_p = 15^\circ\text{C}$ $T_f = 40^\circ\text{C}$ $T_p = 30^\circ\text{C}, 25^\circ\text{C},$ $20^\circ\text{C}, 15^\circ\text{C}$ $T_f = 70^\circ\text{C}$ $T_p = 30^\circ\text{C}, 25^\circ\text{C},$ $20^\circ\text{C}, 15^\circ\text{C}$	~10 – 35 $\text{L}/\text{m}^2/\text{h} *$ ~5 – 10 $\text{L}/\text{m}^2/\text{h} *$ ~28 – 35 $\text{L}/\text{m}^2/\text{h} *$	[15 0]
AGMD	PVDF/ Flat Sheet	0.45	Simulate d Seawater (Cl, Na, Mg, Ca, K, Br, B, F)	Cl (18,600 mg/L), Na (10,400 mg/L), Mg (1,290 mg/L), Ca (410	5.5 L/min	-	$T_f = 40^\circ\text{C} - 70^\circ\text{C}*$ $T_p = 7^\circ\text{C} - 30^\circ\text{C}$	~1 – 7 $\text{kg}/\text{m}^2/\text{h} *$	[37]

				mg/L), K (380 mg/L), Br (62 mg/L), B (4.9 mg/L), F (1.9 mg/L)					
VMD	PP/ Hollow Fiber	0.18	CsCl, CsNO ₃ , NaCl	10 mg/L	41.8 L/h	5.05 kPa	T _f = 30°C -70°C	~0.7 – 6.4 L/m ² /h	[156]
AGMD	Electrospun PVDF, PVDF (Commercial)/ Flat Sheet	0.37 (Electrospun PVDF) 0.22 (Commercial PVDF)	Pb(NO ₃) ₂	1000 mg/L	1.5 L/min	-	T _f = 30°C,40°C,50°C,60°C, 70°C T _p = 7°C T _p = 7°C,10°C,15°C,20°C,25°C, 30°C T _f = 60°C	~4.5 – 28 L/m ² /h * (Electrospun PVDF) ~3.5 – 24 L/m ² /h * (Commercial PVDF) ~21.8 – 15.7 L/m ² /h * (Electrospun PVDF) ~16 – 11.5 L/m ² /h * (Commercial PVDF)	[43]
DCMD	PVDF/ Flat Sheet	0.20	NaCl	17.76 wt%	0.145 m/s	-	T _f = 79°C T _p = 20.5°C	~0.002 – 0.013 kg/m ² /s *	[171]

Note: DCMD = direct contact membrane distillation (MD), VMD = vacuum MD, AGMD = air gap MD, PGMD = permeate gap MD, PP = Polypropylene, PTFE = polytetrafluoroethylene, PVDF = polyvinylidene fluoride.

Table 5. Effects of feed stream flow rate/velocity on permeate flux for different MD configurations. (*Values obtained from graphs.)

MD Configuration	Membrane / Module	Pore size/ Mean pore diameter (µm)	Major Feed Constituent	Concentration	Feed Temperature (T _f), Permeate/cold side Temperature (T _p)	Pressure (for VMD)	Feed flow rate/ velocity	Permeate Flux	Ref.
VMD	PP/ Flat Sheet	0.2	Methylene blue dye	18.5 mg/L	T _f = 50°C	5 mm Hg	14, 17, 30, 42, 57 mL/s	4.75, 5, 6, 8.1, 8.2 kg/m ² /h	[57]
VMD	PP/ Flat Sheet	0.2	Remazol Brilliant Blue R (RBBR) dye	50 mg/L	T _f = 50°C	10 mbar	19.1, 26, 34.9, 41 L/h	22.5, 26, 26.5, 28.5 kg/m ² /h	[130]
VMD	PP/ Flat Sheet	0.2	NaCl	100 g/L	T _f = 55°C	40 – 120 mbar	15, 30 mL/s	~5 – 14.5 kg/m ² /h *	[149]
DCMD	PTFE/ Flat Sheet	0.1	Tapioca starch based synthetic wastewater	COD (1240±360 mg/L), NH ₃ -N (512±70 mg/L), VFA (512±112 mg/L), TS (2918±236 mg/L), TDS (3008±172 mg/L)	T _f = 40°C, 50°C, 60°C, 70°C T _p = 10°C	-	250, 500, 600, 800, 1000 mL/min (0.005, 0.008, 0.01, 0.012, 0.014 m/s)	1.41, 1.67, 1.8, 1.82, 2.09 L/m ² /h (for 40°C) 2.66, 2.94, 3.09, 3.34, 3.44 L/m ² /h (for 50°C) 4.51, 4.97, 5.38, 6.4, 6.62 L/m ² /h (for 60°C) 7.22, 7.35, 7.71, 8.98, 9.22 L/m ² /h (for 70°C)	[145]
DCMD	PVDF/	0.421	NaCl	3.5wt%	T _f = 50°C	-	0.82-	~12.5 – 15	[12]

	Hollow Fiber				$T_p = 25^{\circ}\text{C}$		3.06 m/s (9.5 mm housin g) 0.17-1.05 m/s (19.5 mm housin g)	$\text{kg/m}^2/\text{h}^*$ (9.5 mm housing) $\sim 6 - 11$ $\text{kg/m}^2/\text{h}^*$ (19.5 mm housing)	
VMD	PP/ Hollow Fiber	0.18	$\text{Co}(\text{NO}_3)_2$	10 mg/L	$T_f = 70^{\circ}\text{C}$	0.98 atm	10.5-41.8 L/h	$\sim 4.5 - 6.1$ $\text{L/m}^2/\text{h}^*$	[138]
AGMD	PVDF/ Flat Sheet	0.45	Simulated Seawater (Cl, Na, Mg, Ca, K, Br, B, F)	Cl (18,600 mg/L), Na (10,400 mg/L), Mg (1,290 mg/L), Ca (410 mg/L), K (380 mg/L), Br (62 mg/L), B (4.9 mg/L), F (1.9 mg/L)	$T_f = 60^{\circ}\text{C}$ $T_p = 20^{\circ}\text{C}$	-	1-5.7 L/min	$\sim 2.7 - 3.4$ $\text{kg/m}^2/\text{h}^*$	[37]
VMD	PP/ Hollow Fiber	0.18	CsCl , CsNO_3 , NaCl	10 mg/L	$T_f = 70^{\circ}\text{C}$	5.05 kPa	10.5-41.8 L/h	$\sim 4.8 - 6.8$ $\text{L/m}^2/\text{h}^*$	[156]
PGMD	PTFE/ Spiral wound	0.2	Salinity	0-105 g/kg	$T_f = 80^{\circ}\text{C}$ $T_p = 25^{\circ}\text{C}$	-	200-500 kg/h	$\sim 2.5 - 25$ kg/h^*	[77]
AGMD	Electrospun PVDF, PVDF (Commercial)/ Flat Sheet	0.37 (Electrospun PVDF) 0.22 (Commercial PVDF)	$\text{Pb}(\text{NO}_3)_2$	1000 mg/L	$T_f = 60^{\circ}\text{C}$ $T_p = 7^{\circ}\text{C}$	-	0.5-1.5 L/min	$\sim 18.6-22$ $\text{L/m}^2/\text{h}^*$ (Electrospun PVDF) $\sim 13.79 - 16$ $\text{L/m}^2/\text{h}^*$ (Commercial PVDF)	[43]
DCMD	PVDF/ Flat Sheet	0.20	NaCl	17.76 wt%	$T_f = 43.2^{\circ}\text{C}$, 68°C $T_p = 20.5^{\circ}\text{C}$	-	0.08-0.33 m/s *	~ 0.0019 $\text{kg/m}^2/\text{s}^*$ ($T_f = 43.2^{\circ}\text{C}$) $\sim 0.007 - 0.008$ $\text{kg/m}^2/\text{s}^*$ ($T_f = 68^{\circ}\text{C}$)	[171]
DCMD	PVDF/ Flat Sheet	0.22	NaCl	35 g/L	$T_f = 60^{\circ}\text{C}$ $T_p = 20^{\circ}\text{C}$	-	1.85-3.7 m/s	$\sim 30 - 38$ $\text{kg/m}^2/\text{h}^*$	[227]
AGMD	PTFE, PTFE with PP support/ Flat Sheet	0.45 (PTFE) 0.20 (PTFE, PTFE-PP)	Sucrose	150 g/L	25°C (Trans-membrane Temperature)	-	8-58 L/h	$\sim 90 - 156$ mL/h^* (PTFE 0.45) $\sim 78 - 132$ mL/h^* (PTFE 0.2) $\sim 67 - 90$ mL/h^* (PTFE-PP 0.2)	[228]

Note: DCMD = direct contact membrane distillation (MD), VMD = vacuum MD, AGMD = air gap MD, PGMD = permeate gap MD, PP = Polypropylene, PTFE = polytetrafluoroethylene, PVDF = polyvinylidene fluoride.

Highlights

- MD application is gaining interest for reclamation of different types of wastewater
- Complex interactions of contaminants and membranes lead to fouling and wetting in MD
- Pre-treatment lowers membrane fouling and wetting potential of wastewater in MD
- Novel modification approaches of MD membranes mitigate fouling and wetting
- Membrane cleaning recovers flux with fading reusability in sequential treatment cycles