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A review on fouling of membrane distillation

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ABSTRACT

Membrane distillation (MD) has been developed for the past 40 years. Nevertheless, only in recent times, MD technology has shown substantial progress, including the development of a few commercial systems. In this study, a comprehensive review is carried out on the application of MD for the production of drinking water. Based on a broad perspective, this review describes the applications of MD for drinking water production, its advantages, and limitations. Specifically, this review focuses on the scaling and organic fouling phenomena in MD for drinking water production as one of the major challenge to MD implementation. The fouling and wetting phenomena in MD is discussed in detail as well as fouling detection methods, the influence of feed solution characteristics, and operational parameters on MD fouling and related areas requiring future investigations. The study highlights a number of approaches on fouling reduction in MD.

Keywords: Membrane distillation; Fouling; Scaling; Mitigation

1. Introduction

1.1. Global demand for drinking water

The world's increasing population, economic development, and climate change are driving the demand for more drinking water [1]. The current water consumption rate is more than double that of the population increase rate [1]. In view of the limited volume of available and accessible drinking water, it is a challenge for the water industries to meet global water requirement needs. Water industries are consequently shifting technology trends towards seawater desalination process that offers the capacity to produce drinking water from the world's major alternative water source—seawater [2].

Presently, seawater reverse osmosis (SWRO) technology is the most widely used membrane technology in desalination plants [2,3]. SWRO technology is successful due to its low-energy requirements compared

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to thermal technologies; it is also easy to control and retains a good degree of stability in achieving a high rejection rate of dissolved salts in seawater [3]. Large reverse osmosis (RO) desalination plants in countries such as Israel, Algeria, Australia, Saudi Arabia, and Singapore have the capacity to produce drinking water from 300,000 up to 500,000 m^3/d.

1.2. The role of membrane distillation in drinking water production

Fundamentally, RO operations are built as large centralized desalination plants due to energy recovery capacity in large plants [4]. As such, RO units are suitable for high-density population areas. However, numerous low-density population areas located in inland, rural areas lack fresh water, require small-scale, stand-alone desalination units. Further, the high brine production due to osmotic limitation and energy requirements of the RO application in treating brackish, high saline water remains an economic challenge [3]. Recently, membrane distillation (MD) has been identified as a promising alternative technology option for drinking water production [5,6].

MD differs from other membrane technologies as its driving force is vapor pressure across the membrane. As a process not restricted by feed solution salinity and operating at low thermal requirements, MD can operate where RO and thermal distillation technology applications are challenged [7]. The potential of MD technology has been acknowledged by several review papers on state-of-the-art treatment technologies associated with renewable energies for seawater and brackish water desalination [6–9]. MD should not be viewed as a substitute for conventional pressure operated membrane treatment technologies. Instead, it plays an important role in filling the gap of existing treatment technologies. In this regard, the thermal integrated membrane feature of the MD process presents a unique scaling and fouling phenomena compared to conventional membrane process. It is therefore essential to evaluate the feasibility of MD as a drinking water treatment process with emphasis on the fouling and scaling development.

Hence, this paper presents a comprehensive review associated with the application of MD for the production of drinking water. Specifically, this review focuses on the scaling and organic fouling development in MD for drinking water production. The fouling–wetting phenomena in MD is discussed in detail as well as MD fouling detection methods, the influence of feed solution characteristics, and operational parameters on MD fouling and related areas requiring future investigations. The study highlights a number of approaches on fouling reduction in MD namely membrane cleaning, pretreatment, and antiscalant usage.

1.3. MD application in drinking water production

1.3.1. MD configurations

The MD system consists of various configurations, namely direct contact MD (DCMD), vacuum MD (VMD), air gap MD (AGMD), and sweeping gas MD (SGMD).

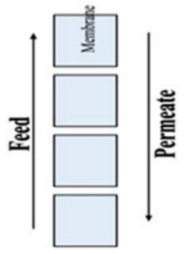
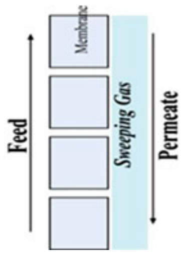
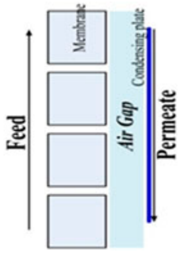
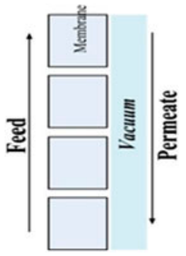
In all four MD configurations (DCDM, AGMD, SGMD, and VMD), the feed solution will be in direct contact with the feed side membrane. The hydrophobic nature of the membrane creates a surface tension force that prevents liquid solutions from entering the membrane pores. Hence, a liquid/vapor interface is formed at the entrance of the membrane pores. The membrane pores should remain dry throughout the MD operation. The MD configuration differs based on the nature of the cold side processing of the permeate as described in Table 1.

1.3.2. Recent development of MD application for drinking water production

The pioneer MD study for the purpose of drinking water production from seawater was conducted as early as 1964. This study reported a low production rate of 1 $kg/m^2/h$ [10]. Following this, a few early investigations acknowledged the potential application of MD for the production of high purity water through the process of desalination [11–13]. MD has a number of attractive features that make it a versatile alternative technology for producing drinking water. As a vapor pressure operated membrane system, MD can be used to treat highly saline feed solution. In this type of operation, partial water vapor pressure will be only reduced slightly due to salt concentration [14,15]. Additionally, the thermal process in MD requires only low operating temperature. This makes it possible to utilize alternative renewable energy sources such as waste heat or solar energy [16–19]. MD system can be constructed as a small-scale and compact unit; a smaller footprint compared to the traditional distillation system [20,21].

In recent times, enhancements such as higher operating cross-flow velocity, the use of acrylic plastic as membrane cell construction material, and the utilization of composite membranes with very thin active layers lead to permeate flux as high as 50–80 $kg/m^2/h$ [14]. Apart from DCMD, the performances of other MD configurations (AGMD, SGMD, and VMD) have been explored for their suitability in producing

Table 1
MD configuration description

	DCMD	SGMD	AGMD	VMD
Configuration				
Permeate-side setting	Cooling water (internal condensation)	Cold sweeping gas (external condensation)	Air gap with condensing plate (internal condensation)	Vacuum (external condensation)
Primary Transport Mechanism	Molecular and Knudsen diffusion	Molecular diffusion	Molecular diffusion	Knudsen diffusion
Main advantage	Simple structure	Lower heat loss than DCMD	Recoverable latent heat	High flux
Main Disadvantage	High heat loss	Additional equipment	Lowest flux due to resistance	Risk of membrane wetting, additional equipment

drinking water. For instance, the VMD configuration was analyzed by a number of researchers who reported promising results for seawater desalination [22–24]. The incorporation of vacuum in the VMD configuration led to achieving a high flux in the range of 12–16 kg/m^2/h, while maintaining lower polarization due to the negligible presence of a boundary layer on the permeate side [25,26]. Meanwhile, the AGMD configuration has also been evaluated in seawater desalination research. The AGMD configuration has an additional air gap interposed between the membrane and the condensation surface. Although heat loss by conduction is reduced by higher heat- and mass-transfer resistances, the penalty is flux reduction. For example, Hsu et al. [27] found that the permeate flux produced by DCMD was higher than that produced by AGMD (5–6 kg/m^2/h).

Presently, a number of semi-pilot-scale plants and pilot-scale plants have been examined for the production of drinking water. Guillén-Burrieza [20] reported a positive outcome from a two-year testing of pre-commercial Keppel Seghers AGMD desalination modules. Meanwhile Gabsi and Chehbouni [16] investigated the feasibility of a solar-integrated VMD configuration for seawater desalination in Mahares, Tunisia. Similarly, Banat and Jwaied [17] observed the performance of an autonomous solar-powered MD with seawater desalination for one year (average of 800 L/d) and highlighted the plant's potential in providing remote coastal areas with clean drinking water. In this regard, Zhao et al. [28] and Naidu et al. [29,30] reported on the development of a modified design pilot-scale VMD system by MemSYS. MemSYS designed its commercial novel unit to incorporate internal heating, enabling it to operate at a low range of feed temperatures between 45 and 60˚C. The solar-driven MemSYS VMD system was evaluated for seawater desalination; it performed well with an average permeate flux at approximately 7 LMH on a sunny day. Testing the pilot-scale plants reflects the emergence of MD as a new and key technology.

2. Fouling phenomena in MD

Despite the promising potential of MD in the production of drinking water, the evidence of membrane fouling development in MD is a major concern. The work of Hsu et al. [27] was one of the initial DCMD studies on drinking water production with seawater that reported permeate flux decline was attributable to fouling. The study highlighted the susceptibility of MD operations to membrane fouling due to thermal application. In two other studies, MD's performance in producing high purity water was evaluated with tap water and these studies observed precipitation of calcium carbonate ($CaCO_3$) onto the membrane surface [31,32]. A long-term DCMD study (for 100 d) with actual seawater reported a permeate flux decline from

23.8 to 14.4 LMH after 30 d of operation and observed membrane fouling due to inorganic scalants [33]. More recently, Shirazi et al. [34] carried out a long-term study to evaluate the feasibility of DCMD as a stand-alone seawater desalination process. After 240 h, the study observed a sharp decrease in permeate flux from around 47 LMH to 37 LMH, and the study attributed this to scale formation on the membrane surface.

Although the challenges associated with fouling are evident from these MD studies, detailed investigation is still lacking in this area. The lack of understanding of membrane fouling development is one of the key constraints to the prospective commercial application of MD. The following sections will focus on the phenomena associated with fouling in MD.

This section is directed towards understanding the fouling phenomenon in MD by reviewing existing studies. Specifically, this section focuses on the relationship of wetting and fouling, fouling detection techniques, and factors influencing organic fouling and scaling development in MD. An understanding on fouling occurrence in MD and its influencing factors will make possible the recommendations for implementing an appropriate mitigation strategy.

2.1. Background of fouling in MD

The term “fouling” is a phenomenon common to all types of membrane processes resulting in the loss of membrane performance. It is a challenge to precisely define membrane fouling as it is an extremely complex phenomenon. In general, during membrane filtration operation, feed solution being transported across the membrane results in the accumulation of foulants (particles and dissolved components) on or inside the membrane. As a consequence, the permeate flux declines with constant operating parameters implying the occurrence of membrane fouling.

According to Vrouwenvelder and van der Kooij [35], it is essential to diagnose the type of fouling to understand the fouling phenomena. In a number of water and wastewater treatment studies, the main fouling categories are classified as organic, inorganic, biological, and particular/colloidal fouling, based on the foulant type [36–39]. The main fouling categories are summarized in Table 2.

In pressure-driven membrane processes, scaling and organic fouling layer on the membrane surface is largely attributable to compaction due to hydraulic pressure [40,41]. On the other hand, due to the application of vapor operation and the absence of hydraulic pressure, membrane fouling in MD is expected to be less severe compared to pressure-driven membrane processes. As such, membrane fouling in MD has not been studied widely in comparison to pressure-driven membrane processes such as ultrafiltration (UF), nanofiltration (NF), and RO [38,41,42]. In fact, initial MD studies dismissed fouling in MD and linked the permeate flux decline caused by organic juice and bovine serum albumin (BSA) concentration the polarization effect only [43,44]. Further, the larger membrane pore size in MD was also associated with minimal fouling/clogging [45].

On the other hand, the direct exposure of the membrane to high concentrated feed solution to meet the near zero liquid discharge coupled with thermal application on a hydrophobic membrane makes MD operation susceptible to membrane fouling.

Most MD studies on membrane fouling development focused on scaling and organic fouling. Biofouling in MD has been examined to date by only two

Table 2
Description of fouling categories

Category of fouling Particle fouling	Scaling	Organic	Biofouling
Type of foulant	*Type of foulant*	*Type of foulant*	*Type of foulant*
Suspended solids/larger particles as well as smaller particles and metal hydroxide in source water	High concentrations of inorganic salts in source water	Natural organic matter (NOM) in source waters.	Aquatic organisms, such as fungi, algae, and micro-organisms in source water
General description	*General description*	*General description*	*General description*
Fouling occurs due to the accumulation of particles on the membrane surface and inside the membrane pores, forming a cake layer	Fouling occurs due to precipitation deposits resulting in bulk and membrane crystallization	Fouling occurs through adsorption of NOM compounds on membrane, causing gel formation of macromolecular substances.	Fouling occurs when biofilm forms on the membrane

studies [46,47]. Microbial growth was deemed to have minimal influence in MD operation. This is due to the high saline concentrate and thermal condition used in MD.

2.2. MD fouling–wetting phenomena

One of the fundamental challenges associated with fouling development in MD is membrane wetting. Membrane wetting is a phenomenon where liquid fills the membrane pores, as opposed to vapor-filled pores. The mechanism for membrane wetting is that water enters the larger pores of the membrane by breaking the surface tension at the interface between liquid and vapor on the membrane surface [48]. For a given pore size, there is a critical penetration pressure, above which the liquid will penetrate the membrane which is known as the liquid entry pressure of water (LEP_w). The degree of membrane wettability differs based on either a surface wetting where the liquid is present only in the pores of the external surface layers (pores inside the membrane wall are dry) or partially wetted, where the majority of pores inside the membrane wall is dry, but a fraction of pores (with the largest diameters) are wetted, or full wetting where all the pores inside the membrane walls are filled by liquid as shown in Fig. 1 [49].

In MD studies, fouling deposition on the membrane accelerates wetting as observed in a number of MD studies [49–52]. Factors such as permeate flux decline, membrane hydrophobicity reduction, and permeate quality deterioration are generally used as indicators of membrane wetting due to fouling [21,50,52].

Although the occurrences of wetting due to fouling are evident from previous studies, the MD fouling–wetting phenomenon is still not clearly represented. To provide a better understanding of MD fouling–wetting phenomena, this review paper classified MD fouling–wetting occurrence based on the main foulant type being inorganic compounds and organic compounds.

2.2.1. Inorganic compound

In scaling studies, it has been observed that crystal deposition on the membrane leads to pore plugging. The pore plugging/clogging of the crystals into the membrane pores, increases the pore diameter size, resulting in membrane wetting. Gryta [53] observed that $CaCO_3$ salt crystals were formed on the membrane surface as well as inside the pores causing wetting as well as mechanical damage of the membrane structure. Similar occurrence of wetting phenomena of pore plugging by salt crystallization leading to permeate quality deterioration and permeate flux decline was established in other studies [50–55].

2.2.2. Organic compound

Franken et al. [56] explained that the presence of high organic contents in the feed would reduce the hydrophobicity of the membrane via adsorption which leads to membrane wetting. In other words, the behavior of organic foulant in MD can be likened to that of absorbents. In this regards, Lv et al. [57] showed that the diffusion of two amine absorbents into PP polymer membrane altered the surface properties and reduced membrane hydrophobicity (membrane contact angle decreased remarkably). Studies on organic fouling leading to wetting have not been carried out in detail. In most MD studies related to protein organic fouling, although prevalent absorption of the protein was established on the membrane surface, the permeate quality TDS/conductivity deterioration was not observed [53,58]. These studies suggest the occurrence of only surface wetting with organic foulant. However, in two recent MD organic fouling studies, the reduction of membrane contact angle as well as permeate organic concentration increment was observed [59,60]. These results established that permeate quality deterioration does occur in MD organic fouling–wetting if measured in terms of organic concentration. Further, both these studies suggest that the type of foulant (not the deposit thickness/amount)

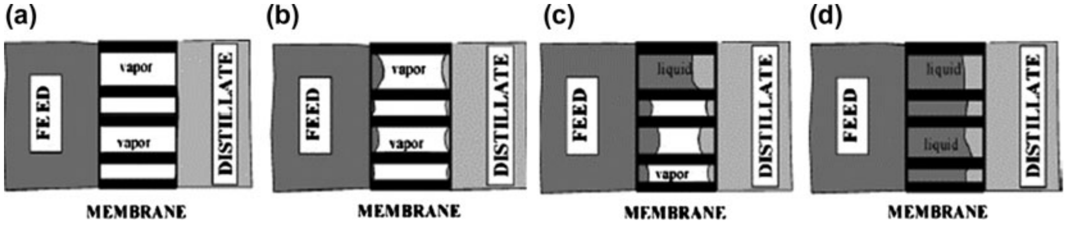


Fig. 1. Illustration of membrane wettability stages: (a) non-wetted, (b) surface wetted, (c) partial wetted, and (d) fully wetted [49].

dictates the rate of wetting. For instance, in comparing the performance of MD and MD-bioreactor, Goh et al. [59] reported on the higher wetting rate in MD due to the presence of retentate organic and high nutrient concentration of wastewater compared to the MD bioreactors which predominantly contained thick accumulated extra polymerase substances. The results highlighted that certain foulant (especially those with amphiphilic structures) accelerates wetting. Similarly, Naidu et al. [60] observed the increased permeate organic concentration with humic substances compared to protein although thicker formation of protein was deposited on the membrane surface. The effect of fouling based on various organic compounds would be discussed in detail in Section 4 of this study. In summary, MD fouling–wetting mechanism can be classified into pore plugging and adsorption onto the membrane surface based on the type of foulant compound as presented in Fig. 2.

Another factor that is worth highlighting is that the permeate flux decline may not be directly influenced by membrane wetting intensity as evidently shown in two recent studies [59,61]. Goh et al. [59] observed higher flux decline with MD-bioreactor compared to MD although the wetting intensity (permeate organic concentration) was higher with MD. The higher flux decline in the MD bioreactor was attributed to the higher mass- and heat-transfer resistance from thicker fouling layer. Guillen-Burrieza et al. [61] in a pilot-scale AGMD study with marine saltwater, showed evidence of membrane wetting based on the on-site permeate conductivity increment over time but did not observe any corresponding permeate flux declining pattern. The study suggested on the likelihood of membrane wetting contributing to permeate flux decline only if membrane structure damage/leakage occurred. The aspect of membrane hydrophobicity recovery is discussed in detail in Section 5 on membrane cleaning.

3. Fouling detection in MD

Generally, the typical mechanism models adopted to describe the fouling phenomena in membrane process are complete blocking, intermediate blocking, and cake filtration [62,63].

There are still limited studies representing fouling models in MD [53,58,64–67]. In most of these fouling models, the approach of transport resistance followed by polarization effect was adopted by fitting the experimental data with constant coefficients. Further, most of these theories are based on empirical fouling equations in linear form of exponential decay.

Srisurichan et al. [58] and Gryta [53] presented a fouling model mechanism for MD by combining the fouling and transport resistance. Model theories by Srisurichan et al. [58] did not take into consideration the real MD fouling scenarios that affect membrane pores resulting in wetting. A combination model of transport resistance as well as MD fouling–wetting phenomena would be a more representative fouling model for MD. Recently, more suitable fouling model theories are being presented based on wetting, depending on operating conditions, and type of solids and membrane characteristics [67,68]. It must be acknowledged that fouling modeling in MD is still at a preliminary stage. One of the factors that can further substantiate MD fouling model theories is the usage of real-time monitoring and detail membrane autopsy as discussed in the following section.

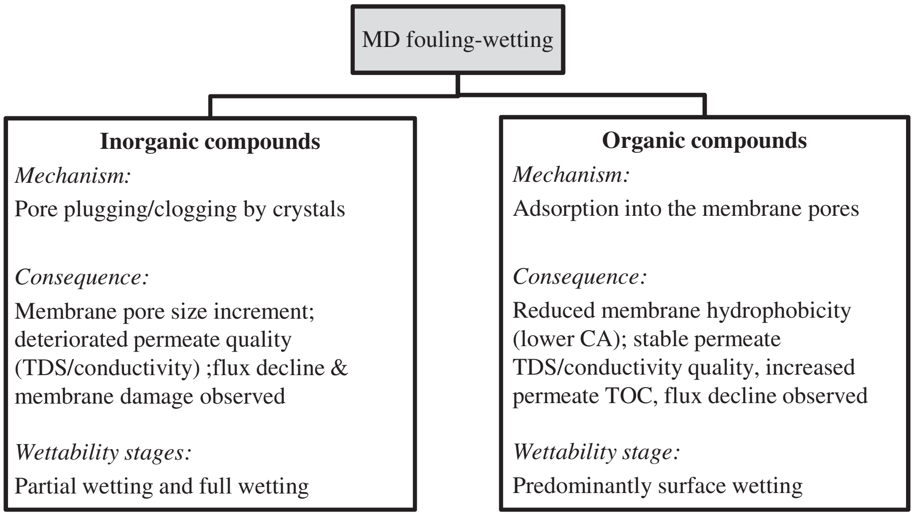


Fig. 2. MD fouling–wetting phenomenon classified by foulant type based on previous MD studies.

In this regard, real-time fouling detection by non-invasive, *in situ*, and rigorous quantification during the membrane operation is pertinent to substantiate current theories and models on fouling development [69–73]. Immediate fouling detection can ensure a more accurate prediction of the membrane fouling as well as the restoration of the membrane. The approach of non-invasive and visual online methods can detect early signs of fouling in real time. However, once fouling occurs on the membrane surface, *ex-situ* methods involving membrane autopsy would be necessary to incorporate future preventative measures. Hence, the application of fouling detection can be categorized by fouling potential tools, *in situ* monitoring, and *ex-situ* observation [74].

3.1. Real-time fouling detection

There are still limited studies that have analyzed scaling development in MD with detailed fouling detection tool. Most of the fouling detection tools used in MD are *ex-situ* tools. It must be acknowledged that these fouling detections are highly beneficial in identifying specific foulant behavior in MD operation. For emerging small- and large-scale MD operations, apart from *ex-situ* tools, membrane analyzes based on *in situ* techniques would be highly beneficial for foreseeing the fouling development.

In a recent DCMD study with salty lake water as feed solution, Hickenbottom and Cath [75] used real-time optimal microscopy to observe the fouling phenomena on the membrane. The real-time detection enabled to prove that salt precipitation on the membrane surface was the main contributor to flux decline. In comparing the DCMD performance with synthetic salt (NaCl) and salty lake water feed solution, the study observed a higher flux decline from point (b) onwards as shown in Fig. 3. The study associated the higher flux decline with the salty lake water to the divalent calcium ions in the presence of humic acid that forms complexes with the carboxyl functional groups, causing prevalent membrane scaling. This study highlighted the beneficial usage of real-time detection tool in preventing scale formation on membrane surfaces, sustaining high water flux and salt rejection as well as eliminating chemical consumption used for membrane cleaning.

3.2. Ex-situ fouling detection

3.2.1. Scaling

Generally in MD studies, the decline of permeate flux is used to represent the inorganic/scaling occurrence [49,54,76,77]. Since many factors can contribute to a flux decrease or product quality change, it is not possible to identify the specific contributing elements. Apart from permeate flux decline, a number of other fouling detection methods have been used to describe membrane scaling in MD namely scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray powder diffraction (XRD) and atomic force microscopy (AFM) as presented in Table 3.

SEM–EDS analysis: SEM imaging coupled with EDS analysis have been effective to characterize the major fouling compounds when MD operation was carried out with synthetic and natural feed solutions containing mixed compounds. For instance, in a study by Gryta [78], SEM–EDS analysis was useful in revealing that $CaCO_3$ was the major compound deposited on the membrane surface during the MD process with tap water (Fig. 4). Similarly, in a seawater study, the compounds contained in a new and used PTFE membrane after duration of one month was analyzed with SEM–EDS. The analysis enabled to reveal that the main seawater compounds that deposited on the MD membrane were sodium, magnesium, calcium, chloride and sulphur. At the same time, SEM–EDS analysis was useful to represent the intensity of the scale formation. For instance, Gryta [76] represented the intensity of scaling using cross section SEM–EDS line analysis as shown in Fig. 5. This approach was useful evidence in revealing that the deposit covered not only the membrane surface, but also penetrated into the pore interior. The similar SEM–EDS approach was used to reflect the influence of feed flow velocity on the intensity of calcium sulfate ($CaSO_4$) membrane scaling deposit [82]. Further, SEM–EDS enabled to establish the effectiveness of MD membrane cleaning as shown in a study that reflected the removal of major compounds after seawater MD operation [26].

Contact angle: Contact angle (goniometer) measurements have been adopted in a number of MD studies to reflect the reduction of membrane hydrophobicity as well as its hydrophobic restoration capacity with membrane cleaning. This is discussed in detail in Section 5 of this paper on membrane cleaning [49,51,52,79].

AFM analysis: A number of MD studies have employed AFM to provide detail morphology of MD membrane [83–86]. In terms of MD fouling analysis studies, AFM measurement has not been adopted widely. In a recent seawater DCMD study with polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) membranes, AFM measurements were carried out to quantify surface roughness and foulant adhesion force [80]. The AFM measurement results were highly useful to evidently display the lower adhesion between the calcium carbonate probe

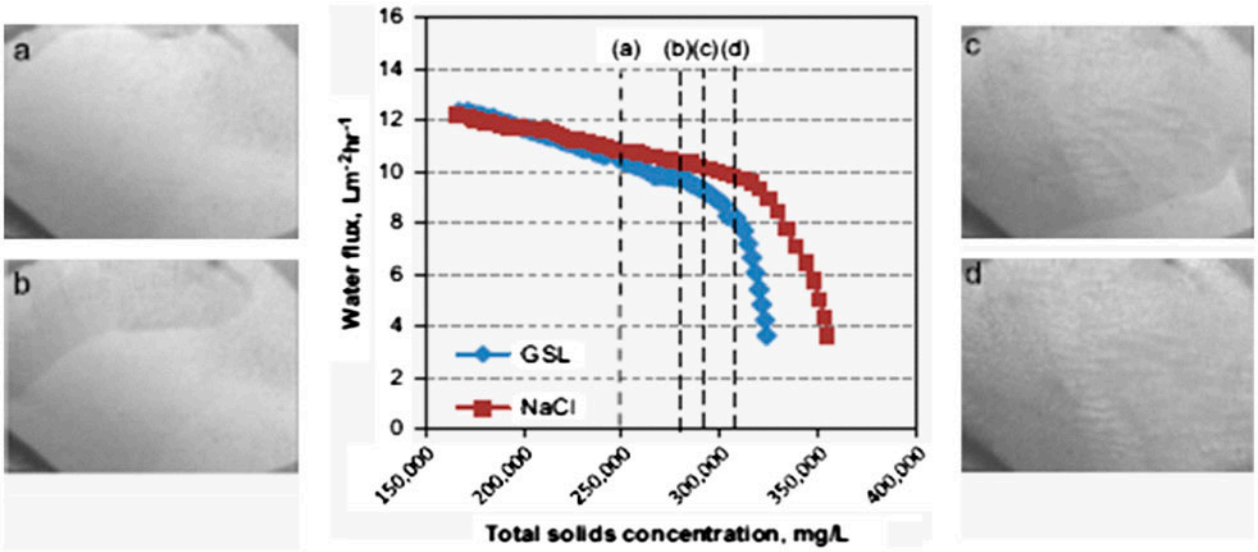


Fig. 3. Real-time stereo microscope images of the feed side of the membrane during the experiment (dashed lines) and the corresponding water flux and total solid concentration using great salt lake (GSL) and NaCl feed solutions on DCMD system [75].

Table 3
Scaling detection methods adopted by MD studies

Detection method	Description	Reference
SEM-EDS	(1) This approach was useful evidence in revealing scalant deposit covered not only the membrane surface, but also penetrated into the pore interior during the MD process with tap water;(2) Useful for reflecting the effectiveness of MD membrane cleaning	[33,53,78
Contact angle	Contact angle analysis was used to reveal the loss of membrane hydrophobicity and subsequent wetting in many MD studies	[49,51,76,79]
AFM	This analysis enabled to explain the lower scaling adhesion observed with the rougher PTFE membrane compared to the smoother PVDF membrane after seawater DCMD operation	[80]
XRD	This analysis was useful to reveal the formation of calcite crystal compounds on a polypropylene membrane without the use of antiscalant, and the effectiveness of using antsicalant to remove calcite peak	[81]

and the membrane surface due to higher membrane surface roughness. This enabled to explain the lower scaling adhesion observed with the rougher PTFE membrane compared to the smoother PVDF membrane.

3.2.2. *Organic fouling*

Similar as scaling analysis, majority of MD studies on organic fouling was based on permeate flux decline pattern [53,87,88]. Apart from permeate flux, membrane autopsy and other fouling detection methods such as Fourier transform infrared (FTIR) have also been adopted. That apart, recently liquid-chromatogram organic carbon detection (LC-OCD) analysis approach was adopted for detailed organic characterization of seawater and synthetic organic solutions. The LC-OCD method displays organic characteristics by size exclusion chromatography of the hydrophilic organic fraction [89]. The summary of the organic fouling detection method adopted by various MD studies is presented in Table 4.

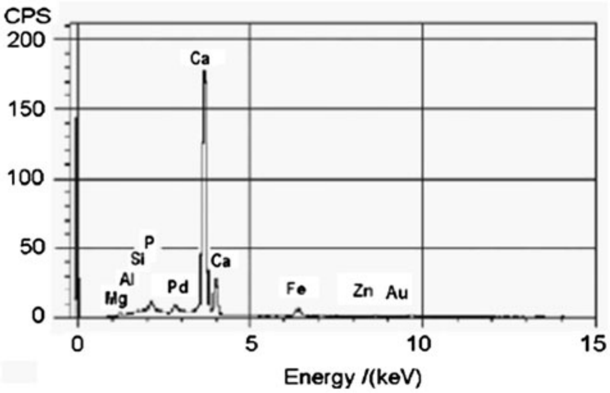


Fig. 4. SEM–EDS analysis displaying the elements deposited on the membrane surface during the MD process with tap water [78].

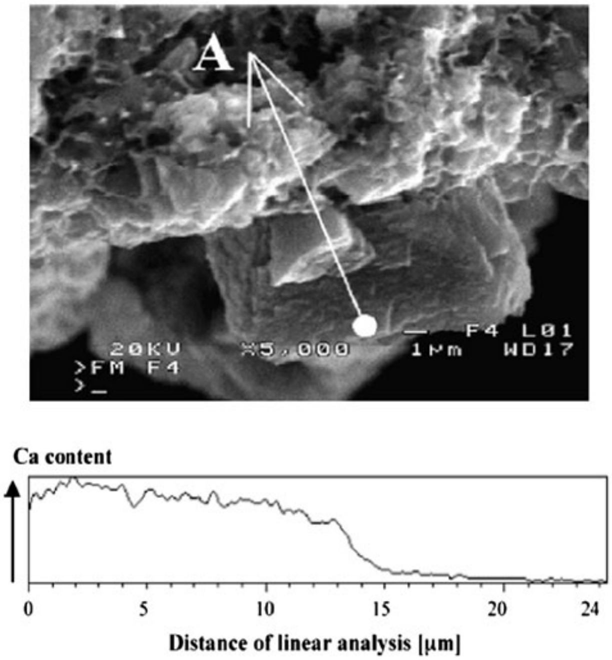


Fig. 5. SEM–EDS cross section line analysis showing $CaCO_3$ penetrated through the membrane pores [76].

SEM–EDS analysis: In a recent DCMD study, Naidu et al. [60] established the usefulness of SEM–EDS to compare the organic fouling intensity between the three main organic foulant of alginate, protein, and humic substances. In this study, the carbon (C) and oxygen (O) element peak were used to represent the organic fouling deposit. The SEM–EDS analysis showed the clear pore penetration of humic substances to protein as BSA and alginic acid (AA) as shown in Fig. 6.

FTIR technique: Gryta et al. [54] used FTIR analysis to establish the presence of protein on the fouled membrane for wastewater MD treatment (Fig. 7). In another long-term DCMD study by Gryta et al. [90], FTIR method was used to evaluate changes in the membrane's structure caused by NaCl solution. The FTIR analysis was useful in revealing the presence of hydroxyl and carbonyl groups on the surface of degraded polymer which reacted with concentrated NaCl solution and formed sodium carboxylate. As a result of the chemical reactions, the membranes soaked in NaCl solutions were wetted faster than those soaked in distilled water.

LC-OCD measurement: In MD studies, the usage of LC-OCD have not been adopted widely. Two recent studies used LC-OCD to characterize the organic compound behavior in MD operation [60,91]. The LC-OCD analysis was insightful in understanding the behavior of humic substances disaggregation to low-molecular weight (LMW)-humic substances under MD thermal operation. The LC-OCD analysis was able to provide a detail characteristic of the organics on the membrane foulant as well as the feed solution as shown in Fig. 8.

In MD, membrane fouling has been shown to compromise membrane hydrophobicity and accelerate wetting as discussed in detail in Section 2.2. The MD fouling–wetting phenomena review in Section 2.2 also clearly showed that the specific concentration and composition of foulants in the feed solution as well as operating conditions may result in different foulant adsorption and wetting rates. Hence, it is important to analyze the factors that influence membrane fouling in MD system. This may assist in delaying membrane wetting which would subsequently reduce the frequency of membrane cleaning and drying. In light of this, in the next section, a detailed review is carried out on the factors that influences scaling and organic fouling in MD.

4. Factors influencing organic fouling and scaling in MD

Studies on fouling caused by other membrane processes such as RO, UF, and NF have well established the key factors that influence scaling and organic fouling development, namely operating conditions, physico-chemical properties of the feed solution, as well as membrane and module configuration [38,92]. Although there are a few available reviews related to MD fouling, the key factors influencing fouling and scaling development have not been examined explicitly [7,21,64].

Table 4
Organic fouling detection methods adopted by MD studies

Detection method	Description	Reference
SEM–EDS	(a) SEM–EDS analysis of the membrane cross section was useful to compare and determine the most intense DCMD organic foulant between polysaccharide, protein and humic substances.	[60]
	(b) SEM–EDS analysis revealed major components deposited on the membrane surface during the MD process with tap water.	[53]
FTIR	(a) The presence of protein on the fouled membrane for wastewater MD treatment was established with the FTIR analysis	[54]
	(b) FTIR investigations revealed that the hydroxyl and carbonyl groups present on the surface of degraded membrane polymer, reacted with concentrated NaCl feed solutions, and consequently sodium carboxylate was formed	[90]
LC-OCD	(a) LC-OCD was useful to obtain detail organic characterization analyses which revealed the intensity of humic substance, polysaccharide and protein.	[60]
	(b) The LC-OCD analyses revealed the intensity of humic substance in seawater DCMD operation	[91]

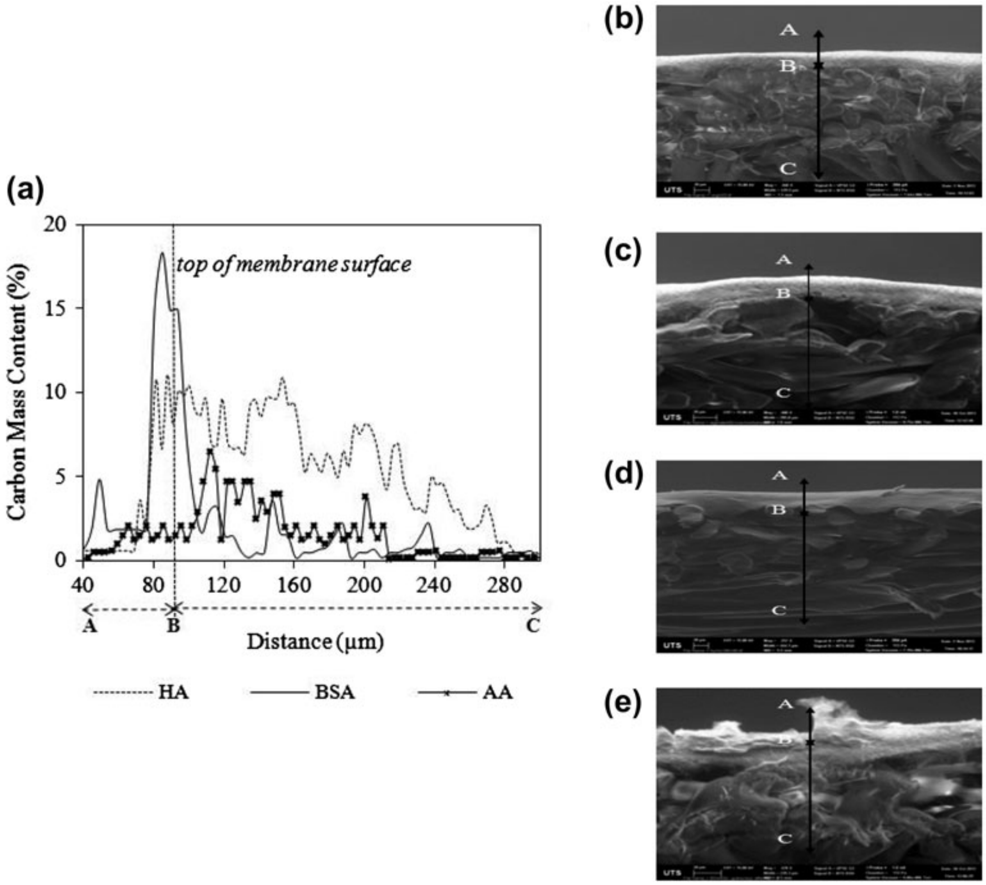


Fig. 6. SEM-EDS membrane cross section line analysis: (a) carbon element mass as a function of membrane depth on humic acid (HA), bovine serum albumin (BSA), and alginic acid (AA) fouled membrane and SEM images of (b) virgin membrane, (c) AA, (d) HA, and (e) BSA [60].

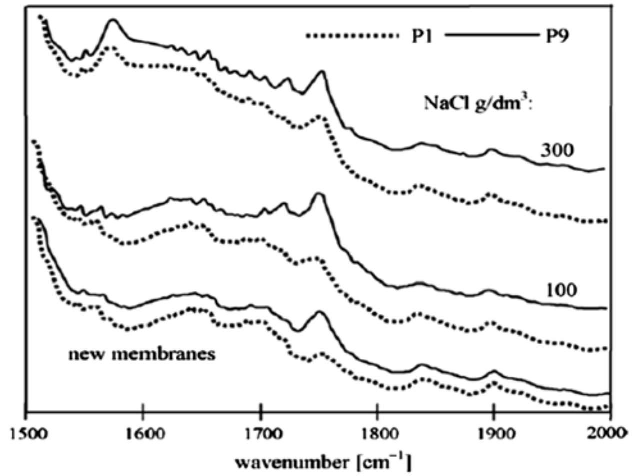


Fig. 7. FTIR spectra of Accurel PP S6/2 membranes stored over a period of 1 year (P1), and 9 years (P9) and these membranes soaked in NaCl solutions for 60 d [90].

To improve the understanding of MD fouling with regards to drinking water production, this review analyzed the factors influencing organic fouling and scaling in MD based on feed physico-chemical condition and operating conditions.

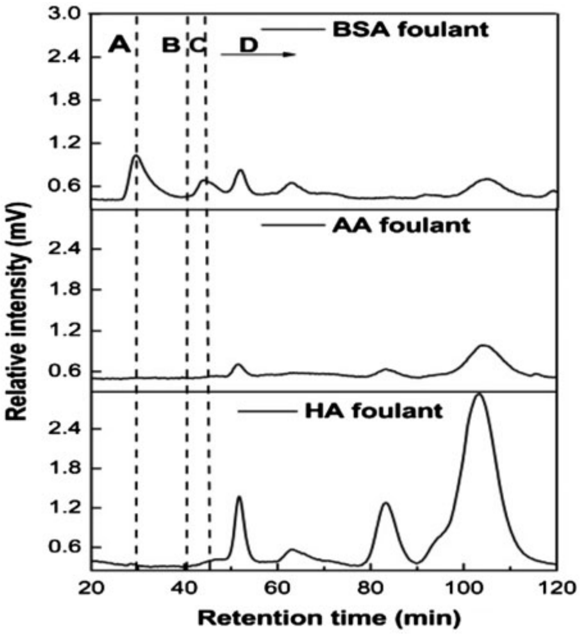


Fig. 8. Comparison of membrane fouling pattern of the three individual organic compound feed solutions using LC-OCD chromatogram (A: biopolymers; B: humics; C: building blocks; D: LMW acids and neutrals) [60].

4.1. Physico-chemical condition of the feed solution

The physico-chemical condition of the feed solution is an important aspect that influences fouling intensity in a membrane separation process [41]. In an MD operation, the consequence of a unique operation combination, namely the presence of a heating condition but the lack of hydraulic pressure compression, will result in selective foulant types exhibiting more pronounced fouling and scaling tendencies. The following sections focus on the influence of the main foulant types in feed solution with reference to drinking water production.

4.1.1. Foulant type

4.1.1.1. Scaling. Studies in MD related to drinking water production have predominantly focused on $CaSO_4$ and $CaCO_3$ scaling, while a few studies examined silica deposition [32,67,77,93–96]. This is because $CaSO_4$ and $CaCO_3$ are the main mineral salts in natural water sources. Furthermore, these salts are also inversely soluble at increased temperatures, thus enhancing the rate of precipitation [77].

Comparatively, a number of studies have established $CaSO_4$ as the more dominant scalant in MD to $CaCO_3$ [93,97]. For instance, Gryta [94] conducted a systematic study of the behavior of $CaSO_4$ and $CaCO_3$ scaling in MD. The study reported a severe case of pore flooding and deterioration of the permeate quality due to membrane scaling when saline wastewater containing $CaSO_4$ was used as the feed solution compared to $CaCO_3$. Similarly, in another study, the SEM analysis of a DCMD fouled membrane using tap water showed predominant $CaCO_3$ deposition occurred only on the membrane surface. Meanwhile, compounds of $CaSO_{4,}$ had penetrated into the membrane wall, indicating more severe scaling contribution [78]. A recent study compared the scaling performance with different mineral salts and highlighted that scaling caused by $CaSO_4$ on MD membrane was much more severe than scaling caused by $CaCO_3$ or silica [97].

4.1.1.2. Organics. Organic fouling is largely attributed to natural organic matter (NOM) in the feed solution as shown in Table 1. NOM is ubiquitous in natural waters, classified by a group of low to high-molecular weight organic compounds, and quantified as dissolved organic carbon. In surface water, ground water, and seawater, humic substances are the major constituents of NOM, followed by carbohydrates (including polysaccharides), protein, and a variety of acidic and LMW species [89,98,99].

The correlation of membrane fouling intensity based on the composition of NOM in a feed solution has been studied widely in pressure driven membrane processes. In these studies, polysaccharides are generally represented by AA compound, humic substances are represented by HA compound, and protein substances are represented by BSA compound [100]. It is important to highlight that in these studies, more detailed methods have been employed to represent organic foulants characteristics such as LC-OCD [89,100].

In MD studies, organic fouling analysis is still limited and primarily based on permeate flux decline trend [53,54,58,87,88]. It is especially essential to understand the detailed characteristics and role of organics in membrane fouling under MD operating conditions. This is because organic foulants, which are generally small in size, are anticipated to cause more significant membrane wetting problems in micro-sized hydrophobic MD pores [48]. In terms of size, biopolymers compounds generally range from 10 to 50 kDa; humic substances are generally in the 0.8 to 1.5 kDa range, while building blocks (BB) are in the 0.5 to 0.8 kDa range, and LMW organics are less than 0.3 kDa [89,100]. Based on the available MD studies that have investigated organic fouling, the implications of the different organic compounds in MD membrane fouling are discussed below.

Polysaccharide: In MD studies, thus far, no clear trend has been drawn concerning the intensity of polysaccharide compound on MD organic fouling. In a MD bioreactor study by Phattaranawik et al. [101], the polysaccharide in the submerged MD bioreactor was observed to result in cake/fouling attachment on the membrane surfaces. Nevertheless, due consideration must be given to the repulsion between the hydrophilic nature of the AA compound and the negatively charged hydrophobic membrane which would result in less adhesion on the membrane surface as mentioned by a UF study [99]. Based on this factor, a recent DCMD study by Naidu et al. [60] established the low-fouling intensity contributed by AA compound compared to protein and humic substances.

Humic substance: The contribution of humic substance onto organic fouling intensity in MD has been investigated by a few studies [58,87,88,96]. Previous membrane studies such as UF membrane have highlighted that humic substance absorbs more favorably onto hydrophobic membrane [102]. In fact, a DCMD study using synthetic HA feed solution with two commercial MD membranes observed higher fouling effect on the more hydrophobic membrane [87]. Further, this study demonstrated that water flushing to clean the HA-fouled membrane was not sufficient to recover the initial permeate flux, suggesting the irreversibility of humic substance fouling in MD. In this regard, a DCMD fouling study with synthetic HA feed solution reported on the organic concentration increment of the permeate solution over time. Using LC-OCD analysis, this study observed the presence of LMW humic substances leading to the occurrence of membrane pore penetration, resulting in permeate organic concentration increment [60]. Meng et al. [103] explained this phenomenon in terms of humic adsorption–desorption mechanism, whereby the humic substances absorbs onto the MD membrane surface via bonding through the phenolic and carboxylic functional groups. The humic substances that adsorbed at the edge of the pores, migrates due to hydrogen bonding between unattached carboxylic or phenolic groups on the molecule and water vapor, which consequently desorbed to the permeate side. These recent MD studies clearly establish the role of humic substances as a prevalent organic foulant in MD operation. Further, humic substances was highlighted to be the major organic foulant in a DCMD study with seawater [91].

Protein: The relationship between BSA foulant and MD membrane fouling intensity was examined by a number of researchers. MD studies acknowledged that feedwater containing NOM compounds of proteins showed a strong tendency to deposit on the hydrophobic membrane [53,54]. These studies indicated that BSA/ protein fouling caused almost 60–70% permeate flux decline in MD. The application of high feed temperature (60˚C and above) in MD operation was related to the intensive protein-based NOM fouling [44,54]. Likewise, in a DCMD study, the highest organic mass deposition on the membrane was observed with BSA compound (0.081 mg/cm^2) compared to HA compound (0.049 mg/cm^2), resulting in higher permeate flux decline with BSA compound [60]. Further, the membrane SEM–EDS analysis detected the thickest carbon contents on the BSA membrane (35.2% higher carbon mass compared to HA foulant) but no pore penetration was observed, while the HA compound as discussed earlier, showed significant membrane pore penetration. At the same time, based on the membrane hydrophobicity measurement, the BSA compound showed easier fouling reversibility with DI water flushing compared to the HA compound.

Most past MD studies have represented fouling intensity in terms of the permeate flux declining pattern. This does not necessarily project the fouling intensity of the organic compounds as clearly highlighted in this review of this study. In recent studies, more detail representation of organic fouling such as organic characteristics changes with LC-OCD, membrane autopsy and hydrophobicity, as well as fouling reversibility were useful approaches in understanding the behavior of specific organic compound under MD operation.

4.1.2. pH and ionic strength

The influence of feed solution pH on fouling development in MD has been investigated by only a few studies. In one study, Karakulski and Gryta [32] highlighted that $CaCO_3$ precipitation on the membrane surface was significantly limited by the acidification of the feedwater to pH 4. In another study, Srisurichan et al. [88] investigated HA fouling pattern at pH solutions of 3 and 7 in a DCMD unit. Their study reported no significant difference in permeate flux. The study, however, mentioned that the complexion of HA with Ca^{2+} was affected by solution pH, whereby at pH of 7, a 68.3% precipitation was reduced to 30.1% at pH of 3. Other membrane studies such as RO and UF have indicated the importance of feed solution pH in changing the structure/ and shape of foulant compounds [102,104,105]. To establish the influence of feed solution pH on fouling development under hydrophobic MD operating conditions, more detailed studies must be carried out.

In terms of ionic strength, a few studies observed a slightly higher permeate flux reduction as well as more intense foulant adhesion on the hydrophobic MD membrane in the presence of salt [54,106]. For instance, Khayet and Mengual [106], observed 4.2% higher permeate flux decline when 0.1 M NaCl was added to the HA compound. Using LC-OCD analysis, Naidu et al. [91] observed the presence of significant amount of LMW humic organics with the addition of 1.0 M of NaCl to synthetic HA feed solution. As a result, more prevalent organic pore penetration was observed with saline HA feed solution. The formation of humic substances has been analyzed in past studies using nuclear magnetic resonance spectroscopy and size exclusion chromatography [107]. These studies reported on the disruption of the weak hydrogen and hydrophobic bonding (Van der Walls) of humic substance in the presence of salts, resulting in LMW humic organics. These findings establish the more prevalent behavior of humic substances with increased salinity. This is similarly reflected in saline nature water sources, where the prevalent role of humic substance as an organic foulant in seawater was highlighted in a recent study [91].

4.2. Operating parameters

The performance efficiency of MD attributed to different operation parameters has been widely investigated experimentally and through modeling approaches [26]. Previous studies have established that the key operating parameters in MD are feed temperature, feed flow rate, and permeate side condition such as the presence of vacuum [64,108]. The effect of MD fouling development due to the main operating parameters of feed temperature and feed flow rate is discussed in this section.

4.2.1. Feed temperature

4.2.1.1. Scaling. A number of MD fouling studies have acknowledged the increase of scaling intensity due to thermal heating [53,64,94,97].

Specifically, based on classical nucleation phenomena, the inversely soluble behaviors of $CaSO_4$ and $CaCO_3$ at increased temperature has been investigated in MD. The saturation index reduction of $CaSO_4$ as gypsum and $CaCO_3$ as calcite with increased thermal heating is presented in Fig. 9 [93].

$CaCO_3$ can exist in three different polymorphs forms—calcite, aragonite, and vaterite. Calcite is thermodynamically the most stable form and regular observed on membrane deposition. Nevertheless, there are also reports of systems where the $CaCO_3$ is deposited on membranes as aragonite [109–112]. For instance in a MD study with tap water by Gryta [113], it was reported that besides calcite, the presence of aragonite was detected on the membrane SEM analysis. At increased water temperature, the bicarbonate ions (HCO_3^-) present in the feedwater decompose, resulting in $CaCO_3$ precipitation on the membrane surface, forming more $CaCO_3$ deposits on the membrane surface as shown in Eq. (1) [114].

$$2HCO_3^- + Ca^{2+} \overset{\text{heat}}{\rightarrow} H_2O + CO_2 \uparrow + CaCO_3 \downarrow \qquad (1)$$

Meanwhile, He et al. [93] established the dominant presence of $CaSO_4$ in the form of gypsum in MD precipitation using an XRD analysis. In terms of the three different $CaSO_4$ forms (gypsum; anhydrite, and hemihydrate), gypsum shows the lowest solubility below 40˚C and is therefore the most thermodynamically stable phase. The transition point of gypsum to anhydrite is located at about 40˚C, and that of gypsum to hemihydrate lies at 80˚C [113]. The dominant occurrence of gypsum prescription in MD was associated to the significantly slower nucleation of anhydrite in comparison to gypsum; and the lower interfacial tension between gypsum and solution (higher solubility of gypsum) than that between anhydrite and solutions. In scaling studies, the induction time is defined as the time taken to form detectable crystals (between the creation of supersaturation and the appearance of a new solid phase) [63,93]. He et al. [93] used thermodynamic model and experimental results to establish the shorter induction period (217–0 min) for $CaSO_4$ (gypsum) at saturation index of 1.35 when the temperature was increased from 60 to 90˚C as shown in Fig. 10.

MD scaling studies have observed the significant changes in crystal structure and scaling deposition intensity at different feed temperature ranges. Table 5 summarizes the influence of feed temperature as reported by MD scaling studies.

4.2.1.2. Organic fouling. In terms of organic fouling, the influence of feed temperature has been generally linked to BSA compound [55, 56]. For instance, wastewater albumin protein as feed solution operated with DCMD at a high feed temperature of 85˚C indicated a significant gel-like formation on the membrane surface and significant flux decline (from 558 to 156 $dm^3/m^2/d$).

Humic substance is one of the major organic compounds in natural water sources used for drinking water production [99]. Studies on humic substance characteristics (using HA compound), have highlighted its tendencies to disaggregate at high temperature [115,116]. These studies used methods such as dynamic light scattering and ultrasonic velocimetry and observed the decrease of humic substance molecular size due to the disaggregation by thermal agitation. It is important to highlight that at these temperature ranges, the structure characteristics of humic substances was not altered. This is because HA compound retained most of its original structure up to high temperatures of 200–400˚C, as detected by FTIR. In this regard, one MF fouling study indicated that the rate of humic aggregation increased with temperature, resulting in increased fouling development, as observed on the fouled SEM image [98]. An initial MD study on humic fouling indicated that the feed temperature affected the permeate flux decline [58]. This particular study investigated the fouling phenomenon in MD using HA solution (100 mg/L) containing 3.775 mM $CaCl_2$. The permeation flux was much higher at 70˚C than that of 50˚C. As a consequence, at 70˚C, more amount of HA coagulates were retained at the membrane surface, significantly reducing the induction time. Recently, Naidu et al. [60] used LC-OCD organic analysis to show the detailed characteristic of humic substances in MD. In this study, the thermal disaggregation of HA to LMW HA organics was exhibited. These LMW HA organics showed tendencies to penetrate into the pores of the membrane, increasing permeate organic contents over time.

4.2.2. Feed flow rate

4.2.2.1. Scaling. Previous MD studies have indicated the correlation between scaling development and feed flow rate. Gryta [53] highlighted the fact that hydrodynamic conditions significantly influenced the size, structure, and morphology of scale formation. The study indicated that a porous thin deposit was formed at high feed flow velocity (e.g. 1.2 m/s), reduced heat-transfer resistance on the membrane, while a non-porous and thick deposit was formed at low feed flow velocity (e.g. 0.35 m/s). Similarly, He et al. [93] recommended a high flow velocity for reducing the flux decline in the presence of a significant amount of precipitate in their MD study using hollow fiber membrane. Nghiem and Cath [97] used high feed flow velocity as a mitigation strategy of membrane surface crystallization of $CaSO_4$.

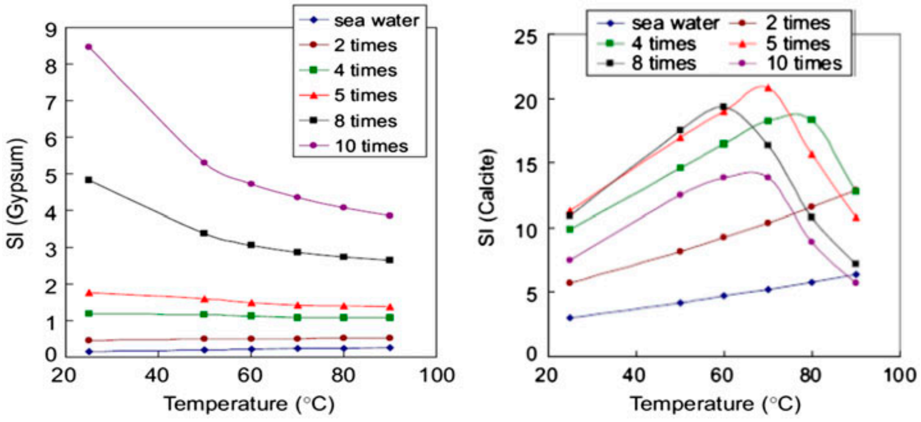


Fig. 9. SI values of gypsum and calcite for seawater concentrated 1–10 times at different temperatures [93].

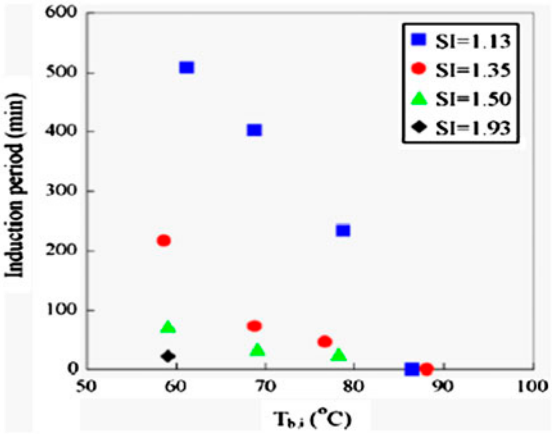


Fig. 10. Effects of brine inlet temperatures and SIs of gypsum on the induction periods during DCMD. Membrane module #25 was used in the experiments with $T_{b,i}$ = 60 or 70˚C; and membrane module #23 were used in those with $T_{b,i}$ = 80 or 90˚C [93].

In pressure-driven membrane separation processes, optimizing hydrodynamic conditions is a general approach to control fouling [41]. Similarly, in MD studies, high flow velocity will reduce the loose crystal deposit that has accumulated on the membrane surface. However, it is important to point out that in MD, the pressure of high flow velocity will increase the risk to membrane wetting as shown by other studies [117].

Hence, more detailed investigations must be carried out on a suitable operating feed flow velocity combination that will achieve sustainable performance while reducing membrane surface deposits and membrane wetting.

4.2.2.2. Organic fouling. The influence of hydrodynamic effect on organic fouling reduction in MD system has not been explored in detail. A DCMD study carried out with HA solution combined with calcium and salt as feed solution acknowledged the advantage of using high cross-flow velocity to reduce polarization in MD system [88]. However, the study also noted the risk of membrane wetting at high cross-flow velocity. This could be explained in terms of adsorption tendency of organic foulant that can substantially reduce the liquid surface tension, causing membrane wetting especially at high cross-flow velocity.

5. Approaches to reduce fouling in MD

5.1. Membrane cleaning

In terms of the severity of the scaling and organic fouling in MD, some studies have reported only loose

Table 5
Influence of feed temperature on scaling development in MD

Ref.	Configuration	Scalant type	Feed temperature, T_f (˚C)	Fouling impact
Nghiem and Cath [97]	DCMD	$CaSO_4$	T_f = 40; 50; 60	SEM crystal formation/induction time 40˚C—thin needles/long induction time 50˚C—large needles 60˚C—very large needles/short induction time
He et al. [93]	DCMD	$CaSO_4$	T_f = 60; 90	As F_t increases from 60 to 90˚C, induction period declines from 217 to 0 min.
Gryta [53]	DCMD	$CaCO_3$ from tap water	T_f = 80; 90	80˚C Induction time = 100 h 90˚C Induction time = 80 h
Gryta [113]	DCMD	Tap water (alkalinity 2.1 mmol HCO_3/dm^3	T_f = 80	SEM image of $CaCO_3$ revealed the: (1) formation of both aragonite and calcite was observed when membrane surface T_f = bulk T_f; (2) formation of only calcite was observed when membrane surface T_f < bulk T_f; (3) membrane surface temperature similar to bulk F_t,: the formation of both aragonite and calcite is observed; (4) membrane surface temperature less than the bulk F_t : formation of only crystallization of calcite is observed.

deposits on the membrane surface which was reversible through simple flushing [53,58,93]. The different membrane cleaning approaches used in MD studies and the description of its effectiveness is summarized in Table 6.

Mainly, these MD studies showed that a combination of acid and alkaline cleaning was effective for cleaning specific types of foulant deposited on the membrane surface. For instance, Srisurichan et al. [88] reported that only a 87% flux recovery was obtained with deionized water (DI) water cleaning of membrane with a thick fouling deposit formation due to a feed solution containing a combination of organic (HA) and inorganic calcium ion. The fouling layer on the membrane surface was able to be completely removed with sodium hydroxide (NaOH) cleaning. Although a thick layer of deposit was formed on the membrane surface, the gel-like coagulated foulant from humic and calcium combination did not cause a membrane pore penetration. This could be associated with the full recovery of the flux with chemical cleaning. Comparatively, upon pore penetration, flux recovery with membrane cleaning was a challenge. For instance, Gryta [78] reported that hydrochloride acid (HCL) cleaning enabled to achieve complete removal of $CaCO_3$ deposits on the membrane, while only partial removal of $CaSO_4$ was achieved. This was attributed to the pore penetration tendency of $CaSO_4$ compared to the membrane surface deposition of $CaCO_3$.

5.1.1. Limitation of membrane cleaning

It must be acknowledged that although membrane cleaning in MD is a straight forward and effective approach to restore the hydrophobicity and performance of the membrane, this approach does have its limitations. For instance, Martinetti et al. [5] suggested that although majority of scales from RO concentrate feed solution was removed by membrane cleaning and permeate flux was restored to its initial level, the residual scales that remained on the membrane provided sites for crystallization, leading to more rapid scale formation and earlier onset of flux decline after cleaning. Similarly, Gryta and Barancewicz [49] reported rinsing PVDF membranes several times with distilled water and drying to remove salt from the pores was effective to reduce the degree of membrane wetting and the leakage of feed to distillate. As a consequence, the electrical conductivity of the obtained distillate was almost at a constant level. However, a progressive decrease in the permeate flux was observed indicating that the wettability of the surface pores still occurred after 200 h as shown in Fig. 11. Similarly, Gryta [78] reported that the repetitions of module cleaning were indicated to cause a gradual flux decline, which was also observed during periodic investigation.

In another study, Gryta [76] reported that rinsing the module with a concentrated HCl solution was effective in dissolving the deposits of iron oxides. On the other hand, the pattern of HCl solution penetration into the pores occupied by the deposit, followed by membrane wetting was observed. As a consequence, the permeate flux decreased from 800 to 650 $dm^3/m^2/d$ during the 100 h of MD. Moreover, the electrical conductivity of the obtained distillate was increased from 3 to 20 μS/cm.

It can be highlighted that for MD operation, loosely deposited crystals on the membrane makes membrane cleaning a suitable mitigation approach. However, these results systematically reflect the shortcoming of membrane cleaning approach, as the procedure of rinsing and drying of the wetted membranes does not guarantee the recovery of membrane hydrophobicity. Further, more long-term MD membrane cleaning studies must be carried out to analyze the wetting phenomena especially when chemical cleaning is utilized.

5.2. Pretreatment

Generally, in pressure-driven membrane processes, a pretreatment of raw feedwater is adopted as a fouling reduction strategy [118]. Pretreatment enables to remove undesirable compounds from the raw feed solution, which otherwise could adversely affect the membrane operation and lead to membrane fouling.

Pretreatment is broadly categorized into two types —conventional pretreatment and membrane-based pretreatment [119]. Conventional pretreatment technologies includes coagulation, multimedia filtration, deep-bed filtration, and dissolved air flotation while membrane-based pretreatment methods include nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF). The appropriate pretreatments are selected based on the raw feedwater characteristics (suspended solids, turbidity, organic matters, etc.) and the cost incurred [120].

The main advantage of conventional pretreatment such as deep-bed filtration is the strategic ability to control organic fouling and biofouling [121]. Physicochemical adsorption by the media in the filters coupled with the presence of biological activity can remove dissolved organic matter, thereby reducing membrane fouling. These pretreatments are especially

Table 6
Summary of different membrane cleaning approaches in MD studies

Membrane cleaning approach	Description	Reference
DCMD scaling mitigation by regular DI water membrane flushing	Reset the induction period of $CaSO_4$ feed solution by regular flushing of DI water. Constant removal of the nucleation sites at the membrane surface before rapid crystallization was effective in controlling membrane scaling.	Nghiem and Cath [97]
Ultrasonic irradiation technique	Fouled membrane with seawater cleaned with ultrasonic effectively resorted the initial flux rate. PTFE membrane was indicated to be strong enough to sustain the impaction of irradiation power.	Hsu et al. [27]
Chemical cleaning of membrane (2 h water, with 0.1 M NaOH)	Fouled membrane with HA mixed with calcium was chemically cleaned. The permeate flux was recovered to 87% of initial flux with DI water cleaning and 100% with NaOH.	Srisurichan et al. [88]
Chemical cleaning of membrane (2–5 wt.% HCl solutions)	Fouled MD membrane with tap water was rinsed with HCl solution enabled the removal of $CaCO_3$ deposit while a complete removal of $CaSO_4$ was not possible.	Gryta [78]
Chemical cleaning of membrane (0.029 M Na_2EDTA and 0.058 M NaOH)	Fouled PTFE MD membrane with RO concentrate was chemically cleaned enabling to restore the initial flux.	Martinetti et al. [5]
Chemical cleaning of membrane (citric acid followed by NaOH)	MD membrane fouled with synthetic seawater showed complete recovery of both flux and hydrophobicity upon chemical cleaning	Curcio et al. [96]
Chemical cleaning of membrane (HCl)	Rinsing the module with a concentrated HCl solution dissolved deposit of iron oxides.	Gryta [76]

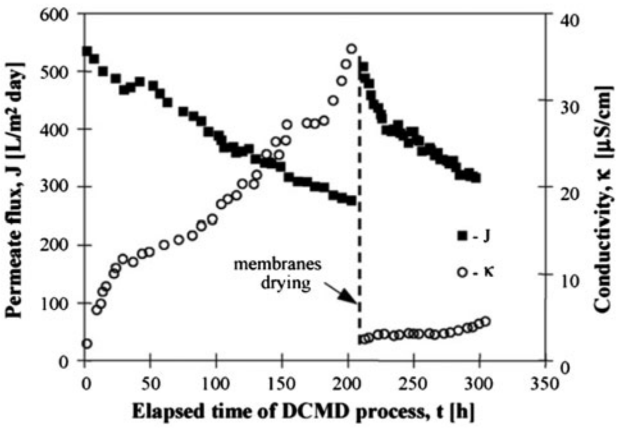


Fig. 11. Changes on permeate flux and the distillate electrical conductivity during cyclic DCMD process with PVDF membranes [49].

sustainable and cost effective enough to support the production of drinking water in small communities. The main disadvantages of the conventional pretreatment, for instance flocculation are the intensive consumption of chemicals and inconsistency in operation [122]. At the same time, the requirement of regular backwashing and inconsistent water quality are associated with media filtration systems [123].

Meanwhile, the main advantages of membrane-based pretreatments such as MF and UF are the capacity to maintain a consistent and stable performance compared to conventional pretreatments [119]. However, the performances of membrane-based pretreatments are compromised when treating feed solution with highly concentrated organic and inorganic compounds. It results in severe membrane fouling and plugging of fibers as observed in a number of studies [124,125].

5.2.1. Pretreatment in MD

Studies have evaluated the performance of MD with pretreatment in the fruit juice processing industry and wastewater [126,127]. Nevertheless, the use of pretreatment in the MD system for the production of drinking water has not been explored in great detail.

A few studies have indicated improved MD permeate fluxes with the incorporation of NF, UF, and MF membrane pretreatment for producing drinking water [27,31,32]. These studies highlighted that membrane pretreatment ensured the production of continuously good permeate water quality. For instance, Karakulski et al. [31] observed significant deposition of $CaCO_3$, on the MD membrane surface with tap water. The scaling deposition was effectively reduced with preliminary softening of the tap water in NF process. Similarly, Hsu et al. [27] reported improved permeate flux by about 25% with seawater pretreated with MF. Nevertheless, this study highlighted that MF as a membrane pretreatment, did not address the issue of organic removal in the seawater, which resulted in long-term permeate flux reduction. Hence, due consideration must be given to the specific purpose of the pretreatment as well as the additional costs incurred.

In another study, Kesieme et al. [128] reported on the effectiveness of cartridge filter to capture calcium scales, reducing scaling deposition on membrane surface and thus allowing high recovery of groundwater RO concentrate with MD. Contrarily, in a MD pilot-scale system, cartridge filter was deemed to be insufficient for the desalination of concentrated brines from thermal plants [129]. The study observed the occurrence of membrane wetting (increased permeate conductivity with decreased permeate flux) caused by residual chemicals from antiscalant/antifoam agents present in the brine, that were not able to be removed by the cartridge filters. In this study, the usage of granular-activated carbon filter was deemed to be effective for this purpose. These results highlight the necessity to select the appropriate MD pretreatment based on the feedwater characteristics. Further, long-term operations would be necessary to establish the effectiveness of specific pretreatment processes for MD application.

Similarly, a wastewater MD treatment study reported on the effectiveness of MF in reducing suspended solids, compared to the relatively mild to weak improvement from ferric chloride coagulation/flocculation [126]. On the other hand, a few MD studies related to drinking water production reported on the effectiveness of coagulation as a pretreatment approach [130,134]. Gryta [130] showed the improved permeate flux pattern of MD system using groundwater feed solution with the addition of contact clarifier pretreatment. In this study, the groundwater was chemically pretreated in a clarifier, involving coagulation with ferrous sulphate heptahydrate and softening with calcium hydroxide followed by sand filtration. In another study, Wang et al. [131] indicated that the pretreatment with chemical coagulant, poly-aluminum chloride, was effective for the desalination of recirculating cooling water by MD process. After 30 d of operation, about 23% improvements of MD permeate flux coupled with the formation of large distorted rhombic magnesium–calcite scale on the membrane surface was observed when coagulation was employed. Bigger crystal deposits were formed on the membrane surface because the coagulation pretreatment removed most of the NOM and antiscalant additives in the feedwater. The formation of bigger crystal reduced partial wetting of membrane, as it was rather difficult for the bigger crystals to enter the membrane pores. These results suggest the suitability of the pretreatment is highly dependent on the feedwater characteristics. For the wastewater treatment, the pretreatment was directed towards total solids removal; therefore, the usage of coagulation was observed to less effective. On the other hand, for scaling mitigation, coagulation pretreatment plays an effective role in the formation of large crystals; reducing pore penetration and wetting, thus maintaining a stable permeate flux in MD operation.

Further, another approach that was reported to be effective for membrane scaling reduction was the usage of net-filter [51,113]. The net filter element (50 mesh) assembled directly to the MD module inlet allows to significantly limit the amounts of $CaCO_3$ precipitation on the membrane surface with tap water [113]. This is because, the heterogeneous crystallization performed inside a net filter decreased the saturation ratio of the concentrated feed solution and as a result, the amount of deposit formed on the membrane surface was reduced.

As a whole, it can be summarized that the potential of MD application for drinking water production can be effectively increased with suitable pretreatment based on various feed solution characteristics and for different purposes. Further, it must be highlighted that although due consideration has been given to scaling mitigation pretreatment systems for MD, there are still limited studies on pretreatment options for organic fouling reduction.

5.3. Antiscalant

Antiscalant is a widely adopted method for membrane scale deposition control. One of the benefits of using antiscalant is its low-cost and small dosage requirement [132]. Hence, the usage of antiscalant is common not only in membrane processes such as RO but also in thermal operations of multistage flash desalination as well as multi-effect desalination. The usage of antiscalant as an inorganic scaling mitigation approach has been explored by some MD studies. He et al. [114] was the pioneer MD study to apply antiscalant as a scaling mitigation approach. The summary of the types of antiscalants used, dosages, and its effectiveness in MD are presented in Table 7.

Table 7
Antiscalant application in MD studies

References	Antiscalant details	Effectiveness
He et al. [114]	• Hollow fiber DCMD operated at 75°C with $CaSO_4$ and $CaCO_3$ feed solution • Performance of difference antiscalant K752 (polyacrylic acid and sodium polyacrylate-based compound) and GHR (organo-phosphorus-based compound were tested	• Antiscalants at low dosages of 0.6 mg/L prolonged the induction period of $CaSO_4$ and $CaCO_3$; • Antiscalant K752 was effective in inhibiting $CaSO_4$ scaling compared to the other tested antiscalants; and • No significant pore-wetting problem was observed with the usage of antiscalant
Martinetti et al. [5]	• Vacuum-enhanced DCMD operated at $T_f = 40$°C with RO concentrate; • Performance of $CaSO_4$ scale inhibitor (Pretreat Plus 0,400) was evaluated	• The highest batch recovery occurred with a scale inhibitor dose of approximately 4 mg/L
Gryta [81]	• Hollow fiber MD operated at 85°C with surface lake water spiked with bicarbonates • Performance of a commercial polyphosphate-based antiscalant ((Name and composition of the commercial antiscalant not provided) and compared with laboratory-grade sodium polyphosphate	• Effectiveness: Formation of CaCO3 crystals eliminated at low dose of antiscalant 7.2 mg/L • Side effect: Thin non-porous layer deposited on the MD membrane; higher flux decline with antiscalant at increased concentrations. Increased feed temperature accelerates the hydrolysis of polyphosphate antiscalant • Recommendation: Regular HCl cleaning with an antiscalant was effective. Residence time in MD should not exceed 1 h to avoid orthophosphate antiscalant breakdown
Hou et al. [133]	• DCMD operated at 80.5°C with seawater • The performance of polyacrylic acid (PAA) antiscalant as a of $CaSO_4$ scale inhibitor was evaluated at dosages between 5 and 15 mg/L	• Addition of PAA antiscalant delayed the formation of scale deposits • No negative effect of the antiscalant on the membrane was observed (membrane hydrophobicity remained intact) • A 10 mg/L was optimal PAA dosage

From these studies, it can be acknowledged that antiscalant at low doses can be effectively used in MD operation for scaling mitigation. A number of factors must be considered for utilizing antiscalant in MD operation. Firstly, it is important to identify the appropriate antiscalant for different scalant mitigation purposes. For instance, He et al. [114] reported that antiscalant K752, a polyacrylic acid (PAA) and sodium polyacrylate-based compound, was more effective in inhibiting $CaSO_4$ scaling, compared with other organo-phosphorus-based antiscalants tested such as GHR and GLF. Secondly, it is important to identify the optimum dosages of antiscalant. For example, Hou et al. [133] used PAA antiscalant for scale deposition control in seawater DCMD. The study observed that increasing the dosage of PAA antiscalant from 5 to 10 mg/L was effective in extending the permeate flux declining period from 9.5 to 10.3 concentration factor of the seawater. However, a higher dosage of 15 mg/L did not significant contribute to further delay the

Table 8
Composition of elements accumulated on the membrane surface at different PAA antiscalant dosages [133]

	wt.%		
Element	ρ(PAA) = 5 mg/L	ρ(PAA) = 10 mg/L	ρ(PAA) = 15 mg/L
Calcium	17.79	15.76	13.27
Sulfate	14.54	12.15	10.84
Oxygen	27.84	28.07	26.05
Carbon	10.31	8.16	9.03
Sodium	10.26	14.91	14.64
Chloride	17.71	20.54	25.32
Magnesium	1.55	0.41	0.85

formation of deposits while the composition of Mg, Cl and carbon elements on the membrane deposits increased at 15 mg/L dosage as shown in Table 8.

It is worth highlighting that the carbon element is a representation of increased organic content on the membrane surface. Increase of organic contents with antiscalant, typically organic in nature, has been highlighted by other studies [56,134]. Due consideration on this aspect is important for MD application as adsorption of organics would reduce the hydrophobicity of the membrane surface resulting in wetting [56].

At the same time, due consideration must be given to the complex chemical reactions that could occur with the usage of antiscalant which is a challenge to be monitored. For instance, Gryta [81] reported that although application of polyphosphates antiscalant at 7.2 mg/L was effective in reducing the deposits formed on the MD membrane surface during the desalination with bicarbonate enriched surface water, the deposit morphology on the membrane surface was changed. An amorphous, low porous scaling layer was formed on the membrane surface instead of crystallites. As a consequence, a decline of MD process efficiency was larger in the case of antiscalant addition as shown in Fig. 12. This phenomenon was overcome with periodical HCl rinsing enabling to maintain a stable performance for 260 h.

In MD, the effect of feed temperature and the feed pH would also affect the antiscalant behavior. For instance, Gryta, [81] analyzed the effect of heating on the hydrolysis of polyphosphate antiscalant ($NaPO_3$) and thermal decomposition of HCO_3^- ions present in surface water enriched with bicarbonate. The results indicated that increase feed temperature accelerates the hydrolysis of polyphosphates and therefore, suggested that the residence time of water in the MD installation should not exceed 1 h to avoid the possibility of formation of orthophosphates. Higher temperatures increases the rate of hydrolysis as the long chain polyphosphates would be broken down into shorter ones, as described in Eq. (2) [135]. As a consequence of the hydrolysis process, the scale inhibition efficiency would be decreased and the risk of calcium phosphate scaling formation increases as shown in Eq. (3) [136].

$$PO_3^- + H_2O \rightarrow H_2PO_4^- \rightarrow HPO_4^{2-} \rightarrow PO_4^{3-} \quad (2)$$

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \quad (3)$$

Overall, the antiscalant application showed positive results in MD scaling mitigation with appropriate antiscalant compound choices. However, the side effects of antiscalant application in MD must be given due evaluation, especially in terms of the breakdown (hydrolysis) of antiscalant with high feed temperature and the possibility of reducing the surface tension of the water as well as the increased organic contents.

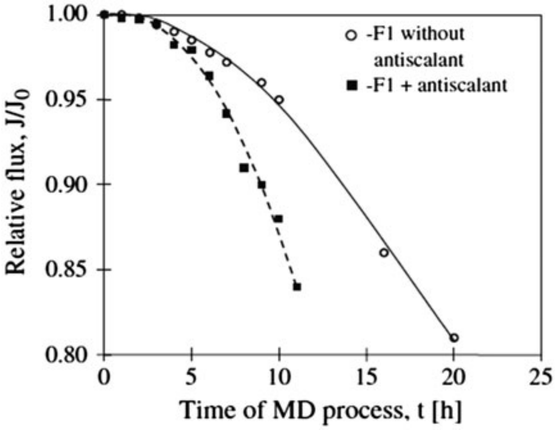


Fig. 12. Changes of the relative permeate flux with the addition of antiscalant during DCMD tap water desalination [81].

6. Conclusions

In this review, the suitability of MD technology for producing drinking water was highlighted. MD fits as a potential alternative candidate attributed to its unique beneficial features namely vapor pressure, compact membrane system, and minimal liquid discharge. In spite of the promising potential of MD in the production of drinking water, the evidence of membrane fouling development is a major concern. Hence, a detailed investigation on organic fouling and scaling development and the related wetting phenomena are essential to evaluate the feasibility of MD operation. The general lack of information makes it a challenge to substantiate MD fouling modeling theories. Thermal condition and concentrated feed solution are perceived to be the main factors influencing fouling intensity in MD operation. For scale formation, reducing the feed temperature and maintaining a turbulent flow rate appear to be effective in reducing membrane scale deposits, namely $CaCO_3$ and $CaSO_4$ that are inversely soluble at increased temperature. Meanwhile, humic substances show a tendency to adsorb and penetrate through the membrane as LMW-humic substances. Hence maintaining a suitable operating condition is an important factor in MD system. At the same time, more precise fouling detection method, long-term operation, and real-time monitoring would be highly beneficial to accurately predict the fouling phenomena in MD. This apart, the wide availability of mitigation strategies does provide possible fouling reduction solutions such as a simple approach of membrane cleaning, and sustainable pretreatment such as flocculation and media filter. Nevertheless, the challenges of some of these approaches for MD application such as antiscalant usage must also be acknowledged. Therefore, a suitable mitigation strategy can only be recommended based on the accurate fouling prediction. Additionally, research on new membranes enhancing the performance of MD as well as integrated MD systems will allow a wider growth of MD technology. Nonetheless it is important for the performance of these new MD membranes to be evaluated in terms of its fouling reduction capacity.

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