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Fouling mitigation strategies for different foulants in membrane distillation

Amira Alkhatib^a, Mohamed A. Ayari^{a,b,*}, Alaa H. Hawari^a^a Department of Civil and Architectural Engineering, College of Engineering, Qatar University, 2713 Doha, Qatar^b Technology Innovation and Engineering Education (TIEE), College of College of Engineering, Qatar University, Doha, Qatar

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ABSTRACT

Providing clean water to a rapidly growing population is an issue that is currently getting lots of attention to offer a sustainable solution for water scarcity. Membrane distillation (MD) is one of the latest technologies that provides great potential in water treatment. Even though there is a tremendous amount of research done during the past two decades on membrane distillation, the long-term use of this process is still restricted by membrane fouling. Membrane Fouling can be defined as the accumulation of various materials in the pores or surface of the membrane that affect permeate's quantity and quality. This review highlights the recent observations on various foulants in MD process. Moreover, different fouling mechanisms of inorganic fouling, organic fouling, biological fouling, and colloidal fouling were investigated for better understanding and prevention of membrane fouling. In order to achieve a sustainable MD process, various techniques to mitigate fouling were discussed comprehensively including pre-treatment processes and cleaning methods. The benefits and disadvantages of these approaches have been investigated and reviewed in order to provide an overall understanding of fouling minimization in membrane distillation process. Fouling mitigation strategies have been suggested for different foulants in membrane distillation.

1. Introduction

Membrane distillation (MD) is a promising solution for water treatment that is gaining lots of interest in the last decade. MD is a thermally driven process, in which a semi-permeable hydrophobic membrane separates the hot feed solution from the cold distillate. Only vapor molecules can pass through the membrane from the feed side to the distillate side. The temperature gradient between the hot feed solution and the cold distillate creates vapor pressure difference that drives vapor molecules to penetrate through the membrane.

MD technology can be used in different water treatment processes such as wastewater (e.g., textile, pharmaceutical, metallurgical, petrochemical), removal of organic matters from drinking water, food processes (e.g., fruit juices, olive mill, liquid foods), natural colors and biological fluids, removal of contaminants, and recovery of other minerals [1,2]. However, seawater desalination is the main application of MD process.

Membrane distillation performs several advantages over other water treatment processes. When comparing MD to conventional thermal technologies, it shows advantages in terms of operating temperature. It is not required for the feed solution in a MD system to reach the boiling

temperature like in conventional thermal technologies. That means lower energy consumption and lower negative environmental effects that can be achieved in MD process. Moreover, combining MD process with any waste heat or conventional source of energy like solar energy provides an additional decrease in energy consumption. On the other hand, MD process is operated with the absence of applied pressure compared to pressure-driven processes which means reduced operating cost and membrane cost due to membrane replacement [3]. Therefore, membrane distillation can provide a sustainable, cleaner, safer, and more energy-efficient process in terms of treatment process intensifications. Despite all the advantages that MD process can perform, the industrial implementation of MD is still lacking. The main factors that stop MD process from large-scale application are the low permeate flux comparing to thermal and pressure-driven processes. Therefore, research work is still required for MD process to reach the real-life industrial application.

Like all separation processes that require the use of a membrane, MD suffers from membrane fouling caused by several factors. The decreased hydrophobicity of membrane material with time and membrane damage are factors that accelerate membrane fouling. Consequently, decrease the permeability through the membrane, and thus reduce the permeate flux. Moreover, membrane fouling reduces the efficiency of the lifecycle

* Corresponding author at: Department of Civil and Architectural Engineering, College of Engineering, Qatar University, Doha, Qatar.

E-mail address: ArslanA@qu.edu.qa (M.A. Ayari).

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Nomenclature			
AA	Polysaccharide	MF	Microfiltration
AGMD	Air gap membrane distillation	MSF	Multi-stage flash distillation
APS	Accelerated precipitation softening	NF	Nanofiltration
BSA	Protein	NOM	Natural organic matters
BWRO	Brackish water reverse osmosis	PP	Polypropylene
DCMD	Direct contact membrane distillation	PTFE	Polytetrafluoroethylene
DI	Deionized water	PVDF	Polyvinylidene fluoride
EfOM	Effluent organic matter	RCW	Recirculating cooling water
EDTA	Ethylene diamine tetra acetic acid	RO	Reverse osmosis
EPS	Extracellular polymeric substances	SDS	Sodium dodecyl sulfate
HA	Humic acid	SEM	Scanning electron microscope
LMW	Low molecular weight	SGMD	Sweeping gas membrane distillation
MD	Membrane distillation	SHMP	Sodium hexametaphosphate
MBA	Microbubble aeration	SS	Suspended solids
MBR	Membrane bioreactor	TOC	Total organic carbon
MDBR	Membrane distillation bioreactor	TP	Total phosphorus
MED	Multi-effect distillation	TS	Total solids
		UF	Ultrafiltration
		VMD	Vacuum membrane distillation

of the membrane. Thus, an increase in energy usage, frequent membrane cleaning, substitution of the membrane, and an increase in running costs are required to maintain the treatment process. Besides, an increase in water contamination can occur from pore wetting and a reduction in salt rejection that affects treated water quality [4,5].

Fouling in MD process is a complex phenomenon and still not well understood compared to the pressure-driven process. It involves several mechanisms such as adsorption, accumulation, or precipitation that can occur simultaneously to result fouling. In fact, the variety of parameters that influence membrane fouling such as membrane characteristics (i.e., pore size, membrane thickness, membrane material, and

hydrophobicity), operating conditions (i.e., feed temperature, pH, and flowrate), the nature of feed solution, and the lack of experimental fouling data play an essential role in the complexity of this phenomena. The nature of the feed water solution determines the type of membrane fouling. Hence, the identification of different foulants and analyzing fouling mechanisms is believed to contribute to the determination of the adequate fouling mitigation process.

Several researchers have shown the undesirable consequences of membrane fouling in MD process, addressing different types of fouling and their mechanisms [6,7,8]. In order to minimize the fouling phenomena in MD and enhance the performance of the MD process,

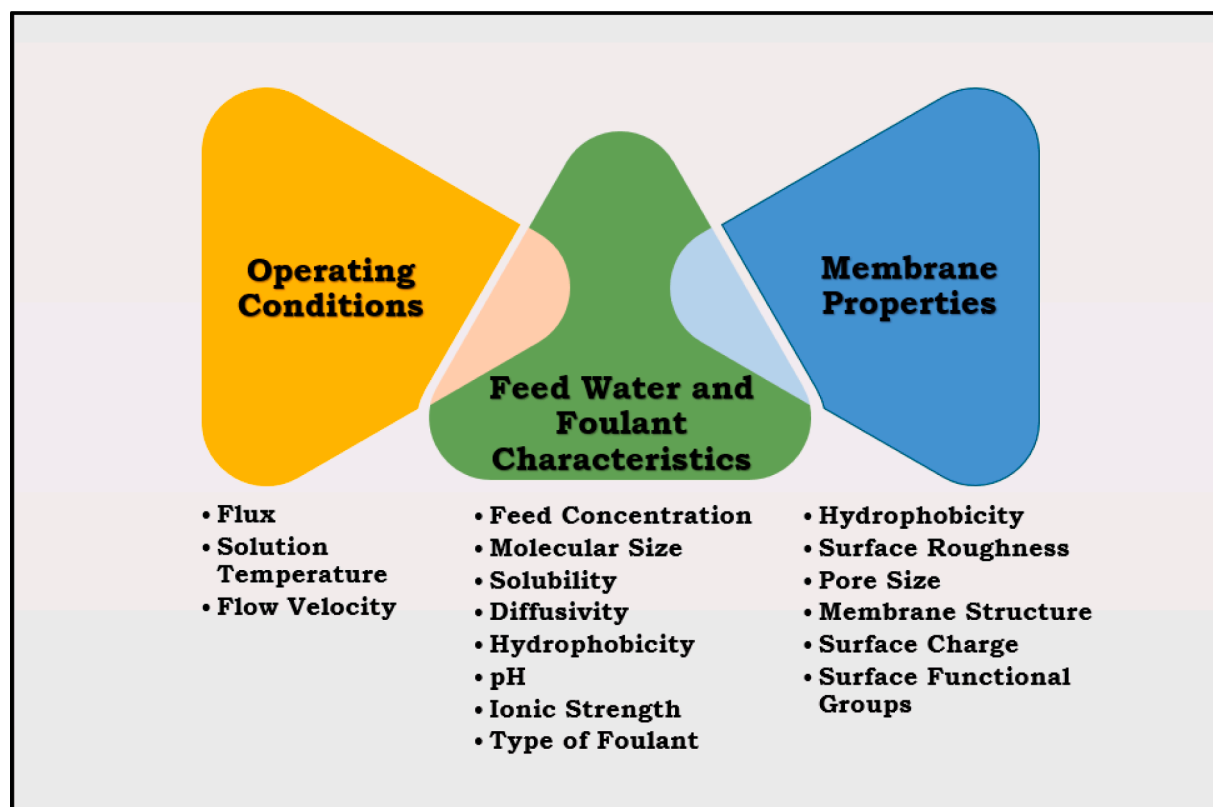


Fig. 1. Factors affecting fouling formation.

researchers have investigated several approaches to enhance membrane characteristics (i.e., membrane surface modification) and improve the operating conditions of the MD process (i.e., flowrate and temperature) [9,10]. In addition, several researchers investigated the impact of pre-treatment and cleaning methods on the performance of the MD process.

This review paper gives a broad overview of membrane fouling in MD and different mitigation methods. The type of fouling were identified according to the feed water source whether colloidal fouling, biological fouling, organic fouling, or inorganic fouling. Up-to-date research findings and observations for each type of fouling are summarized in tables. Then, various fouling mitigation methods are reviewed through the existing literature to propose the most suitable mitigation method for each foulant. This step will provide an effective strategy for proposing the optimum fouling mitigation method for each foulant. The mitigation methods include fouling pre-treatment methods and fouling cleaning methods. Finally, the future trends of addressing membrane fouling, the limitations, and the challenges of this review are discussed.

2. Membrane fouling

Membrane Fouling can be defined as the accumulation of unwanted materials on membrane surface or within membrane pores, that cause the decline of permeate flux and salt rejection [11]. According to the literature, membrane fouling in pressure-driven membrane process is more severe than in MD process [12]. However, fouling in MD is known to be one of the key issues that hinder the long-term application of MD technology. While comparing fouling in MD process to the fouling in pressure-driven membrane process, it is found that fouling in MD is still less researched and not thoroughly known [13]. However, all recognized forms of fouling occurring in any membrane-based process are present in MD process too. Membrane fouling that is observed in MD can be classified according to the source of feed water: biological fouling, colloidal fouling, organic fouling, and inorganic (scaling) fouling. There are two more types of fouling that are less known and have been found in specific feed solutions which are chemical membrane degradation [14], and chemical oxidation by residual chlorine [15].

The four major types of fouling will be addressed in detail. Previously, it is important to explain the principles of fouling mechanisms (Section 2.1) and the different factors affecting the fouling formation.

2.1. Fouling mechanism in MD

Membrane fouling is a complex phenomenon. It is not easy to explain the mechanism of fouling occurrence as it is affected by different parameters that are closely related to each other [16]. In order to ensure a comprehensive understanding of fouling mechanism, a detailed approach should be used to minimize, mitigate, and clean the formation of fouling [7]. As an appropriate mitigation method diverges from each type of fouling to another, it is more practical to analyze each type of membrane fouling independently. The factors that can affect fouling formation are classified by Tijing et al. [7] into three groups [17,16] that are summarized in Fig. 1.

Feed water and foulant characteristics identify the form of membrane fouling. This is due to the characteristics of the feed water, its concentration, the properties of the foulants, and the chemistry of feed water. Different membrane properties also affect the fouling formation in terms of particles' interactions with each other and with the membrane surface, causing deposit formation on the membrane. Surface roughness is one of the membrane properties that highly influence membrane fouling by regulating the hydrophobicity of the membrane. Higher surface roughness can trap more air molecules in micro- and nano-sized membrane surface pores [18], provoking fluid drop suspension from the surface of the membrane. As a result, the membrane surface becomes more hydrophobic with an expanded proportion of the

solid-gas interface in the total combination of solid-liquid and solid-gas interfaces on the membrane surface [17]. Consequently, solid particles can quickly adhere to the membrane surface and cause membrane fouling. Zhao et al. [19] have observed that increasing membrane roughness reduces the contact strength between the floc particle and membrane surface. Therefore, floc particles can easily adhere and detach from the membrane surface. Process operating conditions are the most known and studied factors that affect membrane fouling.

For further clarification of membrane fouling formation, the interactions between foulant particles and the membrane surface should be comprehensively analyzed. It was found that the DLVO Theory [20] gives the best explanation of the interactions between particles in aqueous media. Theoretically, the net particle-surface or particle-particle interactions is a description of Van der Waals, acid-base, and the electrical dual-layer interactions [21]. If the particle has an opposite charge to the surface or another particle, they will attract to each other. While particles with similar charges will repulse from others. In order to reduce fouling, the particle and the surface charges should be kept similar to ensure repulsion. Another process of fouling formation is the agglomeration process, which is a natural phenomenon in which solid particles stick to each other or membrane surfaces. The accumulation rate of the particles on the membrane surface depends on the particle collision and the coefficient of attachment, where large attachment coefficient and frequent particle collisions will lead to higher aggregation [22]. At high ionic strength; as in the case of seawater, the interactions between the particles are directed by acid-base interactions, since the interactions between the electrical double layers are negligible in this case [23,24] and the interactions based on Van der Waals are not capable to sustain different pH and solution concentration shifts.

Fouling formation on membrane surface affects the mass transfer across the membrane, causing a decline in permeate flux. When a fouling film is created on membrane surface, additional hydraulic and thermal resistance is added to the mass transfer coefficient. The degree of resistance is calculated based on the characteristics of the fouling film, such as the thickness and the porosity of the deposited layer [25,26,27]. The fouling layer decreases temperature variation across the membrane and results in temperature polarization [28]. Temperature variation across the membrane is known to be the driving force for flux production. Another cause for flux decline in MD is membrane pores blockage by fouling layer which refers to hydraulic resistance. The fouling layer can be porous or non-porous. The non-porous fouling layer responds to both thermal and hydraulic resistance, while porous layer provides thermal resistance only. Gryta et al. [5] had investigated the creation of fouling layers of different feed solutions, such as protein wastewater, brine, bilge water, and the processing of demineralized water. Non-porous fouling layer with protein and organic foulants demonstrate permeate flux decline due to the thermal and hydraulic resistances. Instead, scale deposition which is considered as porous fouling layer decreases the permeate flux due to thermal resistance only.

It was found that the hardest type of fouling to be cleaned comes from the feed solutions that contain hydrophobic contaminants such as oil and hydrophobic organics. These contaminants produce a non-porous layer of fouling that involves tight hydrophobic-hydrophobic bonds between the contaminants and membrane surface that is very hard to remove [29]. On the other hand, cleaning the porous layer from membrane surface due to salt crystallization is not an easy process too. Cleaning salt crystallization from membrane surface can cause mechanical damage to the membrane [5].

2.2. Types of membrane fouling

Membrane fouling is described as the aggregation of rejected molecules or other undesirable substances on a membrane's surface. The main forms of fouling that can occur in MD process can be classified into four groups according to the foulant category:

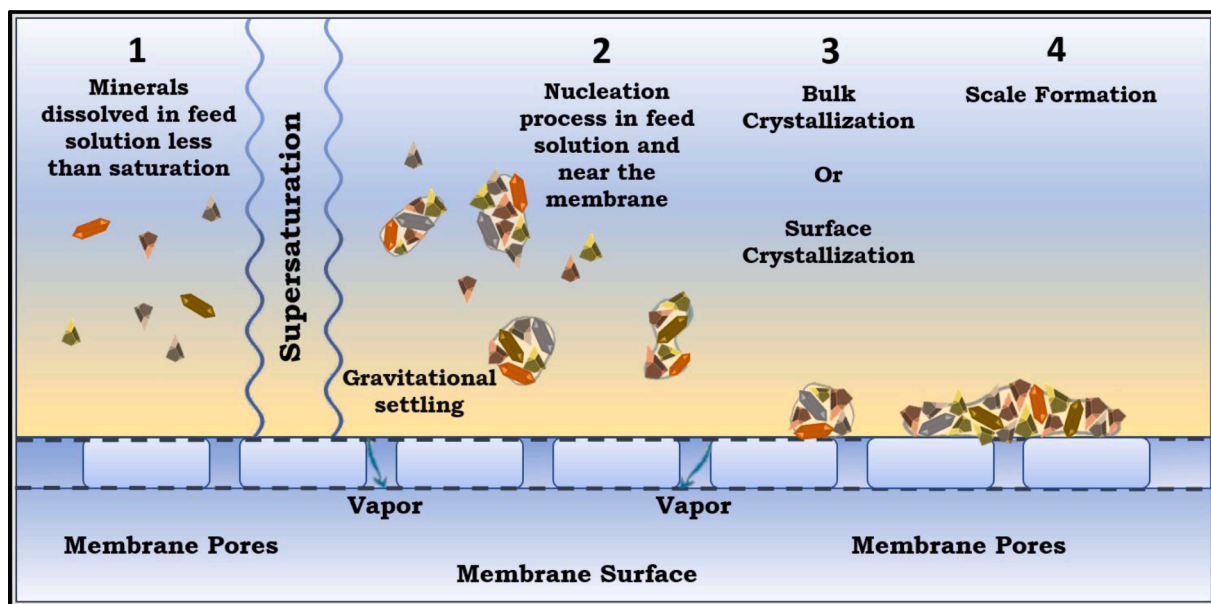


Fig. 2. General steps for Inorganic fouling formation in MD System.

- Inorganic fouling (scaling)
- Organic fouling
- Biological fouling
- Colloidal fouling

The following subsections describe the various forms of fouling encountered in the MD process, their mechanisms, the impacts on membrane surface, properties, and performance.

2.2.1. Inorganic fouling (Scaling)

The study of inorganic fouling in MD is widely discussed in the literature [6]. Inorganic fouling or scaling generally refers to the accumulation of solid inorganic compounds such as calcium carbonate, calcium sulfate, silicate, sodium chloride, aluminum oxide, iron oxide, calcium phosphate, $MgCl_2$, $MgSO_4$ [30], ferric oxide, $SrSO_4$, and $BaSO_4$ on the membrane surface or inside the pores [17,31,32,33]. The source of inorganic components is the feed solution that undergo scale formation by complex mechanisms of crystallization and transport process [7, 15].

Most common scale deposits occur with the presence of sparingly soluble salts such as $CaSO_4$, $CaCO_3$, and CaC_2O_4 in the feed solution [34]. These salts have a limited solubility level in the water, but are not totally insoluble. Due to changes in temperature, solvent evaporation, concentration polarization, or degasification, the concentration of dissolved salts increases in the feed solution. When the concentration exceeds the equilibrium solubility product, supersaturation on the feed side occurs, leading to nucleation process [9]. Nucleation can be characterized as a process in which a limited number of ions, atoms, or molecules are organized in a typical pattern of a crystalline solid. This pattern creates a site where additional particles can accumulate as the crystal grows continuously. Therefore, nucleation is considered as the initial stage of crystallization process [35].

During supersaturation, different ions start to attract to each other forming crystals in the bulk solution. These crystals can be formed on the membrane's surface or inside the pores of the membrane by gravitational settling or transfer of particles [36]. Therefore, crystallization process can happen by either surface crystallization or bulk crystallization, or both [6]. Surface crystallization, also known as heterogeneous crystallization [37], is more dominant at high operating pressure with low feed flowrate. While, bulk crystallization, which is known as homogeneous crystallization [37], is observed at high operating pressure

and average feed flowrate [15]. Even though membrane distillation process is operated in the absence of pressure, both crystallization processes can occur in MD. Surface and bulk crystallization processes are responsible for the surface blockage that prevent vapor molecules from penetrating through the membrane [33]. Both crystallization processes are coexisting in MD system, making inorganic fouling a complex process [7]. Research conducted by Lee et al. [38] concludes that heterogeneous crystallization is more dominating in unstirred batch systems, while in continuous flow systems, scaling is occurring due to both homogeneous and heterogeneous crystallization processes. Concentration polarization is known to be the primary source of increased concentration of the feed solution, leading to crystallization processes occurrence [15].

During the crystallization process, multiple layers of deposits are formed on the surface of the membrane. The deposition layer has both thermal tolerance and an increase in temperature polarization which decreases the driving force throughout the membrane. Accordingly, leading to a reduction in permeate flux [39,40]. Fig. 2 illustrates the general steps of inorganic fouling formation in membrane distillation systems. Table 1 provides a list of research studies on inorganic fouling in MD process.

It is important to understand the inorganic fouling crystallization process to avoid fouling formation on membrane surface. Preventing fouling formation acts as fouling mitigation method for inorganic fouling as it is difficult to clean inorganic scalants from the membrane surface and pores [61]. Therefore, inorganic fouling is considered one of the main challenges that stop MD process from operating in a large-scale capacity for desalination application [62]. In addition to the kinetics of crystallization process, many other factors, such as membrane morphology, the type of feed solution, and the operating conditions are responsible for inorganic fouling [63].

Inorganic fouling is classified based on the alkalinity of the feed solution into three categories; alkaline, non-alkaline, and uncharged molecular scales (silica-based) [61].

Alkaline scale in MD

The most famous type of alkaline scalant is carbonate which can present in the form of bicarbonate and calcium ions in MD feed solution [6]. Calcium carbonate is a widely spread scale that reaches the supersaturated conditions one of the first components among different other ions in various feed solutions [64]. It can be found in industrial water, groundwater, brackish water, and seawater [64]. It is normally formed

Table 1
Published research studies on inorganic fouling in MD processes.

Foulant	MD set-up	Membrane Type	Poor Size (μm)	Porosity (%)	Feed Composition	Inlet Temperature (Feed/Permeate) ($^{\circ}\text{C}$)	Flow Rate (Feed/Permeate) (m/s)	Flux (Kg/ m^2h)	Observation	Ref.
CaSO_4	DCMD	Capillary PP	0.22	73	Brine from ion exchanger regeneration	80/20	0.11/0.046 (m/s)	14.6–18.8	Rinsing the membrane with 2–5% HCl solution removed the accumulated CaCO_3 deposits from membrane surface	[37]
CaSO_4	DCMD	Hollow fiber PVDF	0.16	90.8	36.2 g/l brine from RO	55–77/35	0.205/0.011 (m/s)	2.5–5.8	Higher membrane fouling was noticed at high feed temperature and long term operating conditions	[41]
Ca^{2+}	DCMD	Hollow fiber PP	0.2	–	Pig slurry with 5 M NaOH and 0.5 M H_2SO_4	40/40	0.004/0.003 (m^3/min)	3–42	Biological and inorganic fouling is noticed due to the microorganisms and minerals such as S, Fe, Na, Mg, K available in feed water	[42]
NaCl	DCMD AGMD	Flat-sheet PTFE	0.18	64.05	10 g/l NaCl 35 g/l NaCl	30–60/24 60–80/15–37	0.012/0.012 (m ³ /min) 0.010/0.020 (m ³ /min)	5–35	This research had focused on cleaning strategies for removal of fouling layer	[43]
NaCl	DCMD	Flat sheet PP	0.22	70	Brine from the Great Salt Lake (GSL)	30–70/20–30	1.6 / 1.6 (Lmin-1)	10–35	A reduction in (ΔT) between feed and distillate temperature less than 20 $^{\circ}\text{C}$ improve the performance of flux and reduce inorganic fouling of NaCl	[44]
NaCl and CaSO_4	DCMD	Flat sheet, PVDF	0.22	65	Real seawater from China with an average conductivity of 42–49 mS/cm	60/20	21 L/h feed and permeate flowrates	19.5–23	This research noticed that superhydrophobic (PVDF) membrane with a high contact angle of 154.5 $^{\circ}$ improved wetting resistance and reduce membrane fouling	[45]
NaCl, CaSO_4 and CaCO_3	VMD	Flat sheet, PTFE	0.20	–	solutions from natural sea salt and CaSO_4	50–60/	0.01–0.03 m/s	–	NaCl crystal growth on membrane surface was studied using an incident light microscopy setup where rapid nucleation occurs and inhibits mass transfer.	[46]
CaCO_3	submerged vacuum membrane distillation and crystallization (VMDC)	Hollow fiber, PP	0.20	73	Synthetic solution	50–70/	0.0055 m/s	~ 2 – 13	CaCO_3 scaling was studied using CFD numerical simulation by using CaCO_3 scaling mechanism model that helps in predicting temperature and concentration polarization.	[47]
CaCO_3	submerged vacuum membrane distillation and crystallization (VMDC)	Hollow fiber, PP	0.20	73	Synthetic brine solution	60–80/	–	~ 12	periodic air-backwash was applied and resulted in 150% permeate productivity improvement	[48]
CaSO_4	AGMD	Flat sheet, PVDF	0.20	–	Synthetic solution	40–70 / 20	0.044–0.32 / 0.2 kg/s	5–40	Calcium sulfate scaling was studied by developing a model that reflects thermodynamics, kinetics, fluid mechanics, and	[49]

(continued on next page)

Table 1 (continued)

Foulant	MD set-up	Membrane Type	Pore Size (μm)	Porosity (%)	Feed Composition	Inlet Temperature (Feed/Permeate) ($^{\circ}\text{C}$)	Flow Rate (Feed/Permeate)	Flux (Kg/ m^2h)	Observation	Ref.
Colloidal silica, CaCO_3 NOM	DCMD, VMD, SGMD	Flat sheet, PTFE	0.5	90	Synthetic solution	40 / 10	0.56 m/s	~ 9 - 30	experimental validation. It was found that supersaturating conditions are not affecting MD process if nucleation induction time is long. VMD was suggested not to be used for feed solutions containing calcium bicarbonate or carbonate foulants. DCMD had the greatest fouling rate, although the highest flux. SGMD showed the best fouling resistance of all configurations.	[50]
–	vacuum-enhanced air-gap membrane distillation (V-AGMD), AGMD	spiral-wound modules, low-density polyethylene (LDPE)	0.32	76	Saline solutions	80 / 25	1100 l/h	~ 1.4 – 8.5	Represent the best experimental performance so far by an increase of up to 234% in permeate flux.	[51]
CaSO_4	submerged vacuum membrane distillation (SVMD)	Hollow fiber membranes, PTFE	0.186	41.1	Synthetic solution of Calcium chloride and sodium sulfate	70–80/	–	–	Surface crystallization process was compared to bulk crystallization to study the fouling rate. Air backwash was proved to reduce fouling rate by 54%	[52]
CaSO_4 and MgSO_4 .	AGMD	flat-sheet low density polyethylene (LDPE) membrane	0.30	85	Seawater	35–60 / 25–50 with $\Delta T = 10$	0.5 L/min	~ 2.4 – 5	More needle-shaped and larger crystals scaling occurred at high feed temperature. Scaling mitigation techniques like antiscalant and vinegar cleaning were studied showing that vinegar cleaning was less effective for high feed temperature.	[53]
–	DCMD	Flat sheet, PVDF	0.2 – 0.3	50 - 64	35 g/L sodium chloride solution	83 / 20.0	–	49.37 kg/ m^2h	The effect of calcium carbonate nanoparticles was studied that increases the contact angle of membrane and causes membrane wetting.	[54]
CaCO_3	DCMD	PP polypropylene hollow fibers	0.20	70	Synthetic seawater solutions	40 / 20	7 l/min	2.0 l/ m^2h	The effect of humic acid presence on CaCO_3 scaling was studied. It was found that Humic acid delays the nucleation and growth of crystals at low supersaturation	[25]
CaSO_4 And MgSO_4	DCMD	PTFE Flat-sheet	0.20	75	Seawater	40–50–60/25	0.03–0.06 m/s	12–18	Increasing feed temperature double up the initial water flux of the process. However, it also magnified polarization effect and promoted membrane scaling due to supersaturated CaSO_4 .	[55]
	DCMD	PVDF Flat-sheet	0.45	N/A	Synthetic water	60/20		2.3–9.3		[56]

(continued on next page)

Table 1 (continued)

Foulant	MD set-up	Membrane Type	Poor Size (μm)	Porosity (%)	Feed Composition	Inlet Temperature (Feed/Permeate) ($^{\circ}\text{C}$)	Flow Rate (Feed/Permeate)	Flux (Kg/ m^2h)	Observation	Ref.
Gypsum, CaCl_2 Na_2SO_4							0.085–0.17 m/s		The modified slippery PVDF membrane surface showed that MD performance is less affected by gypsum scales among other scales.	
N/A	DCMD	PVDF Hollow fiber	0.34	83.31	Dyeing solution treatment process	60/20	Feed:0.016 Cold:0.01	8–11	Deposits formed at the inner surface of the doped membrane with PVP additive and pore wetting were induced.	[57]
MgSO_4 And CaSO_4	DCMD	PP Hollow fiber	0.46	80	Fermentation wastewater with high organic concentrations	55–60/30	2 L/min	4.3–8.7	The deposits consist of organic components combined with inorganics and were found to be hardly flush off by water rinsing. Ca and Mg content could make deposits more compact.	[58]
NaCl	AGMD	PTFE Flat-sheet	0.2–0.45	80	Concentrate synthetic brine solution	45–82/25	1.7 L/min	3.8–36	Salts were deposited over the membrane surface with a significant flux decline rate of 2.37%/h and 4.10%/h at 82 $^{\circ}\text{C}$ for the membrane of 0.2 μm and 0.4 μm respectively.	[59]
MgSO_4O_3 CaCO_3	VMD	PP Capillary	0.2	73	Coal seam gas produced water	70 P $_v$: 6abs kPa	N/A	5.5	Calcites and magnesium silicates were found on membrane surface and caused rapid flux decline.	[60]

Note: AGMD: Air Gap Membrane Distillation, DCMD: Direct Contact Membrane Distillation, SGMD: Sweeping Gas Membrane Distillation, VMD: Vacuum embrane Distillation, PP: Polypropylene, PTFE: Polytetrafluoroethylene, PVDF: Polyvinylidene Fluoride.

after the bicarbonate breakdown (HCO_3^-) as shown in Eqs. (1-4):

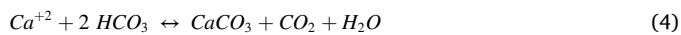
The carbonic mechanism in feed solution is resulting from the dissolution of carbonate minerals and carbon dioxide (CO_2) in water (Eq. (1)).



Bicarbonate (HCO_3^-) ions will lose their hydrogen ion and break down to carbonate ions (CO_3^{2-}) that will react with calcium ions (Ca^{2+}) available in feed water and produce calcium carbonate (CaCO_3).



Combining all the previous Eqs. (1-3) is leading to calcium carbonate equilibrium reaction represented in Eq. (4).



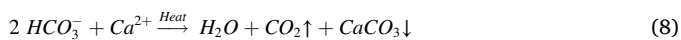
In general, the breakdown of bicarbonate in MD process has an essential influence on calcium carbonate scaling, but it is not as simple as represented in the previous equations. Eq. (4) indicates that an increase in calcium or bicarbonate content in feed solution contributes to an increase in calcium carbonate formation. The increase of bicarbonate (HCO_3^-) ions in feed water can happen due to different factors such as high carbonate concentration, high feed temperature, high alkalinity, and an increase in pH of the feed [65].

Therefore, feed water temperature plays a significant role in the precipitation process of CaCO_3 . It was found that increasing feed water temperature escalates CaCO_3 scaling. This is happening due to the inverse solubility property of aqueous CaCO_3 that decomposes to bicarbonate (HCO_3^-) ions and then to carbonate (CO_3^{2-}) ions. At higher temperatures, carbonate ions have the potential to hydrolyze into carbon dioxide [66] as follows:



where the produced carbon dioxide gas will be withdrawn from the feed solution. This reaction converts feed water into a basic solution and influences the dissolved minerals to leave their dissolved state, re-solidify, and precipitate. Magnesium ions can be an example of this reaction that will precipitate in the form of $\text{Mg}(\text{OH})_2$. In other words, when the pH and the temperature are high enough, different minerals will try to stabilize in the feed solution, forming the scale. The same principle is used in thermal water softening Section 3.1.1) which is one of the pre-treatment methods to mitigate fouling. The only disadvantage of this process is that in some cases the degassing of CO_2 can be transported to the permeate side through membrane pores and reduce the permeate quality. Eqs. (6-9) explain the degassing process of CO_2 .





Generally, these salts are named alkaline salts because they produce more basic solution when dissolve. Therefore, hydroxide ions will be generated. Hydroxide ions can be mitigated by different pre-treatment methods such as chemical water softening or membrane filtration that can limit CaCO_3 scaling [25]. Chemical water softening acidify feed solutions to pH 4 and cuts the affinity of various alkaline salts to precipitate [67,68].

A minimum temperature of 37 °C is needed to forming the CaCO_3 scale [69]. For MD systems that mainly operate at high feed temperatures (60 – 80 °C), CaCO_3 scaling can not be avoided. In addition to high feed temperature, other factors induce CaCO_3 scale formation such as the feed concentration and flow conditions [70]. Several researchers [25,48,60,71] showed that calcium carbonate scale causes rapid flux decline that can reach up to 66%. Increasing feed flowrate was a solution suggested by Gryta et al. [71] to reduce crystallization growth and make the carbonate scales more porous and loosen. However, in a real MD process, CaCO_3 is not found as a pure scale. Other impurities contribute to the fouling formation and complicate the prediction of scaling behavior. Therefore, the simple increase in feed flowrate is not the best solution to mitigate CaCO_3 formation. In reality, CaCO_3 scaling is usually observed with calcium sulfate (CaSO_4) [46,71]. In some studies, the combination of CaCO_3 with CaSO_4 resulted in a dramatic permeate flux decline [13]. However, Gryta et al. [71] concluded that CaCO_3 precipitation together with CaSO_4 produces a fouling layer that reduces membrane wetting, but causes membrane damage. Several researchers [25,72] indicated that other impurities like magnesium, sodium, barium, and sulfate ions in addition to humic acid, and fulvic acids inhibit the precipitation of CaCO_3 in various degrees of inhibition. Impurities are not only affecting the growth rate, but also indicate the type of CaCO_3 scale formation. For example, magnesium ions can lead to several formation of CaCO_3 forms and stop the formation of others.

The temperature polarization and the concentration polarization have a significant effect on MD inorganic fouling. Feed temperature and salt solubility are highly dependent on each other in an inversely proportional relationship. In the case of salts whose solubility decreases with increasing feed temperature such as BaSO_4 , CaCO_3 , and CaSO_4 ; temperature polarization facilitates the creation of salt crystals in bulk solution where the temperature is higher than the membrane surface. Crystals are deposited on the membrane surface by gravitational settlement. On the other hand, crystal salts whose solubility rises with increasing feed temperature (i.e. NaCl), will be created on the membrane surface where the concentration is higher and the temperature is lower than the bulk solution [1].

Consequently, an increase in pH happens as the temperature of the feed solution increases. As mentioned before, this process will result in the withdrawal of CO_2 molecules and the conversion of feed solution into a more basic solution [66,70] leading to changing the solubility of CaCO_3 with the change of CO_2 concentration.

Calcium carbonate can take various forms. Three anhydrous crystalline polymorphic forms of CaCO_3 are classified as vaterite, calcite, aragonite, and three other hydrated forms. Both types of calcium carbonate scale are different in the type of crystal morphology, color, and hardness. Calcite is known to be the most thermodynamically stable form of scales that occurs in MD systems. It forms cubic crystals or round shape crystals [73]. The average calcite particle size is 10 μm and it forms at ambient temperature (i.e. less than 30°C). Gryta et al. [74] mentioned in his research that laminar flow can induce calcite formation. Aragonite is less stable than calcite, but it is still observed in MD systems [75]. It exists in a needle-like structure and occurs at feed temperature higher than 30°C. Vaterite takes the shape of spherical crystals with a particle size of (0.05 – 5.0) μm . As mentioned before, different ions present in feed solution can control CaCO_3 scale formation. Magnesium ions, for example, contribute to the aragonite formation and prevent vaterite

formation [76].

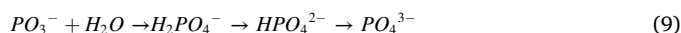
Non-alkaline scale in MD

Non-alkaline salts are ions dissolved in water, but not contributed to the rise of water pH [77]. Calcium sulfate (CaSO_4), gypsum, Calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), magnesium, and sodium chloride (NaCl) are examples of non-alkaline scaling. Calcium sulfate (CaSO_4) is the most popular non-alkaline scale occurring in membrane distillation process [70]. Calcium sulfate is formed according to three crystallographic forms; anhydrite (CaSO_4), hemihydrate (Bassanite- $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), or dehydrate (Gypsum- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) [78]. Regardless of the form of CaSO_4 scaling, it is known to be very cohesive and adherent to the membrane [37]. Among all the three forms, gypsum has the most acute form of CaSO_4 scaling due to its low solubility and high stability. Lee et al. [79] found that gypsum starts precipitating at feed temperature of 20 °C. Other experiments have shown that gypsum crystals occur in the shape of needles and platelets in orthorhombic and hexagonal prismatic structures [80]. The gypsum structure specification is based on the supersaturating ratio and crystallization kinetics. When surface crystallization is dominated, needle-like gypsum crystals occur. While platelets are observed when bulk precipitation is dominating.

While **gypsum** can precipitate at a feed temperature of 20 °C, anhydrite and hemi-hydrate precipitations are found at higher feed temperatures. Calcium sulfate solubility peaks are found to be around 40 °C [37]. In order to prevent gypsum formation, Gryta et al. [37] proposed that the concentration of sulfate ions in feed solution should be kept below 600 mg/L. At this concentration level, a thin layer of accumulated particles exists on the surface of the membrane which can be easily removed by washing the membrane with HCl. An increase in sulfate ions concentration in feed solution will challenge fouling mitigation methods. Comparatively, it is more difficult to clean CaSO_4 scale than alkaline scale from the membrane. Therefore, optimizing feed composition and the operating conditions play an essential role in mitigating calcium sulfate scale in MD.

A research study showed that during MD process when vapor molecules are penetrating through the membrane and feed solution is gradually reaching supersaturation, flux decline is observed [81]. Another research conducted by Nghiem et al. [82] on CaSO_4 scaling using hollow fiber membranes in DCMD system proposed that supersaturation alone is not enough to cause surface crystallization. Long induction time and high feed concentration (i.e. 30, 43, and 53 h for 2000, 1000, 500 mg/L of CaSO_4 , respectively) are the main reason for scale deposition on membrane surface.

Calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) is another non-alkaline scale found in MD process. It mainly occurs in wastewater treatment processes with a high concentration of phosphate ions that dissociate from phosphoric acid. The basic solution simulates the dissociation process of phosphoric acid to produce phosphate ions [70]. Therefore, maintaining a low pH of the feed solution is considered as a mitigation method to prevent calcium phosphate scale formation. As membrane distillation process is not a common process in wastewater treatment, thus calcium phosphate scale has not been addressed in MD literature. However, it can appear in processes where anti-scalants are used for CaCO_3 scale mitigation [83]. These anti-scalants use sodium hexametaphosphate (SHMP) to inhibit the growth of CaCO_3 and sulfate-based scale. Membrane distillation processes usually operate at high feed temperature and neutral pH. These conditions simulate the hydrolysis process of (SHMP). The hydrolysis process lowers the inhibition efficiency of the scale and simulates calcium phosphate formation [84]. Eqs. (9-10) summarize the hydrolysis process of (SHMP) and calcium phosphate scale formation.



Another scale that has been observed in MD processes is **magnesium** scale. Guillen-Burrieza et al. [85] and Cheng et al. [86] had studied the

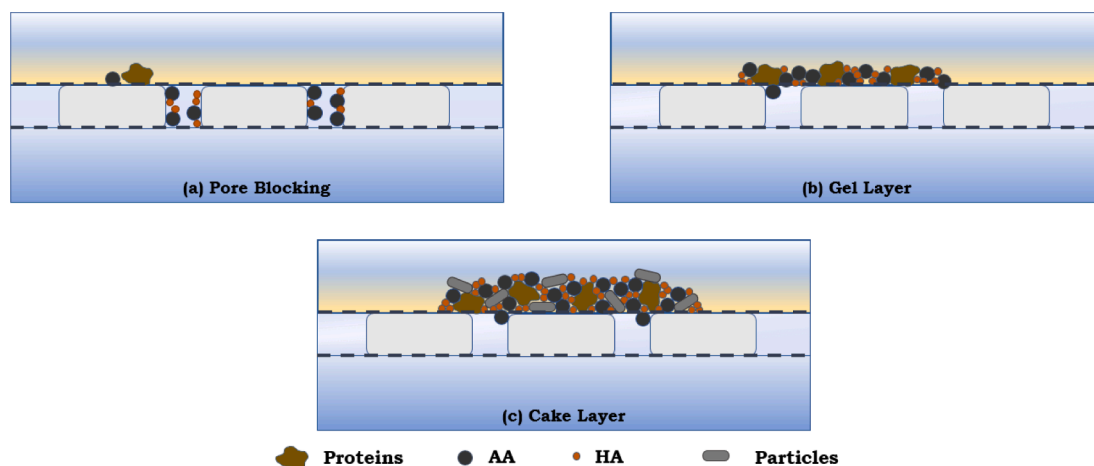


Fig. 3. Fouling mechanisms caused by NOM.

impact of different salt deposition (i.e., MgSiO_3 , MgCO_3 , MgCl_2 , or MgSO_4) on two different commercial membranes; one is polytetrafluoroethylene (PTFE) and the other is polyvinylidene fluoride (PVDF). Although both membranes did not show significant resistance to salt deposition, Cheng et al. [86] found that more scale was deposited on (PTFE) than on (PVDF) membranes. It was concluded that the decline in permeate flux is due to magnesium salt precipitation on the membrane surface rather than the increase in feed solution concentration and concentration polarization effect. Guillen-Burrieza et al. [85] had measured the thickness of the deposited salt layer on PTFE and PVDF membranes and observed that the salt layer thickness on a $50\ \mu\text{m}$ PTFE membrane is $7\ \mu\text{m}$ and about $4\ \mu\text{m}$ on a $23\ \mu\text{m}$ PVDF membrane. Similarly, the thickness of salt deposition layer on a $200\ \mu\text{m}$ PTFE membrane was found to be $15\ \mu\text{m}$ and about $10\ \mu\text{m}$ on a $125\ \mu\text{m}$ PVDF membrane. It was concluded that magnesium fouling not only reduces the quality of MD performance, but also deforms membrane properties.

The essential salt that appears in MD process used for desalination application is **sodium chloride (NaCl)**. It precipitates as cubic crystals of NaCl known as halite. Even though it is extensively used in the literature that addresses MD scaling, it is not a common scale for many MD applications due to its high solubility in water [6]. Cheng et al. [86] investigated the effect of NaCl concentration on permeate flux in DCMD system. It was concluded that increasing the concentration of feed solution from 4.5% to 10% by weight results only in a 3–4% flux decline. It was found that the flux reduction is caused by the decrease of the mole fraction of the water near the membrane surface and not due to scaling problem. Thus, the permeate flux in MD process is not affected by the feed solution concentration in terms of NaCl. These findings have been verified by a research study conducted by Tun et al. [81]. The study concluded that even at extreme conditions of high feed concentration, only the reduction in vapor pressure across the membrane is causing the dramatic decline of the flux. Therefore, there is no natural source of water fed into MD process that will have a severe NaCl scale.

2.2.2. Organic fouling

Organic fouling is associated with the accumulation of natural organic matter (NOM) on membrane surface. NOM consists of humic acid (HA), carbohydrates (including polysaccharides), proteins, lipids, and several acidic and low molecular weight (LMW) species, such as nucleic acids, amino acids, organic acids, fulvic acids [7], carboxylic acid, alginate acid, cell components [87], and polyacrylic polymers [88]. NOMs can be in the form of dissolved particles or colloidal materials that are abundant in natural waters such as groundwater, surface water, and seawater. It can also occur in wastewater sources, but known as effluent organic matter (EfOM) [89]. Organic fouling is a big issue in wastewater treatment since the concentration of EfOM (10–20 ppm) is

far greater than the normal concentration of NOM in surface water (2–5 ppm) [11]. In surface water and seawater, NOMs are released by the aquatic organisms or produced from the degradation and decomposition of living organisms. Due to the sticky properties of these components, they can attach to each other and exist in different structures like clouds, sheets, filaments, and blobs [15]. They also play a key role in forming biofouling as it often provides nutrition to the bacteria present in water bodies.

Feed water with rich organic content decreases membrane hydrophobicity and induces membrane wetting in MD process [8]. In general, hydrophilic surfaces are less exposed to organic fouling due to the presence of a hydration layer that prevents organic foulant from adhering directly to the membrane surface [90,91]. However, in MD system, hydrophobic membranes are essential, making organic fouling a challenge.

Organic matter adsorption on the surface of the membrane can occur due to various mechanisms, such as hydrophobic interactions, chemical affinity, and electrostatic [92]. Guo et al. [93] mentioned that there are at least three fouling mechanisms caused by NOM:

- The NOM might adsorb to membrane pores leading to narrow or block the pore, accordingly reduce water flux.
- It can block the access to the pores by forming a gel layer on membrane surface, accordingly block the pores.
- In situations where both NOM and other particles are present, a low permeability particle/NOM cake sheet is formed on the membrane surface.

Fig. 3 summarizes fouling mechanisms caused by NOM.

Metal ions such as Ca^{2+} , Fe^{3+} , Mg^{2+} , Al^{3+} may also contribute to NOM fouling by forming a cake layer on the membrane surface. These cations increase the electrolyte or ionic strength of the feed solution causing metal ion-induced aggregation. Divalent cations, which are cations with a valence of 2+, such as Ca^{2+} or Mg^{2+} , serve as binding agents for carboxyl functional groups present in NOM. This leads to a reduction in particle charge and the electrostatic repulsion forces between NOM macromolecules and encouraging particulate precipitation that leads to a complex formation [25,94]. These complexes consist of humic macromolecules with reduced charges that are coiled together in a spherical shape, forming a more compact fouling layer [95]. They affect not only the quality of water, but also the permeability. Still, complexes can be removed easily without the use of chemicals [96].

Nevertheless, there are contradicting observations regarding the effect of organic fouling on the quality of permeate. Some studies [5,97] indicated that organic fouling did not affect the quality of water even when membrane wetting was observed. Other studies [88,98] found that

Table 2
Published research studies on organic fouling in MD processes.

Foulant	MD set-up	Membrane Type	Poor Size (μm)	Porosity (%)	Feed Composition	Inlet Temperature (Feed/Permeate) ($^{\circ}\text{C}$)	Flow Rate (Feed/Permeate)	Flux ($\text{Kg}/\text{m}^2\text{h}$)	Observation	Ref.
Protein	DCMD	Capillary PP	–	–	11–12 g/l proteins 2–3 g/l Cl	(50- 70)/20	350/430 (cm^3/min)	1.5–11.3	The decrease in feed temperature affect reversibly on the concentration of proteins and lactose in the feed solution	[103]
Carbohydrates, proteins	MDBR	Flat-sheet PVDF	0.22	75	COD:0.67, TN:0.04 (g/l)	55.5/19.5	–	4.0–8.5	As the thermal and hydraulic resistance of the fouling layer increases in MDBR system, rapid flux decline occurs.	[98]
Human urine	VMD	Flat-sheet PTFE	0.2	–	Human urine	Feed: 50, 60, 70	Feed:0.030 (m^3/h) Vacuum: 74–92 (kPa)	5.0–13.5	VMD process showed efficient results in treating human urine	[104]
Skim milk, whey	DCMD	Flat-sheet PTFE	0.5	–	Skim milk and whey	54/5	200/200 (cm^3/min)	22	Organic fouling is starting by the accumulation of proteins on membrane surface that emphasis other salts and lactose to deposit	[105] [106]
Humic Acid (HA)	DCMD	Flat-sheet modified PVDF	0.45	–	Synthetic water: $\text{NaCl}+\text{HA}+\text{CaCl}_2$	60/25	0.2/0.4 (m/s)	12–15	It was found the organic foulants can penetrate through the original and modified PVDF membrane by an adsorption-desorption mechanism	[107]
Sodium alginate, humic acid, bovine serum albumin	DCMD	Flat-sheet PTFE	0.2	70–80	10–20 mg solution	70/24	1.1/0.3 – 2.2 (m/s)	12–35	HA can break into low molecular weight HA particles when feed temperature is increased.	[88]
Humic Acid (HA)	DCMD	Flat-sheet PTFE	0.2	70–80	Seawater, synthetic HA feed solution	70–50/25	1.1/ 1.1 (m/s)	16.0–35.7	Organic fouling was studied in seawater and HA feed solutions. It was found that HA can penetrate through membrane pores making organic fouling irreversible while using seawater feed solution. But (CaSO_4) scale reduces the disaggregation of HA due to the binding effect and prevents penetration.	[108]
Synthetic wastewater	DCMD	Flat-sheet PTFE	0.22	70	Synthetic wastewater	40/20	11.7/11.7 (cm^3/s)	–	Results indicated that the rejection and rate are controlled by the volatility in addition to the hydrophobicity of the membrane.	[109]
RO concentrated wastewater	VMD	Hollow Fiber, PVDF	0.16	82 - 85	RO concentrated wastewater	Feed: 70	Feed: 1.0 m/s Permeate vacuum: 0.085 MPa	–	Contaminants that are accumulated on membrane surface after VMD process usually consist of CaSO_4 , CaCO_3 , and trace organic matter	[110]
Humic Acid (HA)	DCMD	Nanofiber membrane, PVDF	–	–	Brackish water	60 / 20	0.75 L/min	~ 12 – 37	PVDF membranes that were modified and coated with superhydrophilic layer showed decrease in flux decay and cake formation. This finding indicated that the superhydrophobic properties of membranes do not address the issues of fouling.	[111]
Humic Acid (HA)	DCMD	superhydrophilic polyethersulfone (PES) membrane	–	–	Simulated water: $\text{NaCl}+\text{HA}+\text{CaCl}_2$	$\Delta T = 40$	0.6 / 0.3 (L/min)	12 – 18	Polydimethylsiloxane (PDMS) and SiO_2 were selected as the variable factors in coating materials	[112]
Humic Acid (HA)	Ultrasonic DCMD process hybrid	Hollow Fiber, PTFE	0.26	45	Synthetic solution with HA + CaCl_2	53 / 20	0.25 / 1.0 (m/s)	~ 2.5	Ultrasonic irradiation can be used to improve flux performance in DCMD process with synthetic HA feed solution. However, the addition of CaCl_2 to the feed causes a thick layer of organic fouling.	[113]

(continued on next page)

Table 2 (continued)

Foulant	MD set-up	Membrane Type	Poor Size (μm)	Porosity (%)	Feed Composition	Inlet Temperature (Feed/Permeate) ($^{\circ}\text{C}$)	Flow Rate (Feed/Permeate)	Flux ($\text{Kg}/\text{m}^2\text{h}$)	Observation	Ref.
Humic Acid (HA)	DCMD	Flat-sheet, PVDF	0.22	75	Simulated surface water: NaCl+HA+CaCl ₂	45–65 / 15	0.4 / 0.4 (L/min)	~ 27	Rejection efficiency of different contaminants such as ibuprofen, boron, and arsenic, in the presence of HA, calcium chloride, and sodium chloride was studied. A negligible quantity of HA was detected in the permeate (less than 1% of the initial amount in the feed), but the trace of HA observed suggests that some of the non-volatile compounds can also penetrate through the membrane.	[114]
Protein, polysaccharide (AA)	DCMD	Flat-sheet PTFE	0.22	75 – 80	Synthetic solution with CaCl ₂	75 / 25	10.5 / 10.5 (mm/s)	–	Differently charged lysozyme (LYS), sodium alginate (SA), and bovine serum albumin (BSA) were studied. LYS and SA displayed a more severe flux decline. SA was deposited on the membrane surface, while LYS penetrated through the pores, causing more severe membrane fouling.	[115]
Humic Acid (HA)	–	Flat-sheet PTFE and PVDF	PTFE: 62 PVDF: 75	PTFE: 0.187 PVDF: 0.209	Synthetic solution of HA with CaCl ₂	~ 50 / ~ 23	0.4 / 0.4 (L/min)	–	25–63% flux decline was observed on PTFE and PVDF membranes due to HA accumulation.	[116]

Note: AGMD: Air Gap Membrane Distillation, DCMD: Direct Contact Membrane Distillation, SGMD: Sweeping Gas Membrane Distillation, VMD: Vacuum Membrane Distillation, MDBR: Membrane Distillation Bioreactor, PP: Polypropylene, PTFE: Polytetrafluoroethylene, PVDF: Polyvinylidene Fluoride.

organic foulants reduce membrane hydrophobicity and penetrate to the permeate side. Consequently, reducing permeate water quality. The common fact between all these studies is that each type of organic foulants will have a different degree of wetting on the membrane surface. Compared to polymeric organic foulants, fine organic foulants are expected to cause more serious wetting problems due to their micro-size [99]. For example, the study carried by Naidu et al. [88] showed that small-sized HA in feed solution accelerates membrane wetting more than big-sized protein particles. It can be concluded that the nature of organic matter also affects the organic fouling formation. Besides, the uncertainty in research findings could be due to the lack of organic fouling analysis used in MD studies where fouling is mainly observed by monitoring permeate flux reduction only [26,97,100,101].

More factors are involved in organic fouling formation such as the ionic strength, membrane surface structure and its chemistry, different ions present in feed solution, process operating conditions, the properties of the feed solution (pH), the molecular weight of feed particles, and the polarity of the components [102].

Table 2 provides a list of research studies on organic fouling in MD processes.

There are three main NOMs that cause organic fouling in MD; Humic Acid (HA), Polysaccharide (AA), and Protein (BSA) that are discussed in details in the sections below:

Humic Acid (HA)

The main component of NOM is humic acid (HA) and it is a common name for complex mixtures of organic acids that contain functional phenolic and carboxylic groups [117]. As mentioned earlier, HA is produced from the biodegradation and decomposition processes of organic matter present in water bodies. It can be recognized by a yellowish or brown color appearance in water bodies [77]. HA is very complex in structure and varies in size. Its molecular weight can vary between 700 and 200,000 Da [118] and can achieve a size beyond this range too. As highlighted before, HA can nourish bacteria and lead to

significant biological fouling [119].

HA fouling in membrane distillation system has been studied widely [105–118]. Even though, it has fewer occurrences in MD compared to other membrane processes. Jucker et al. [91] found that HA tends to adsorb more on hydrophobic membranes which are essential in a membrane distillation process. This finding was also proved by Khayat et al. [101] who tested synthetic HA feed solution in DCMD process using two commercial membranes; one hydrophobic and one hydrophilic. The results showed that more HA fouling occurs on the hydrophobic membrane than on the hydrophilic membrane. In addition to membrane hydrophobicity, HA fouling in MD is dependent on the feed components, feed temperature, pore characteristics of the membrane, and pH of the feed [101,107]. As previously discussed, the accumulation of HA and thus the membrane cake forming is emphasized by the addition of multivalent cations and the rise in the concentration of electrolyte (NaCl) in the feed solution.

A research study performed by Srisurichan et al. [26] on a dense layer of cake formation on a flat-sheet membrane in a direct contact membrane distillation system where HA is combined with CaCl₂ in a wastewater feed solution. It was found that the fouling layer blocks the membrane pores and increases the heat transfer resistance [26]. Similar results were observed by Hou et al. [113] using a hollow fiber membrane. The initial HA concentration did not affect permeate flux properties, but when CaCl₂ was introduced, a heavy and dense HA clogging layer occurred and resulted in a significant flux decline. It is important to point out that in more acidic feed solutions, the dissociation of HA particles occurs less as fewer Ca²⁺ cations present in these conditions [94]. In addition, HA can affect other forms of fouling such as inorganic fouling by inhibiting the effects of scaling on calcium carbonate [25].

HA fouling occurs on the surface of the membrane without impacting the internal structure of the membrane. Srisurichan et al. [26] found that the deposited layer of HA fouling on the membrane surface was loosely packed and porous, and was easily removed mechanically by

backwashing or cleaning with water and 0.1 M sodium hydroxide solution.

The large aggregates of HA that are formed on membrane surface block the pores only, leading to flux reduction. Flux reduction due to organic fouling was studied by many researchers. Khayet et al. [95,101] mentioned that a flux reduction of 8% approximately occurs in DCMD process of treating HA solution for 30 continuously operating hours with commercial PTFE and PVDF membranes. Similar membranes were tested by Tan et al. [116] and performed a flux reduction of 25–63%.

Other studies [88,108] showed that HA particles can also penetrate to the permeate side through membrane pores due to their low molecular weight, thus reduce permeate water quality. However, (CaSO₄) presence in the feed solution reduces the disaggregation of HA due to the binding effects and prevents penetration to the permeate side [108].

Another factor that affects the process of HA aggregation is the pH of the feed solution. The humic substance has a negative charge for a broad range of pH [120]. It attaches favorably to membrane surface at low pH and forms bigger aggregates in acidic solution. This happens due to the reduction of intermolecular and intramolecular electrostatic repellent forces because of the protonation of the HA carboxylic groups [94]. Yet, it was found that the quantity of permeate flux does not change much. Srisurichan et al. [26] found that permeate flux does not change a lot when fluctuating the pH of the solution between pH 3 and pH 7. It can be explained by the low tendency of HA to dissociate and penetrate through the pores of the membrane at low pH. The HA fouling layer that occurred on the membrane surface, did not penetrate through membranes' pores. The cake layer was loosely packed and was easily removed by rinsing the membrane with 0.1 M NaOH solution.

The penetration of HA to the permeate side is also affected by feed temperature. Naidu et al. [88] showed that raising feed water temperature from 50°C to 70°C will increase the tendency of HA compounds to disaggregate into low molecular weight particles that can reach the permeate side.

Polysaccharide (AA)

Polysaccharides (AA) are larger particles than HA with molecular weights in the range of hundreds to the range of thousands kDa. They have rod-shaped structures or rigid fibrillary with weak negative charges [121]. Polysaccharides represent an important component of organic fouling related to water treatment processes that involve microalgae [8]. Phattaranawik et al. [122] studied the organic fouling caused by polysaccharides. It was found that AA components are poorly attached to the membrane surface due to the repulsion force between hydrophilic AA and hydrophobic membrane. Other research studies [88, 115] reached similar results and concluded that AA components have a lower fouling tendency when compared to humic substances and proteins.

Protein (BSA)

Bovine serum albumin (BSA) is a type of protein with a molecular weight of 66,000 Da approximately. High operating feed temperature is one of the main factors that cause protein fouling in MD [123,62]. Tijjing et al. [7] mentioned that BSA fouling that occurred in MD process is negligible when the BSA feed concentration and feed temperature (i.e., 20–38 °C) are low. In another study, it is observed that 60%–70% of permeate flux reduction was caused by BSA fouling [100]. A high feed temperature of 85 °C will decline the permeate flux by 72% because of a gel-like structure on the membrane surface [124]. In a research study conducted by Naidu et al. [88], a comparison between BSA, AA, and HA fouling is performed in DCMD system. It was reported that the dominant fouling comparing to other components was BSA. Moreover, due to its hydrophilic nature, AA showed minimal fouling. Even with permeate flux reduction of 50%, no pore wetting was observed and BSA deposits were on the membrane surface only. Therefore, it was concluded that BSA fouling appears to be reversible and can be cleaned with normal flushing. Nevertheless, HA foulants cause pore wetting and penetrate to permeate side.

2.2.3. Biological fouling (Biofouling)

Biological fouling or Biofouling refers to the multiplication and accumulation of bacteria or living microorganisms on the membrane surface. Biofilm creation is an essential problem that affects membrane performance and application. Biofouling lowers membrane permeability, leading to productivity reduction and eventually causing long-term operational problems [125]. Comparing to other membrane processes, biofouling is less found in MD, making it not well understood as other forms of fouling. The limitation of understanding biofouling involves several factors such as feed water chemistry, foulant-surface (membrane) interactions, and foulant-foulant interactions [15]. Although, biological fouling is more likely to appear in reverse osmosis (RO) and MD bioreactors (MDBR), it is only recently extended to MD systems [119]. In MD bioreactors (MDBR), bacteria are used to break down and consume solutes to maintain the functionality of MD system. In other words, MDBRs have the same concept as membrane bioreactors (MBRs). Goh, et al. [98] mentioned that permeate flux decline of 6% approximately is observed during the first 3 days of treating wastewater in MDBR using PVDF flat sheet membranes. Flux decline of 51% is observed after 23 days of operating. The thickness of biofilm was measured after 7 days and 20 days of operating and it ranged between 2 and 8 mm and 20 mm, respectively. However, regular cleaning methods and process optimization were enough to control biofouling. In addition, reducing nutrient concentration in feed solution delayed membrane pore wetting.

The type of feed water used in MD process determines the type of microorganisms. Microorganisms with the potential to make a biofilm on the surface of the membrane are *Lactobacillus*, *Mycobacterium*, *Cytophaga Flavobacterium*, *Bacillus*, and *Pseudomonas*. [126]. For the marine source of water, *proteobacteria*, *bacteroidetes*, *firmicutes*, and *cyanobacteria* are the most common types of bacteria [127,128]. These microorganisms are classified into two types; aerobic and anaerobic bacteria. The operating conditions such as the high temperatures applied in MD are unfavorable for aerobic bacteria (*pseudomonas faecalis*) growth. However, in the case of anaerobic bacteria and fungi such as (*Streptococcus faecalis* and *Aspergillus* fungi), the high temperatures used in MD are encouraging their growth and reproduction. Bacteria can have a varied range of sizes. *Streptococcus faecalis* can get through the pores of the membrane. In general, microorganisms attached to membrane surface tend to grow rapidly forming a cake layer called biofilm. Compared to the alkaline solid scale, these biofilms are typically made of 75–95% water and are relatively porous [129]. Biofilms occur only when there are enough nutrients in the feed solution. As stated earlier, organic fouling can play an essential role in biofilm formation. Extracellular polymeric substances (EPS) which are high-molecular-weight natural polymers produced by bacteria are the major structural components of biofilms [6]. Simply, EPS consists of living, inactive, dead, or decomposed microorganisms accumulated in a form of multilayers that are hard to remove. EPS comes in different forms, mainly consist of nucleic acids, aromatic amino acids, polysaccharides, glycoproteins, lipoproteins, proteins, lipids, and humic substances [126,130,131]. Bacteria present in water adhere to the biofilm and start to grow by consuming EPS nutrients [132]. Similar to organic fouling, biofouling can cause pore wetting leading to penetration of other foulants to the permeate side [7]. Therefore, the formed biofilm can partially or completely block membrane pores making this type of fouling irreversible and the hardest to remove [133]. It is concluded that biological fouling inhibits membrane distillation process by two mechanisms:

- (a) pore wetting that allows some particles to penetrate to the permeate side and cause distillate contamination [119].
- (b) pore blockage by biofilm that reduces water diffusion and adds more resistance to the mass transfer leading to permeate flux reduction. Additionally, biofilm increases the temperature and concentration polarization effect [134].

Microorganisms' attachment and growth on the surface of the membrane is affected by different factors such as feed flowrate, membrane properties, microorganisms properties, pH, and feed water source [8]. Biofilm formation undergoes several stages in terms of bacteria activity and mobility:

a) Formation of conditioning film

The organic particles and colloidal materials that exist in the feed solution are adsorbed to membrane surface causing the creation of a thin organic conditioning layer. As mentioned in (Section 2.2.2), the formed organic layer consists of nucleic acids, lipids, polysaccharides, proteins, and humic acids with a thickness of (<300 nm) [135]. The conditioning film layer is considered as a good environment for the adhesion of microorganisms [136].

a) Attachment of microorganisms

Environmental signals will attract microorganisms to approach the conditioning film and attach to it through weak bonding. Other factors, such as surface characteristics of the membrane (e.g. charges and hydrophobicity) [137], electrostatic repulsive force, hydrogen bonding, and operating conditions [138] will also affect the attachment bonding between the conditioning film and microorganisms. Although the bonding is weak, this stage is considered as the most critical stage in the formation process of biofilms [33]. During the experiment conducted by Krivorot et al. [119] using seawater as feed solution in DCMD process and operating at 40°C, it was found that conditioning biofilm was formed within 4 h of operating time.

a) Excretion of Extracellular Polymeric Substances (EPS)

The microorganisms that are attached to the conditioning film absorb nutrients and excrete EPS [126]. The extracted EPS is essential for the constant growth of the biofilm, strengthening its structure and making it not easy to clean [139,140]. Excretion of EPS acts as a bridge between the microorganisms and the conditioning layer which will result in an irreversible attachment of microorganisms to the membrane surface [135].

a) Biofilm formation

The growth of microorganisms will continue as long as there are enough nutrients and more EPS is excreted. This stage allows larger organisms that flow in feed water to stick to the biofilm. Therefore, an additional nutrient source will be provided to the microorganisms and cause an increase in biofilm size. Continuous nutrient sources will enhance biofilm formation. The settlement of larger organisms is defined as biofouling which will later affect the performance and mechanical strength of the membrane [141]. Consequently, membrane pore wetting will occur and cause microorganisms penetration to the permeate side. Thus, relative to earlier stages, the later stage of biofouling is more difficult to control. [142].

a) Detachment of microorganisms

Due to lack of nutrients or increase in bacteria population, some microorganisms can leave the biofilm and move to another spot where more nutrients are available. The existence of dead zones or low flux regimes attracts the microorganisms to grow and develop new biofilms or stay in the water as contaminants.

Fig. 4 summarizes the five stages of biofilm formation.

Referring to the literature, not many research papers are available regarding biofouling in MD system. Krivorot et al. [119] studied biofouling in seawater desalination application by DCMD process operated at two different feed temperatures. In one experiment, the

temperature of the feed was 70°C and the other one is 40°C. It was found that more biofouling had occurred during the lower feed temperature 40°C where it is less harmful to microorganisms. However, even with high feed temperature, biological fouling can still occur in MD process. Gryta et al. [125] mentioned that the occurrence of biological fouling is limited in MD process if the salinity of the feed is high and it is operating at high feed temperature. Even though the experiment was operating at a feed temperature of 80°C, bacteria and fungi were detected on the surface of the membrane. Microorganisms were not noticed in feed water at a temperature of 90°C. However, high feed temperature can affect membrane functionality. Recent research conducted by Liu et al. [143] had contradicted previous findings. In a DCMD process of treating real lake water and operating at two different feed temperatures; 40°C and 60°C, more severe and faster flux decline was observed at feed temperature of 60°C. Moreover, the membrane surface operated under feed temperature of 60°C revealed more attachment of organic substances and salt crystals (Si and Ca). The high operating temperature can indeed kill microbial cells and microorganisms, but it cannot get rid of EPS that was already produced by microorganisms. Bogler et al. [144] had studied biofouling at different feed temperatures of 47°C, 55°C, and 65°C using PVDF membrane in a DCMD system. The obtained results showed a 30% flux decline under operating feed temperature of 47°C, and 78% flux decline at 55°C. Although bacteria activity was very weak at feed temperature of 65°C, the produced EPS caused serious pore wetting in MD system. In addition, Zodrow et al. [147] concluded that some microorganisms will live in high-temperature feed solutions by developing spores that will accumulate at lower temperature zones on the membrane surface.

In summary, different conclusions were reached out by different researchers. While, several researches [119,125] had concluded that biofouling is not significant at high feed temperature, other researches [143,144,145] established that biofouling can still occur at high feed temperature due to EPS production by microorganisms. The disparity in conclusions can be attributed to the big variety of the experimental conditions of the previous researches, such as feed water source, feed composition, salt concentration, membrane properties, operating parameters, species of bacteria, and the duration of the experiments. The impact of feed concentration on biofilm formation was studied by Liu et al. [146]. Experiments on real lake water were carried on DCMD system at 47°C feed temperature and under two different modes; mode O and mode C. Mode O used a continuous stream of deionized water (DI) to feed solution to maintain the initial concentration of feed solution, while mode C did not use a diluted stream of DI. Therefore, the feed solution got more concentrated with time in mode C. It was found that during mode C where an increase in feed concentration is happening with time, more organic deposits occur on the membrane surface compared to mode O. The organic deposits form a dense nutrient layer that stimulates microorganism colonization at the early stage of MD activity. On the other hand, during mode O less nutrients were observed on membrane surface with stable microbial community and milder flux decline.

Due to the controversy of conclusions and lack of experimental data, more experiments on different factors affecting biofouling are needed such as the effect of water source, operational conditions, and bacterial conditions. This will help in further understanding biofouling in MD process.

Additionally, feed water solution typically involves a mixture of different components in the real MD process; organic, inorganic, and different microorganisms. Therefore, biological fouling is not observed separately in MD process. A mixture of fouling mechanisms would occur together in MD with a collaborative effect of each type of fouling on another. Unlike other types of fouling, biological fouling is difficult to be excluded completely by a pre-treatment process because microorganisms can grow and multiply. Therefore, if the pre-treatment will not eliminate the microorganisms completely, the remaining ones will reproduce and cause biofouling. Theoretically, biofouling requires two

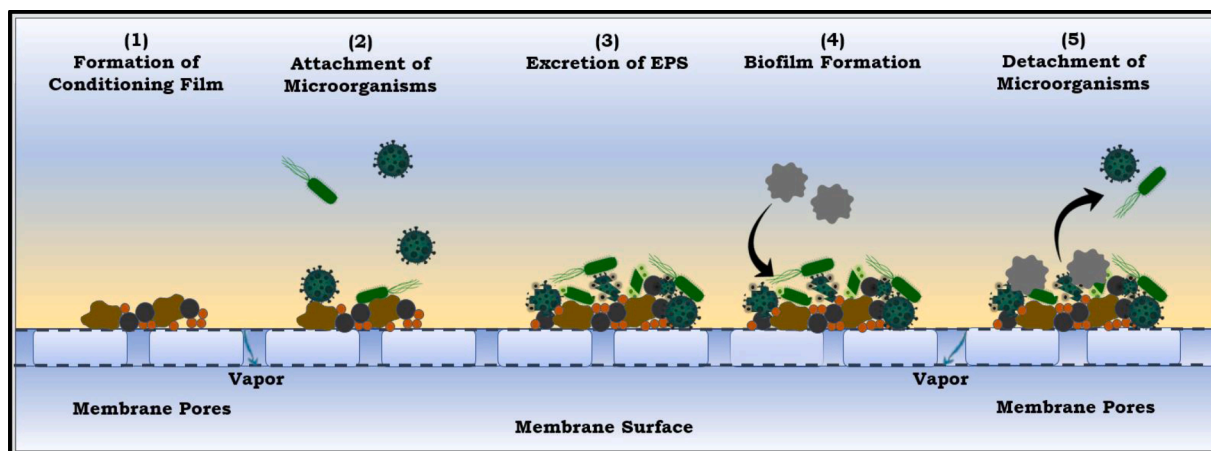


Fig. 4. Five stages of biofilm formation.

essential conditions; microorganisms present in water solution and nutrients availability. If one of these factors is eliminated, biofouling will terminate. This is the principle of a pre-treatment process for mitigating biological fouling. As it is difficult to remove all the microorganisms from feed water, the focus should be on removing the nutrients, which means other types of fouling. Pre-treatment methods for other types of fouling, such as organic, inorganic, and colloidal, will work on reducing nutrients availability. Therefore, preventing biological fouling and pore wetting that reduce the quality of distillate.

Table 3 provides a list of research studies on biofouling in MD processes.

2.2.4. Colloidal fouling

Colloids are suspended fine particles that cause fouling in many feed water solutions. The size of colloids can range from few nanometers to few micrometers [150]. Although larger particles can be removed by different membrane technologies, fine particles can cause serious fouling problems. Sometimes in literature, colloidal fouling is considered as inorganic and organic types of fouling. Therefore, colloidal particles can be divided into inorganic foulants and organic macromolecules that have been mentioned in the previous sections. Silica, Aluminum silicate minerals, clay, silt, iron oxides/hydroxides, and debris, are the predominant inorganic sector of colloidal foulants that are found in natural water sources. Similarly, organic macromolecules are predominantly made of materials such as polysaccharides, proteins, as well as natural organic matter and represent the organic part of colloidal fouling [129,151]. The type of colloidal particles varies according to the source of water. Lakes, rivers, and groundwater treatment processes may have colloidal fouling more than desalination processes where pre-treatment technologies are used for screening large molecules [152]. Many factors can affect colloidal fouling, such as the characteristics of the colloids (i.e., size, shape, charge) [121], the force of electrostatic interaction between the colloids, other foulants, and membrane surface, and the frequency of particulate collisions [151].

Feed water characteristics such as feed concentrations, physicochemical characteristics, pH, membrane properties, and hydrodynamic and operating conditions [153,154,155] affect the degree of colloidal fouling on the surface of the membrane, similar to the other types of fouling. The formed colloidal fouling layer causes an increase in concentration polarization and additional mass transfer resistance that will lead to permeate flux decline [156].

Silica

Silica is considered the most famous colloidal particle found in desalination processes and petroleum production. It can be found as colloidal silica, particulate silica, or dissolved silica in natural feed water supplies. Pre-treatment methods (i.e., MF) usually are insufficient in

extracting colloids due to their small size. The precipitation process of colloids depends on silica concentration and the pH of the feed solution. When supersaturation is reached (concentration > 100 ppm at pH 7.0) in the feed solution, insoluble silica starts to polymerize and precipitate on membrane surface [157,158] in a gel-like layer [70]. Even though the polymerization process of silica can be avoided by monitoring feed concentration below 120 ppm, other consequences appear.

It was found that when reducing feed concentration, other foulants with lower solubility start to nucleate [159]. Consequently, produce other types of fouling. On the other hand, the pH of the feed solution plays an essential part in the ionization and polymerization process of silica. Silica is unionized in most natural water bodies at a pH of 8.5 with minimal risk of fouling [160]. Conversely, silica particles are more likely to be ionized at pH higher than 10 or pH value less than 5 [161]. As silica belongs to particles with standard solubility, it precipitates at low temperatures. Since silica's solubility increase with increasing feed water temperature, it means that silica deposition is not a common issue in thermal treatment processes like MD.

Table 4 summarizes the list of colloidal fouling research studies in MD processes. Qin et al. [50] studied silica fouling in three different membrane configurations; DCMD, SGMD, and VMD. It was found that silica fouling has minimal effect in both DCMD and SGMD. In both configurations, silica was deposited on the membrane surface in a porous gel layer. Similar results were observed by Singh et al. [162] where silica fouling was not detected on membrane surface while treating de-oiled produced water in DCMD system using hollow fiber membranes. In contrast, Karakulski et al. [163] found that silica precipitation had a major effect on hollow fiber membranes used to treat tap water. Silica deposits clogged the pores of the membrane and reduced permeate flux. It happened even when nanofiltration was used as a pre-treatment process to the MD. The decline in the permeate flux reached 30%. Another research [164] indicated that flux decline can reach 70% in hollow fiber membranes due to silica deposition. The use of acidification was suggested as a post-cleaning process to remove silica particles from the membrane surface, although it restored the permeate flux only partially.

Unlike the other types of fouling that cover membrane surface and block membrane pores, silica fouling causes membrane clogging in hollow fiber membranes. Clogging can result in an increase in temperature and concentration polarization across the membrane, which reduces the permeate flux [163]. The use of flat sheet membranes in DCMD system was also tested in the same research with simulated water containing silica. The results indicated flux and salt rejection decline, but not as significant as in hollow fiber membranes [165]. Therefore, the authors suggested avoiding hollow fiber membranes when the feed solution has significant silica present.

Table 3
Published research studies on biological fouling in MD processes.

Foulant	MD set-up	Membrane Type	Pore Size (μm)	Porosity (%)	Feed Composition	Inlet Temperature (Feed/Permeate) ($^{\circ}\text{C}$)	Flow Rate (Feed/Permeate) (m/s)	Flux (Kg/ m^2h)	Observation	Ref.
Bacteria	DCMD	Hollow fiber PP	0.6 (maximum pore size)	70%	Real seawater	40/20	0.03/0.22 (m/s)	<3.9	In cross flow experiments, flux decline was noticed after 180 h of operating compared to parallel flow experiments where stable flux was observed.	[119]
Bacteria	DCMD	Capillary PP	0.22	73%	Glycerol 1% (v/v), Extract 5 g/l, peptone K 20 g/l and lag phase 10% (v/v)	36/(20–24)	Permeate: 0.78–0.85 (m/s)	<1.3	An increase in bioreactor productivity was observed after improving operating conditions for microorganism growth.	[147]
Sludge	MDBR	Flat-sheet PVDF	0.22	–	$\text{K}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$: 22.2, KH_2PO_4 : 7.26, urea: 18, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.1 M NaOH	55/19.5	Permeate: 7.4	3.4–8.4	Flux decline by 60% was observed in cross flow MD process due to biological fouling	[98]
microorganisms	MDBR	Flat-sheet PVDF	0.22	–	Synthetic Wastewater	55.5/19.5	Permeate: 350 cm^3/min	4.1–8.3	Mass transfer resistance is more significant than heat transfer resistance with organic fouling and biofouling	[98]
Synthetic Wastewater	DCMD	Hollow fiber PP	0.2	–	Synthetic Wastewater	40/20	0.007/0.007 (m^3/min)	1.4–2.1	Total cleaning and restoration of membrane hydrophobicity can be achieved by cleaning the membrane with a citric acid solution, followed by NaOH solution.	[25]
microorganisms	DCMD	Flat-sheet PTFE	0.22	75 - 80	Lake water	40–60/10	10.5 mm/s	4 – 9.7	A higher amount of (Ca and Si) crystals and organic matter accumulate on membrane surface at high feed temperature causing more severe and rapid flux decline.	[143]
microorganisms	DCMD	Flat-sheet PTFE	0.22	75 - 80	Lake water	60/10	10.5 mm/s	9.67	During C mode: A thick layer of organic fouling is formed on the membrane surface that acts as a rich media for the colonization of microorganisms During O mode: A thinner layer of organic fouling is formed, resulting in Lower flux decline.	[146]
microorganisms	DCMD	nanofibre membranes PVDF	1–2.5	–	bacteria effluent with CaCl_2	60 / 20	0.75 L/min	16- 45	Superhydrophobic membrane was coated with a thin layer containing f-MWCNTs and AgNPs. The presence of the AgNPs on the coating layer inhibited the growth of microorganisms	[148]
Petrochemical wastewater	MDBR	Flat-sheet PTFE	0.45	–	Oil, fatty acids, emulsifiers, corrosion inhibitors, and bactericides	58/30	–	5.5	The main reason for flux decline was inorganic fouling.	[149]

Note: AGMD: Air Gap Membrane Distillation, DCMD: Direct Contact Membrane Distillation, SGMD: Sweeping Gas Membrane Distillation, VMD: Vacuum Membrane Distillation, MDBR: Membrane Distillation Bioreactor, MD: Membrane Distillation, PP: Polypropylene, PTFE: Polytetrafluoroethylene, PVDF: Polyvinylidene Fluoride.

As mentioned in the previous sections, it is common to have more than one type of fouling in MD system. Zhang et al. [167] studied the combination of calcium carbonate and silica fouling. The CaCO_3 formation was found to be rapid and without co-precipitation with dissolved silica. However, polymerized silica formed a non-porous fouling layer on the membrane surface. Silica fouling does not cause a reduction in flux as rapidly as calcium carbonate did, but it is still causing a

problem since it is hard to clean. A research [164] using SEM imaging had shown that silica foulants were found not only on the surface of the membrane, but also inside the pores of the membrane. The mechanism that silica colloids follow producing colloidal fouling is explained in Fig. 5.

The mechanism of colloidal fouling is starting with silica deposits on the surface of the membrane. Then, the colloids are wetting out to the

Table 4
Published research studies on colloidal fouling in MD processes.

Foulant	MD set-up	Membrane Type	Pore Size (μm)	Porosity (%)	Feed Composition	Inlet Temperature (Feed/Permeate) ($^{\circ}\text{C}$)	Flow Rate (Feed/Permeate)	Flux (Kg/ m^2h)	Observation	Ref.
Silica	DCMD	Flat-sheet PVDF, Hollow fiber PP	0.6 Maximum	60–80	BWRO concentrate	75/50	0.030- 0.055 / 0.015- 0.030 (m^3/h)	6–9	The accumulation of silica particles in membrane pores leads to membrane wetting	[164]
Silica	DCMD	Hollow fiber PP	0.22	72	Tap water	(60–85)/22	0.030–0.350 / 0.030–0.350 (m^3/h)	6.25 – 33	Acidification and softening processes improved flux performance and reduce scaling	[163]
CaCO_3 CaSO_4 SiO_2	DCMD	PP Flat-sheet	0.1	65–70	–	60/20	0.6 (L/min)	30	Membrane scaling caused both flux and salt rejection decline.	[165]
Silica Al (OH) $_3$	DCMD	Flat-sheet PTFE	0.45	–	Real silver leaching solution (SLS)	$\sim 60 / \sim 20$	0.3 (L/min)	7.8 - 15.7	Silica fouling is highly dependent on the presence of aluminum ions in feed solution that emphasizes silica polymerization.	[166]
Silica CaCO_3	DCMD	Flat-sheet PTFE	0.3	–	Coal seam gas (CSG) reverse osmosis (RO) brine	$\sim 50 / \sim 25$	1 (L/min)	21.0	Calcium carbonate precipitated faster than dissolved silica which reacts with different ions (Mg^{2+}) to produce other components (magnesium silicate). The produced components form a thick non-porous layer of fouling	[167]
Silica	DCMD	hollow fiber PTFE	0.26	45.07	Synthetic silica solution	$\sim 53 / \sim 20$	0.25 / 1.0 (m/s)	1.80 – 2.00	Silica scaling deposited on membrane surface from the beginning of MD process forming a gel layer that causes permeate flux decline. Ultrasonic can enhance flux performance by 43%.	[168]
Colloidal silica, CaCO_3 NOM	DCMD, VMD, SGMD	Flat sheet, PTFE	0.5	90	Synthetic solution	40 / 10	0.56 m/s	$\sim 9 - 30$	VMD process was not suitable for feed solutions that contain calcium bicarbonate or carbonate foulants. DCMD had the greatest fouling rate, although the highest flux. SGMD showed the best fouling resistance.	[50]

Note: AGMD: Air Gap Membrane Distillation, DCMD: Direct Contact Membrane Distillation, SGMD: Sweeping Gas Membrane Distillation, VMD: Vacuum Membrane Distillation, PP: Polypropylene, PTFE: Polytetrafluoroethylene, PVDF: Polyvinylidene Fluoride, BWRO: Brackish Water Reverse Osmosis.

pores and forming depositions inside the pores of the membrane. Increased temperature and concentration polarization promote deeper pores intrusions. Continuous silica precipitation on membrane surface leads to total pore blockage. Therefore, this mechanism is making silica fouling hard to clean. Moreover, particles or colloidal species that may trap into membrane surface or pores can contribute to biofilm formation [169]. Because of the uncharged property of silica [163], acids that are commonly used to break down the crystalline scales are not very successful in cleaning silica. Another technique is used to minimize silica deposition by limiting aluminum and iron concentration levels in feed water. The use of different pre-treatment methods and acidification process can also help in reducing colloidal fouling. Different pre-treatment methods for colloidal fouling will be discussed in (Section 3.1).

Another research conducted by Chen et al. [166] studied the effect of aluminum ions on colloidal fouling. Experiments were focused on treating real silver leaching solution (SLS) in DCMD system with flat sheet membranes. It was found that the degree of silica scaling is related to the presence of Al^{3+} in SLS. The amount of $\text{Al}(\text{OH})_3$ produced was dependent on the initial pH of the feed solution. As $\text{Al}(\text{OH})_3$ has a positive charge, it accelerates the aggregation of mono-silicic acids and contributes to the rapid polymerization of silica.

3. Fouling mitigation methods

Several research works are done to address fouling problems in MD process and improve membrane performance. Improving membrane performance can be achieved by optimizing process operating conditions and membrane characteristics modifications. A detailed representation of fouling reduction by these two processes can be found in several review papers [33,8,6,17,15]. However, this paper will focus on other techniques of improving membrane performance which are fouling mitigation methods. They include pre-treatment methods and membrane cleaning methods. Fig. 6 summarizes all fouling mitigation methods that are covered within the scope of this paper.

This section will be dedicated to reducing fouling in MD process by two different methods that will be discussed in details in the coming sections:

- i) **Pre-treatment methods** are used to treat the feed solution to minimize fouling formation and limit the chances of its occurrence (i.e., filtration, water softening, acidification)
- ii) **Cleaning methods** are used to clean a fouled membrane when pre-treatment methods have failed. These methods can cause a partial or total removal of the foulants (i.e., flushing, backwashing, air bubbling)

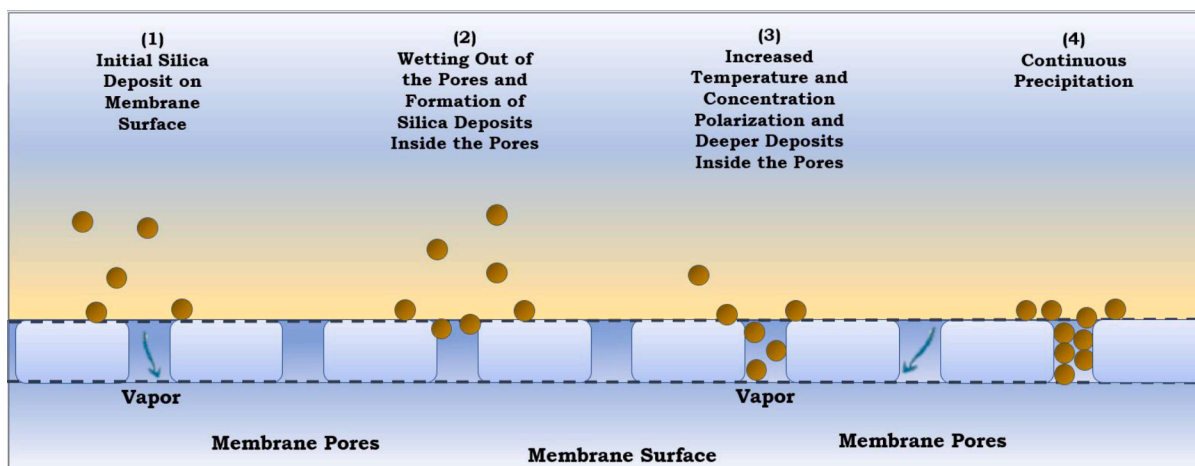


Fig. 5. Mechanism of Silica colloids that cause colloidal fouling.

Both membrane fouling mitigation methods are suitable for all types of fouling if an appropriate approach is used. The difficulty to mitigate membrane fouling appears in choosing a proper method for each foulant, especially in feed solutions where a combination of different foulants exists. As an example, pre-treatment methods are more preferable over cleaning methods for treating inorganic solutes available in the feed solution, as it is very hard to clean inorganic fouled membrane. On the other hand, organic fouling can be easily removed by mechanical cleaning. Cleaning organic fouling can be easily achieved if it is the only type of fouling that is occurring in the feed solution. In reality, organic fouling is usually a concurring type of fouling with biological fouling. When these two types of fouling are combined, pre-treatment methods fail to solve this problem [170]. As per the discussion in (Section 2.2.3), microorganisms available in feed water consume the organic matter and produce EPS that promote biofilm formation. EPS is considered as feed substances for other microorganisms and simulates the continuity of biofilm formation. Additionally, organic matter will continuously accumulate on the membrane providing a rich environment for further biofouling [6]. In fact, effective pre-treatment and cleaning membrane

fouling methods are still very limited.

3.1. Pre-treatment methods

Pre-treatment methods are used to avoid fouling from happening. The purpose of pre-treatment methods is to use various strategies to minimize the amount of foulants in feed solution and reduce the chances of fouling occurrence.

The use of pre-treatment technology in MD process is not as important as in pressure-driven treatment processes. However, it was proven that pre-treatment is considered an effective process in MD [7]. Therefore, a proper choice of pre-treatment technology can play an essential role in reducing fouling formation, increasing the quality of permeate water, improving MD performance, and increasing the lifetime of the membrane [1]. It is an important pre-step for MD process, especially when real feed water (i.e., wastewater, seawater) is used that contains a mixture of different foulants. Pre-treatment methods are used either to remove the particles that cause pore blocking or stop macro-particles and other particulate matter to reach membrane surface and

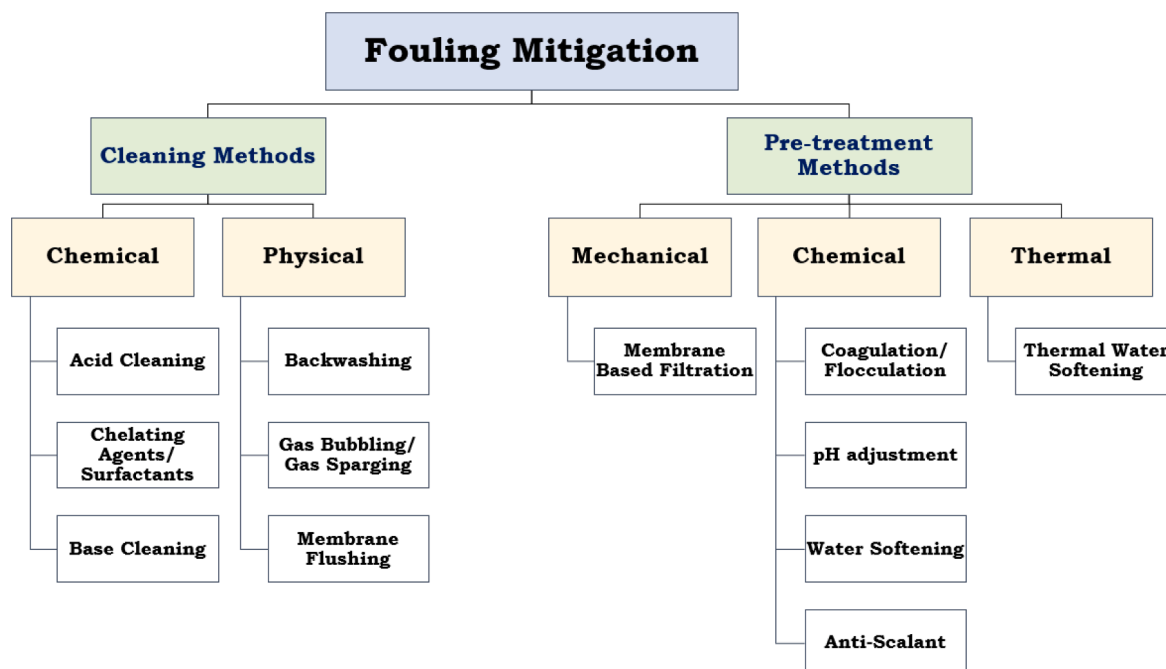


Fig. 6. Different Fouling mitigation methods.

Table 5
Published research studies on pre-treatment methods used in MD processes.

Pre-treatment category	Method	MD Process	Feed Composition	Feed Foulant	Observation	Ref.
Mechanical	NF and filtration net	DCMD (PP hollow fiber membrane)	Tap water	CaCO ₃	NF pre-treatment process at the beginning of membrane distillation can improve long-term DCMD performance up to 1100 h.	[163]
	UF, NF, RO	DCMD (PP hollow fiber membrane)	Surface water (lake)	Organic compounds, suspended solids, colloids	UF was used to reduce colloidal fouling (silt), while NF removes dissolved organic carbon by 60% and reduces hardness up to 87%. However, TDS rejection reached 99.7%.	[175]
	MF	DCMD (PP hollow fiber membrane)	Hot brine, City water containing salt at the level of 3.5, 6 or 10%, Real Seawater	Organic components, colloids, and bacteria	The hydrophobicity of membrane surface was reduced that can lead to membrane wettability. However, very limited flux reduction occurred even with high feed concentration like seawater	[180]
	MF followed by degassing	MD pilot plant (PVDF, PP, UHM-PE)	Polluted seawater	Salts, oil, silt, sludge, and unknown organic compounds	Minimal use of pre-treatment improved distillate quality and increased salt rejection.	[182]
	Forward osmosis	DCMD (PP flat sheet membrane)	Wastewater	Ammonium, COD, arsenic components	More than 99% removal of volatile contaminants was achieved.	[184]
	Forward osmosis	DCMD (PVDF hollow fiber membrane)	Real domestic wastewater	High molecular weight contaminants	More than 90% removal of organic matters, calcium salts, magnesium salts, sodium salts, and silicates was achieved.	[185]
Chemical	pH adjustment using HCl at pH = 4.1	DCMD (PP hollow fiber membrane)	Tap water, Synthetic solution with CaCO ₃ /CaSO ₄	CaCO ₃ /CaSO ₄	Stable vapor flux was achieved during the experimental time of 7 h when the induction period was extended.	[13]
	Accelerated precipitation softening (pH adjustment + calcite seeding + MF)	DCMD (PVDF hollow fiber membrane)	RO concentrate	CaCO ₃ and CaSO ₄	APS pre-treatment achieved 92% removal of calcium, CaCO ₃ , and CaSO ₄ scaling, while the flux declined by 20% only within 300 h.	[67]
	pH adjustment (acidification, alkalization)	MD (PP flat sheet membrane)	Synthetic water	Colloidal fouling - silica	Membrane cleaning with NaOH solution at pH higher than 11 was used to induce dissolution of silica scale as removing silica scale after depositing on the membrane surface is a difficult process to achieve.	[161]
	Coagulation/flocculation and MF	DCMD (PTFE flat sheet membrane)	Olive Mill Wastewater	Suspended solids and organic compounds (Phenolic compounds, Sugar, and Proteins)	MF pre-treatment improved the flux performance in DCMD process more than coagulation/flocculation pre-treatment.	[179]
	- Magnetic Lime coagulation (MLC) - Chemical precipitation-coagulation-flocculation-sedimentation integrated technology was used. The use of anti-scalant	DCMD (Self-made PVDF- TFE membrane)	Flue gas desulfurization wastewater (FGDW)	High suspended solids (SS), TOC, anions, cations	More stable flux performance and high salt rejection was achieved for 440 h continues MD process	[186]
		DCMD (PVDF flat sheet membrane)	Synthetic RO effluent	Gypsum	Three different anti-scalants were tested in DCMD process. All anti-scalants showed stable performance in terms of surface tension and distillate quality. However, high feed temperature adversely affected scaling inhibition performance because of the dependence of anti-scalants on temperature.	[187]
	Acidification	DCMD (PVDF flat sheet membrane)	Anaerobic digestion effluent	The anaerobic digestion effluent contained large amounts of suspended solids (SS), organics, ammonia, and phosphates	Feed acidification process significantly increased the rejection of ammonia (from 66% to 99%) and postponed the crystallization of Mg, Si, and Ca related scaling	[188]
	Different chemical pre-treatment processes (i.e., alkalization, etc.)	DCMD (PTFE flat sheet membrane)	Effluent of RO brine	Calcium hardness and sulfate ions	Increase of salt rejection from 58.6% to 97.9%	[189]
Thermal	Thermal water softening followed by filtration	DCMD (PP hollow fiber membrane)	Tap-water Groundwater lake water	Hardness (bicarbonate)	HCO ₃ ions that appear in groundwater were decreased by 2–3 times only by boiling feed solution for 15 min.	[183]
Combined	Sedimentation and UF Thermal Pre-treatment and filtration		Bilge water, saline wastewater	Hardness, organic compounds, and proteins	Using sedimentation and UF pre-treatment processes showed a	[5]

(continued on next page)

Table 5 (continued)

Pre-treatment category	Method	MD Process	Feed Composition	Feed Foulant	Observation	Ref.
		DCMD (PP hollow fiber membrane)			decline in flux performance. However, thermal and MF pre-treatments minimized the rapid flux decline due to the removal of protein by boiling the feed	
	UF with coagulation	VMD (PVDF hollow fiber membrane)	RO-concentrated wastewater from steel plant	Hardness and organic matter	Permeate flux increased by 30% when coagulation and ultrafiltration pre-treatment was used and the COD removal reached 40%.	[110]
	FMX-B (Vortex-based anti-fouling membrane system used in high density, high viscosity, and high TDS applications) flocculation-sedimentation (FS) flocculation-sedimentation-microfiltration (FSMF)	DCMD (Hollow Fiber membrane)	Real Shale gas wastewater	High concentration of salt and total dissolved solids (TDS)	The FSMF was more efficient to restore permeate flux than the FMX-B and FS. FSMF pre-treatment was also the most effective to suppress fouling at high-temperature differences	[190]
	Oil/water separation, photocatalysis	DCMD (Flat Sheet membrane)	Synthetic petrochemical wastewater	Organic (TDS, oil/grease, and volatile organics)	The two-stage pre-treatment could effectively remove 99.5% oil and SVOC from the wastewater.	[191]
	Precipitative softening (PS) and walnut shell filtration (WSF)	DCMD (Flat Sheet membrane)	Real Shale oil and gas produced water samples	Organic (volatile organics)	PS and WSF processes removed various particulates, organic, and inorganic foulants. Therefore, decreased the volatile organic contaminants.	[192]
	Coagulation, filtration, acidification, and degasification	DCMD (PVDF hollow fiber membrane)	Recirculating cooling water	Total organic carbon, total phosphorus (TP), organic matter (NOM), and suspended substance (SS)	MD flux performance was improved by 23% after employing coagulation.	[193]
	Lime precipitation by Ca(OH) ₂ , sedimentation and filtration	DCMD (PP hollow fiber membrane)	Saline wastewater from ion-exchanger	CaSO ₄ and silica	The fouling was significantly diminished	[194]

Note: AGMD: Air Gap Membrane Distillation, DCMD: Direct Contact Membrane Distillation, SGMD: Sweeping Gas Membrane Distillation, VMD: Vacuum Membrane Distillation, PP: Polypropylene, PTFE: Polytetrafluoroethylene, PVDF: Polyvinylidene Fluoride, RO: Reverse Osmosis, NF: Nanofiltration, MF: Microfiltration, UF: Ultrafiltration.

accumulate on it [16].

Several procedures can be carried out for reducing fouling occurrence, such as feed pre-treatment, the optimization of process operating conditions, and membrane characteristics. The optimization of process operating conditions and membrane characteristics modifications are not within the scope of this paper, but they are classified as fouling pre-treatment methods. This paper will only focus on feed pre-treatment techniques to avoid fouling of the membrane.

Pre-treatment methods are including coagulation/ flocculation, water softening, anti-scalant, membrane filtration, thermal water softening, and pH adjustment [171,172,173,174] and can be classified into three main categories:

- i **Mechanical** (i.e., membrane-based filtration);
- ii **Chemical** (i.e., coagulation/flocculation, pH adjustment, water softening, anti-scalant);
- iii **Thermal** (i.e., thermal water softening)

Or a combination between these processes (i.e., mechanical and chemical, mechanical and thermal) [1]. The most commonly used pre-treatment methods in MD system will be covered in the sections below. Table 5 summarizes some of the pre-treatment methods adopted in MD process.

3.1.1. Mechanical pre-treatment process

3.1.1.1. Membrane-based filtration (NF, UF, MF). Mechanical pre-treatment implements membrane filtration technologies to reduce the content of colloids, suspended particles, microorganisms, organic matter, in addition to bulky particles available in the feed solution. Using membrane-based filtration with MD process is a common procedure to

minimize membrane fouling and prevent membrane damage. Karakulski et al. [175] mentioned that inorganic fouling in MD was reduced after using NF pre-treatment process. Small amount of carbonate still observed in NF permeate stream, but it was easily eliminated by the acidification process. It required just adding a small amount of HCl (pH = 5) to NF permeate stream. Another effect of NF on inorganic fouling is that the negative charge of NF surface tends to stop the permeation of sulfate molecules that cause CaSO₄ scale formation on the membrane [8]. Therefore, NF can be used to limit the less soluble components like divalent salts (Ca²⁺, Mg²⁺) from accumulating on membrane surface in MD system [176].

Nanofiltration, ultrafiltration, and microfiltration are the main three processes that are used in the mechanical pre-treatment process. Nanofiltration is responsible not only for removing hardness from the water, but also can reject organic matters. Microfiltration is also used as a pre-treatment method to remove biological matters and solutes from MD systems. Inorganic scale such as calcium scale was efficiently eliminated from groundwater using microfiltration as a pre-treatment method to MD [177]. El-Abbassi et al. [178,179] had shown that microfiltration is more effective for extracting total organic carbon (TOC) and total solids (TS) from the wastewater of raw olive mills than the pre-treatment method of coagulation/flocculation. For experiments that involve saline water or brine, membrane filtration was also tested. Song et al. [180] demonstrated that extremely saline water can be operated on a daily basis in a DCMD process for 3 months without fouling. Before evaluating the water in MD system, it was pre-treated in a membrane filtration unit to remove the macro-particles and biological matters. On the other hand, biofilm formation required only 28 h of operation to occur when raw seawater from the Mediterranean Sea was used without filtration [119].

Ultrafiltration is not commonly used as a pre-treatment method for

MD process, but it can effectively remove suspended solids and colloids [6]. Ultrafiltration with MD process can be used for other applications like the recovery of valuable components from the feed solution. Zhong et al. [181] had conducted a research on achieving a complete separation from the Traditional Chinese Medicine (TCM) wastewater using ultrafiltration and MD hybrid system.

For better results, researchers suggest using more than one pre-treatment process before the MD. Jansen et al. [182] operated a microfiltration (i.e., 10 μm pore size) unit followed by degassing section prior to liquid gap MD (LGMD) process. Seawater was used as feed solution and a distillate with excellent quality was achieved. Nonetheless, the effect of the degassing system was not fully understood, even though positive results were observed. Other researchers [183] suggested the same pre-treatment procedure for MD as practiced in RO which consists of chemical coagulation and membrane-based filtration.

3.1.2. Chemical pre-treatment process

Chemical pre-treatment processes involve coagulation/flocculation, pH adjustment, precipitation, softening, anti-scalants, or disinfection. All chemical processes have the same technique in minimizing membrane fouling that is based on adjusting and neutralizing the charge of different particles. These processes can be used for various forms of fouling such as inorganic, colloidal, biological fouling, and different oxidizing agents [1]. As an example, colloidal particles and suspended solids are required pH adjustment to shift the foulants far from their isoelectric point. This process helps in reducing gel layer formation and enhancing the agglomeration of these particles into bigger and heavier molecules to prevent their penetration through membrane pores.

3.1.2.2. Coagulation/Flocculation. Coagulation is considered a simple and cheap pre-treatment process. The principle of coagulation/flocculation process is to stabilize different particles present in feed water such as colloidal particles, divalent ions, and bacteria to form bigger foulants that will minimize the risk of scale development on the surface and pores of the membrane. For example, divalent ions cause fouling by bonding to other ions and creating macromolecular chains that accumulate on the membrane surface. Ion-exchange is required for these molecules to be eliminated from the feed solution, but this process is not working with monovalent ions that may escape from precipitation.

Wang et al. [193] explored the impact of pre-treatment coagulation technologies on MD process performance by re-circulating cooling water (RCW) as a feed solution. Usually, RCW contains various contaminants such as chemicals that are added for limiting corrosion, for biofouling control, and for scaling prevention [195,196,197]. Therefore, a sequence of different pre-treatment processes is required to mitigate fouling. Wang et al. [194] used coagulation, precipitation, filtration, acidification, and degasification pre-treatment processes to eliminate fouling. Poly-aluminum chloride (PACl) was used as a coagulant for RCW and it was able to remove most of the natural organic matter (NOM), antiscalant additives, total phosphorus (TP) substances, total organic carbon (TOC), and suspended solids (SS) from feed solution. The removal process of these foulants was by converting them into bigger magnesium-calcite scales that deposit on the membrane surface and prevent them from penetrating to membrane pores. The formation of larger size deposits reduces the tendency of membrane wetting, reduces permeate flux decline, and improves permeate water quality. After coagulation pre-treatment, a microfiltration process was used to clean feed solution from large-sized foulants. In order to minimize the volume of CO_2 content in RCW, feed solution was sent through acidification treatment followed by degassing. Results had demonstrated an improvement in permeate flux by 23% when coagulation pre-treatment is used before MD process. Poly-aluminum chloride (PACl) was also used in another study as a coagulant for biologically treated coking wastewater (BTCW) fed into MD process [198]. The results indicated that (PACl) can effectively reduce the amount of biological contaminants

from BTCW without membrane wetting. Polyacrylamide (PAM) was also used as a coagulant for BTCW and it was proven to decrease the contaminant level. However, the aggregates formed by (PAM) can lead to the creation of a dense cake layer on membrane surface.

In another research, the method of magnetic lime coagulation (MLC) was used prior to MD system for flue gas desulfurization wastewater (FGDW). Lime, magnetic seeds, and different coagulants were used in this pre-treatment process for suspended solids (SS) removal. Poly-aluminum chloride (PACl), polyacrylamide (PAM), and hydrated lime were added to the feed solution as coagulants. Hydrated lime was the first coagulant to be added to FGDW in order to remove hardness from feed solution. Then, magnetic seeds and other coagulants were added, respectively. The findings revealed that the rejection of salts and organic matter was high. However, after operating for 150 h, membrane fouling and wetting was observed where inorganic scale was the main foulant in addition to some biological and organic fouling. During this study, a new fouling mechanism “bricklaying model” was induced where inorganic foulants act like “bricks” and colloids, organic matter, and microorganisms act as the “concrete” providing a thick mixture of different foulants. [186].

3.1.2.3. Acidification (pH adjustment). The pH adjustment of feed solution is a common fouling pre-treatment method. Almost in all cases, pH adjustment means converting the feed into an acidic solution by lowering its pH. Consequently, alkaline salts such as calcium carbonate (CaCO_3), the main component of inorganic fouling, will be dissolving in the acidic solution instead of accumulating on membrane surface. Several researchers [13,163,193,199] report that treating feed solution with HCl to reach pH 4 or 5 will effectively control CaCO_3 scaling in DCMD processes and perform a stable flux. The reason behind a stable flux is that hydrogen ions added to the feed from HCl solution tend to neutralize carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions through the following equation (11):



However, Karakulski et al. [163] mentioned that acidification of feed solution had failed to mitigate colloidal fouling such as silica. Another research conducted by Bush et al. [161] studied silica fouling in MD process. Pre-treatment methods to control silica fouling were proposed. Feed water with a pH lower than 5 or higher than 10 was found to have a negligible decrease in flux efficiency due to membrane fouling. Using NaOH solution as a pre-treatment process at pH above 11 increases the dissolution of silica particles in the feed. Therefore, to eliminate silica fouling, both acidification and alkalization procedures are encouraged to be used. It was found that scaling rates were the highest at neutral pH between 6 and 8. When the scale occurs, it causes membrane pores blockage and limits the mass transfer. On the other hand, silica gel layer reduces evaporation rates at the interface between the scale layer and membrane surface. This process happens because of the adsorption properties and pore structure of silica gel layer. In addition to the fact that silica fouling is not easy to clean, silica fouling occurs more frequently on a cleaned membrane compared to new membranes. Therefore, pre-treatment and careful monitoring of feed water conditions that contains silica is the optimum approach for the long-term implementation of MD process. The only drawback with pH adjustment is that the cost of some acids can be high according to the required quantity to reach a specific pH in large plants.

3.1.2.4. Water softening. Water softening is a similar technique to pH adjustment where lime, soda ash (Na_2CO_3), or caustic soda (NaOH) are used for CaCO_3 precipitating process instead of dissolving it in water. It is usually followed by microfiltration to prevent clogging of the membrane by the produced macro-particles. The key downside of this process is that water softening requires a long period of time for the settlement. To improve the efficacy of this process, an accelerated precipitation

softening (APS) process was introduced by Qu et al. [67]. APS pre-treatment process consists of pH adjustment with caustic soda and CaCO_3 seeding, followed by microfiltration. Qu et al. [67] used ASP to treat RO concentrate before introducing it into DCMD process. It was concluded that APS pre-treatment process demonstrated efficient results by removing 92% of calcium from the feed solution. Consequently, less CaCO_3 and CaSO_4 scale will occur on membrane surface.

3.1.2.5. The use of anti-scalant. Another pre-treatment approach to reduce inorganic fouling in the MD process is anti-scalant. It is usually used to inhibit carbonate scale in addition to phosphate, sulfate, and fluoride scale. In some cases, it can be used for the removal of some colloids and metal oxides [14,71,200]. Anti-scaling products are classified as chemical additives to the feed solution to weaken the scaling adhesive properties.

Different mechanisms are followed by anti-scalants to inhibit the scale such as modifying CO_2 concentration, decreasing the precipitation rate, delaying nucleation growth, and distorting crystal structure [201, 202]. It was proven that the use of anti-scalant is effective in minimizing scale formation in various water treatment processes, not only at low feed temperatures, but also at high feed temperatures. As MD process usually operates at high feed temperatures, it is preferable to use anti-scalant in MD. Moreover, it is considered a low-cost solution when low dosing of less than 10 ppm is used. On the other hand, a high dosage of anti-scalant can reduce the surface tension of water due to the organic nature of anti-scalant that have water-like hydrophilic property. As a result, membrane wetting can be accelerated.

Conversely, a study conducted by Qu et al. [187] on three different anti-scalants had concluded that the performance of anti-scalant is temperature-dependent and the increase in feed temperature can adversely affect the inhibition process of different scalants. DCMD process was used to study the effect of MDC220, PTP-0100, and SHMP anti-scalants on gypsum scaling using synthetic RO effluent feed solution. All three anti-scaling agents did not reduce feed surface tension or aggravate distillate quality. Moreover, it was confirmed that not less than 5 mg/L of MDC220 anti-scalant is needed to control gypsum scaling.

Anti-scalants can vary according to the type of feed solution. One of the earlier anti-scalants used in water treatment was sodium hexametaphosphate (SHMP) to inhibit CaCO_3 and sulfate-based scales. SHMP is considered a very sensitive anti-scalant in usage as the amount of dosing is critical. Any inaccuracy in SHMP dosing can cause the hydrolysis of SHMP and reduce the efficiency of scale inhibition. Moreover, the possibility of calcium phosphate scale formation is increased. Gryta et al. [14] performed that using sodium polyphosphates as anti-scalant can reduce CaCO_3 scale formation, but it can change the morphology of the deposit layer by making it less porous. As a result, permeate flux decline occurs in DCMD when the concentration of anti-scalant is increased. The low-porous layer can be removed by a simple acidification process, similar to what is usually performed in the thermal water softening pre-treatment process. As the non-porous deposit layer is formed on the top of the membrane surface only and not within the pores, it can be easily removed.

Currently, the most common types of anti-scalants used in desalination processes are organophosphonates, polyelectrolytes, and condensed polyphosphates [83]. In general, an effective anti-scalant should compose of a mixture of a hydroxyethylidene diphosphonate (HEDP) and polyacrylate or phosphoric acid and polyacrylic acid (PAA) [14].

He et al. [200] had studied five different types of anti-scalants with different concentrations using PP hollow fiber membrane in DCMD system. The goal of this research was to study the impact of various anti-scalants on CaCO_3 and gypsum scales. All five types of anti-scalants performed good results and indicated no membrane wetting. It was proven that the addition of anti-scalant affects the induction period of

crystal formation and slows down the precipitation process even at a low dosage of 0.6 mg/L. Various induction periods were obtained for different anti-scalants. However, K752 anti-scalant (sodium polyacrylate and polyacrylic acid based compound) showed the most effective gypsum scale inhibition results. For CaCO_3 scale, all anti-scalants performed similar results with little advances of GHR anti-scale (solution of a nitrogen-containing organophosphorus compound) over the others.

With all the advantages of anti-scalants in DCMD process, some limitations should be taken into consideration. As it was mentioned before, the high dosage of anti-scalants can change its role from substances that inhibit the scale to foulants that will accumulate on membrane surface. Some anti-scalants that have amphiphilic properties and work as surfactants usually reduce water surface tension and raise the risk of membrane pore wetting. Consequently, decreasing the lifetime of the membrane [203]. In addition, some anti-scalants (e.g., SHMP, orthophosphate) can increase the potential of biofilm formation by acting as a good source of nutrients for some microorganisms. Other anti-scalants that contain phosphorous can accelerate the growth of microbes and algae [204]. The type of anti-scalant used is also affected by the concentration of feed solution. Some chemical residuals from other pre-treatment processes can react with the anti-scalants and produce an additional fouling layer or reduce the efficiency of the anti-scalant. For example, feed solutions that contain iron molecules experience additional fouling [7]. Besides, the usage of anti-scalant is not easy to be monitored in processes like DCMD systems where temperature and feed solution is varying. Therefore, more research is required in this area.

In general, the efficiency of any chemical pre-treatment process depends on several parameters like chemical agents used, feed temperature, dosing point, membrane characteristics, and foulant properties [205].

3.1.3. Thermal pre-treatment process

Thermal pre-treatment is a process where the temperature of feed water is raised to reach the boiling point. Most thermal pre-treatment processes aim to remove (HCO_3) from the feed solution. Therefore, less inorganic scaling is occurring on membrane surface. In some feed solutions where protein foulants exist, boiling the feed followed by a filtration process reduces the chance of biofilm formation [5]. According to Gryta et al. [5], saline wastewater that is boiled for 30 min and then filtered by filter paper, caused 60% and 79% reduction in TOC and turbidity, respectively [5]. It was concluded that thermal pre-treatment process had avoided the rapid flux decline. Therefore, it was proved that thermal pre-treatment process followed by filtration can minimize protein accumulation on membrane surface.

3.1.3.6. Thermal water softening. Thermal water softening is a process of removing bicarbonates (HCO_3) from feed solution by boiling the water. In some feed solutions with high water hardness such as groundwater, thermal water softening is a good step to break bicarbonate ions. The breakdown of (HCO_3) ions means less CaCO_3 scale development on the surface of the membrane and less degassing of CO_2 which is associated with alkaline scale formation. Gryta et al. [183] examined thermal softening pre-treatment process on groundwater in MD process by using a hollow fiber membrane. It was concluded that filtering the feed solution after boiling it will lower the bicarbonate ions from 2 to 3 times of its original content.

Although thermal water softening pre-treatment process is used in water treatment applications, it has several drawbacks. It was observed that when HCO_3 ions concentration decreases in feed solution after being thermally softened, non-porous scale is formed on the membrane surface. The accumulated scale can lower the permeate flux and decrease the process efficiency [183]. However, this problem can be solved by a simple acidification pre-treatment method by decreasing the

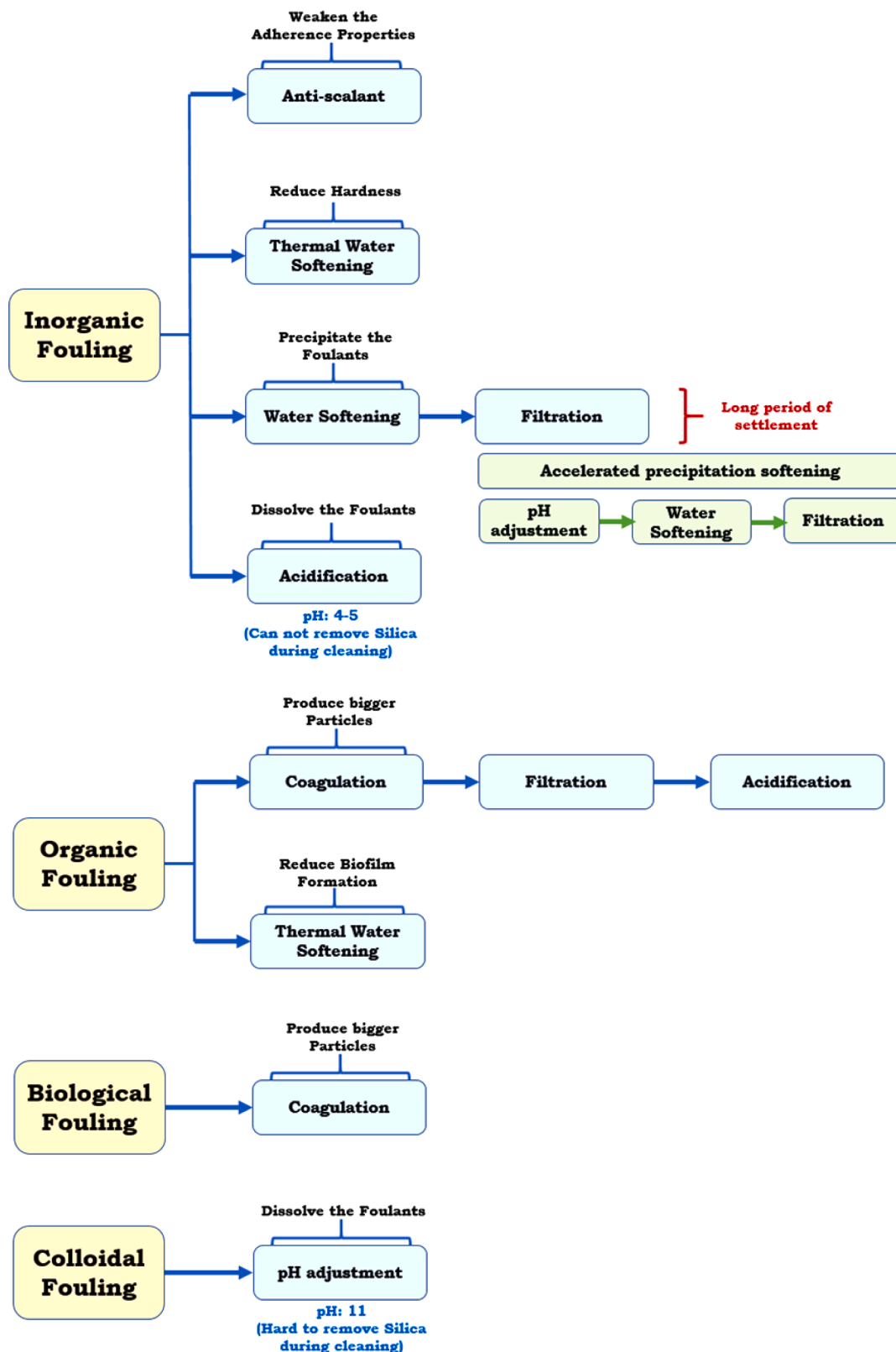


Fig. 7. Suggested different pre-treatment methods for various types of fouling.

pH of feed solution to 4. Another drawback of thermal water softening pre-treatment is that it is considered as a costly choice regarding energy consumption as MD process is trying to operate at minimum feed temperature to minimize energy usage.

Fig. 7 summarizes all the pre-treatment methods for different types

of fouling covered in this review.

3.2. Cleaning methods

Membrane cleaning methods are used to clean a fouled membrane

when fouling pre-treatment methods have failed in minimizing the fouling. Several techniques can be used to clean the membrane by total or partial removal of particles that clog the pores or accumulate on membrane surface. Periodic membrane cleaning is an essential step towards extending membrane lifetime in every membrane water treatment process. [206]. There are various membrane cleaning methods available (e.g., chemical, enzymatic, physical, and biological) to clean the membrane. However, chemical methods and physical methods are the most known cleaning methods. The efficiency of cleaning methods can be measured by resistance removal and permeate flux recovery [207]. Chemical cleaning methods implement the usage of chemical agents such as caustic soda, oxidants, acids, chelates, or proprietary surfactants to weaken cohesion interaction forces between the foulants and the membrane surface [208]. Mainly, these approaches require the use of vast amounts of chemicals that can cause significant harm to the membrane and shorten its lifetime duration. Moreover, a waste stream with the used chemical agents is generated after membrane cleaning process which requires a secondary treatment technology [209]. On the other hand, physical cleaning techniques include the use of hydraulic or mechanical forces to remove foulants from the membrane surface [210].

Membrane cleaning methods are not only used for the removal of the accumulated particles from membrane surface, but it is also used for membrane restoration. Wetted membranes can be restored after being efficiently cleaned as membrane wettability is associated with membrane fouling. In order to restore a wetted membrane to its original form, it should be totally dried before being used again. However, drying the membrane is a challenging process as in many cases it can cause membrane degradation. Moreover, the reduction in hydrostatic pressure will not guarantee the restoration of membrane pores back to unwetted condition [33]. The main problem that occurs while drying the membrane is that some solutes may stay in the membrane pores after evaporating the water. In this case, the membrane can be chemically washed and then dried to be restored.

3.2.1. Chemical cleaning methods

In all chemical cleaning methods, different chemical agents are used. It includes not only metal chelating agents (i.e., organic compounds that form complexes with metal ions), but also surfactants, enzymes, oxidants, caustic soda, acids, and alkalis [150,208]. These chemical agents work to reduce the forces of cohesion between membrane surface and foulants, making foulants easy to be removed. Therefore, foulants will be unattached from membrane surface. Chemical cleaning methods require the use of large quantities of chemicals. Thus, selecting a proper chemical agent is considered the main step in chemical cleaning methods. The selection step is subjected to economic factors, chemical properties, in addition to foulants components and fouling types [211].

3.2.1.7. Acid cleaning. In chemical cleaning process, strong and weak acids can be used according to the foulant type. Acid cleaning is considered as one of the most common forms of chemical cleaning techniques. Safety cautions should be applied while using acids for chemical cleaning in order not to damage the membrane. Moreover, acids can react with different foulants and produce additional byproducts. Sulfuric, hydrochloric, and nitric acids are usually used for cleaning inorganic fouling, especially CaCO_3 [212]. For example, hydrochloric acid (HCl) is famous for eliminating basic crystal salts such as CaCO_3 [71]. Rinsing the membrane with acid is effective when fouling occurs on membrane surface. However, when salt particles accumulate inside membrane pores, the full recovery of initial permeate flux is impossible. The process of acid cleaning starts with rinsing the membrane with distilled water as a feed solution. Then, distilled water is replaced with an acidic solution. Acids in the feed solution dissolve salts deposits on the membrane surface and move them away from membrane surface [213]. During acid cleaning, the collected permeate should be discharged. Gryta et al. [14] had noticed that HCl as a volatile

component, can penetrate with water vapor to permeate side.

A study has shown that rinsing PP hollow fiber membrane with 3 wt% HCl can efficiently dissolve CaCO_3 scale and restore permeate flux to its initial value. Microscopy tests of the cleaned membrane result images with similar characteristics to unused membranes [71]. Yang et al. [214] achieved similar outcomes with the 5 wt% HCl solution. However, it was proved in another study that the frequent rinsing of the membrane with 2–5 wt% HCl solution would result in a steady decrease in overall permeate flux. Acid rinsing is required to be repeated every 30–70 h of DCMD operating process with PP hollow fiber membrane [212].

These results can be explained by another research conducted by Gryta et al. [30] that used concentrated HCl solution to clean iron oxide scale. As iron oxides were challenging to be removed, more concentrated (more than 5 wt%) acid cleaning was required. HCl solutions with 18 wt% and 36 wt% were used to clean PP hollow fiber membranes in this study. Even though high concentrated HCl solution (36 wt%) can fully remove iron oxides from the membrane, it causes permeate flux reduction, serious damages to the membrane, and an increase in membrane wettability. In the previous research, permeate flux was reduced by 21% after acid cleaning. The author suggested for the improvement of the flux, to dry the membrane after 36 wt% HCl cleaning to free the pores from the acid solution. Filled pores with acid solution cause an increase in the area of the wetted membrane. Therefore, it was concluded that partial removal of iron oxide could be a better solution for membrane cleaning which is the case of using 18 wt% HCl solution. While using less concentrated acid, permeate flux was brought back to its initial value approximately with a partially fouled membrane.

3.2.1.8. Chelating agents and surfactants. Chelating agents are chemical agents that react with metal ions such as iron oxides to form a stable, water-soluble complex. They are very sensitive to feed pH and can be affected by feed temperature and flowrate [215,216]. Ethylene diamine tetra acetic acid (EDTA) is the most common chelating agent used in chemical cleaning methods [207]. Other chemical agents that can remove organic foulants are surfactants. Surfactants are organic compounds that contain both hydrophobic and hydrophilic groups. This property of the surfactants helps in attaching them to organic matters from the hydrophobic side, while the hydrophilic side will tend towards water [217]. This process will cause the detachment of the organic matters from membrane surface. The most common surfactant that is used in chemical cleaning is Sodium dodecyl sulfate (SDS). In addition to organic fouling cleaning, surfactants could also remove colloids. Garcia-Fayos et al. [218] found that SDS can effectively eliminate colloidal fouling that occurs after treating seawater, but proper cleaning conditions should be applied.

3.2.1.9. Base cleaning. For organic fouling and biofouling mitigation, alkaline solutions such as sodium hydroxide are very popular in terms of chemical cleaning [150,219]. Feed solutions that contain both organic and inorganic fouling, a two-step cleaning method is used that consists of acidic and basic cleaning. Curcio et al. [25] used both a citric acid solution followed by NaOH solution to clean CaCO_3 and HA fouling. After cleaning, a full recovery of permeate flux and membrane hydrophobicity was achieved. Similar results were achieved by different studies [26,193]. For biofilm removal that consists of organic matter and bacteria, Krivorot et al. [119] used NaOH solution only. The only additional step is to use 70% ethanol solution to disinfect the system from living organisms. After each step, the system is rinsed with distilled water. Results indicated that permeate flux was recovered to its initial value. However, Ang et al. [220] found that NaOH alone is not effective in cleaning organic fouling in the presence of inorganic foulants. Nonetheless, adding EDTA or SDS to feed solution can efficiently remove organic fouling especially at basic feed solution.

Several researchers evaluated different chemical cleaning agents. Guillen-Burrieza et al. [43] studied six different solvents to clean PTFE

flat sheet membrane used in treating saline water. Five chemical solvents at different pH were tested in addition to the distilled water. It was found that the most effective cleaning solvents are at pH equal to 2 containing 0.8 wt% citric acid with 0.1 wt% oxalic acid solution. The Majority of foulants (i.e., Al oxides, Fe, NaCl and Mg) were removed from membrane surface when highly acidic solvents were used. However, a damaged membrane structure was observed due to the chemical cleaning method. Consequently, membrane wetting was detected. Moreover, membrane dry-out periods accelerated membrane wetting. Other researchers had tested other acids used in cleaning membrane fouling. Filloux et al. [219] studied cleaning membrane fouling after seawater desalination process. It was found that cleaning the membrane with nitrous acid can reduce biofouling and CaCO₃ deposition. Other studies [221,222] confirmed that cleaning a fouled membrane and restoring its function can be achieved just by rinsing the membrane with deionized water.

Chemical cleaning methods efficiency has been investigated by different researchers [223]. It varies according to different factors where fouling type is the main factor that affects cleaning efficiency. Moreover, there are other factors such as the resistance of the membrane to the chemical cleaning and the deposit location that affect the cleaning process [2,43]. Overall, chemical cleaning methods on commercial MD membranes is not a very efficient process [1]. Modified membranes are more suitable for chemical cleaning methods. Chemical cleaning can cause severe damages to the membrane and develop membrane wettability. However, factors such as feed temperature and pressure can improve the chemical cleaning process. High feed temperature can increase the solubility of inorganic foulants in feed solution instead of accumulating them on membrane surface. The less pressure used in the process, the less foulants will be pushed toward the membrane surface and stick to it [150]. In addition, the efficiency of different chemical agents can be changed when they are combined together. As each chemical agent is responsible for removing a specific type of foulants, combining more than one chemical agent in the same feed solution can inhibit the process of cleaning [224].

In summary, alkaline scale that tends to dissolve at low pH such as CaCO₃ could be effectively removed by acid cleaning. Other inorganic foulants such as iron oxide require stronger acid solutions to be cleaned from membrane surface [30]. However, some studies had pointed that acid cleaning is not very effective with wastewater feed solutions. The reason behind this could be the existence of some organic matter and microorganisms. Natural organic materials work as a binding agent for inorganic foulants and promote biofilm formation [100,225]. Colloidal fouling can be treated with chemical cleaning too. Silica particles could be removed with NaOH solution, but it is considered a hard process. Therefore, the most suggested chemical cleaning method for colloids is the use of surfactants.

3.2.2. Physical cleaning methods

Physical methods of cleaning refer to the physical elimination of foulants sticking to the surface of the membrane. Hydraulic and mechanical forces are involved in physical cleaning to loosen and release the fouling layer [210]. This cleaning process includes the usage of hose-pipe, brush, or sponge to clean the membrane surface [16]. Physical cleaning methods include backwashing, gas bubbling/ sparging, the usage of turbulent promoters, reversing the flow direction, rinsing the membrane with water, and pulsing. Sometimes electrical field and ultrasonic cleaning techniques are considered as physical cleaning methods too [16]. Some of the main physical cleaning methods are explained in the sections below.

3.2.2.10. Backwashing. Backwashing is a process in which water is pumped back from the permeate side to feed solution through the membrane. It is a common procedure to remove the accumulated deposits from membrane surface. The efficiency of this process is limited to

the elimination of foulants from the surface of the membrane only [16]. In some cases, when the foulants are accumulated deep in the membrane pores, this cleaning method may not be very effective. For more efficient cleaning, the pressure of the backwash has to be higher than the operating pressure. As pressure is not applied in MD process, minimal pressure is essential to surpass the pressure generated on the surface of the membrane. The backwash scheme can be either continuous or pulsed. It is also known as back-pulsing or backshocking [16]. Short duration pulsation (i.e., about 0.1 s or shorter) can be more effective than continuous backwashing. However, either with continuous or pulsed flow, backwashing had showed effective results in terms of cleaning. Backwashing was suggested for the removal of small colloids (i.e., size > 0.45 μm) and proteins where it showed efficient results with colloidal fouling [93]. However, several studies [226] have found that backwashing is effective only during tubular and hollow fiber membranes due to the high-pressure endurance requirements.

Backwashing can be an effective cleaning method for biological fouling too. Meindersma et al. [227] had found that reversing the feed solution direction can restore the declined flux. Water from a natural pond was used as a feed solution into AGMD hollow fiber membrane system in this study. After 2200 h of operating, the direction of the flow was reversed. Results showed that this simple technique can clean the membrane from biofouling and restore the flux.

Sometimes backwashing using air is used to remove crystals and scales from the membrane [49]. It is usually used to restore wetted membranes. However, this technique should be applied when the wetted membrane still contains some water particles in its pores. This will ensure the effectiveness of the de-wetting process by forcing the liquid from membrane pores and preventing other particles from precipitating [228,229]. Warm air can also enhance membrane cleaning process. Shin et al. [230] mentioned that the optimum temperature for backwashing with air is 60 to 70°C. Julian et al. [48] experimented backwashing with air on brine solution in a submerged vacuum membrane distillation and crystallization (VMDC) system. The optimum temperature for air stream was 60°C. Higher air temperature such are 70°C and 80°C can increase crystal formation due to the complexity of temperature influence on the solubility of different solutes. Therefore, a more extensive cleaning procedure than air-backwashing was suggested to deal with scale and inorganic fouling.

3.2.2.11. Gas bubbling/ gas sparging. Gas bubbling had been studied by several researchers as a mitigation process to eliminate fouling [231]. In some studies, this process is identified as gas sparging with the same principle of gas bubbling. The principle of this process is to increase the shear rate and fluid dynamics at membrane surface to minimize concentration polarization and temperature polarization. Consequently, reduce fouling formation. In this process, gas is injected into feed solution to form a two-phase (i.e. liquid-gas) flow. The effect of gas bubbling on PVDF hollow fiber membrane cleaning in a DCMD process was studied by Chen et al. [231]. During the experiments, a nozzle linked to an air pump was mounted inside the module at the inlet side of the feed to disperse air bubbles. The results had shown that air bubbles can decrease concentration polarization and temperature polarization while increasing shear rate and fluid dynamics at membrane surface. Consequently, reduction of inorganic fouling on membrane surface.

Ahmed et al. [16] mentioned that the permeate flux scheme is not affected by the gas injection factor. While increasing the gas injection factor, the fouling will be reduced. However, only the reversible types of fouling will be minimized. The irreversible type of fouling will not be affected and the density of cake layer will be increased. It is important to note that the size of the bubbles can be related to the quality of the cleaning method. Uniformly distributed fine bubbles can provide better results than coarse bubbles [232]. Such bubbles can produce uniform flow circulation, intensity mixing, and increase the shear rate at membrane surface. Similar results were achieved by Ye et al. [233] where

microbubble aeration (MBA) was introduced to VMD system to minimize inorganic fouling after treating synthetic solution with high salinity. It was found that smaller-sized microbubbles can increase permeate flux and reduce salt precipitation, especially when bubbles are produced at large quantity.

Another research conducted by Ding et al. [234] had studied the effect of gas flowrate, bubbling duration, and MD process duration on the effectiveness of fouling mitigation. DCMD system was used with PTFE flat sheet membrane to treat traditional Chinese medicine (TCM) extract, while a fan was connected to the entrance of the feed side to produce air bubbles. At the beginning of the experiment, when gas bubbling was introduced, permeate flux decline was noticed. The reason behind it could be the tendency of gas bubbles to allocate on the top of membrane surface. Thus, reduce the interaction region between membrane surface and vapor molecules. Moreover, the bubbles can be trapped inside membrane pores and prevent vapor molecules to penetrate to the permeate side. The results showed that increasing gas bubbling flowrate and the duration increases the efficiency of fouling mitigation. However, as mentioned before, gas bubbling can deal with external fouling only. These findings are consistent with Kim et al. [235] research work. Even though gas bubbling is demonstrating many advantages, gas-liquid phase flow still requires more studies due to its complexity.

Qaisrani et al. [236] had compared gas bubbling to backwashing processes to study fouling control and membrane cleaning. Suspended solids were used to produce feed solution. Even when the study concluded that backwashing is more efficient than gas bubbling in cleaning fouling and enhancing membrane performance, it was suggested to use a combination of backwashing and air bubbling to clean the fouled membranes. The combination of air bubbling and backwashing had shown the most efficient method for cleaning the membrane and reducing fouling from the five different cleaning methods that were tested. The reason behind backwashing high efficiency could be the type of feed solution. As mentioned before, backwashing is suggested for suspended solids and colloids while gas bubbling is more preferable with inorganic fouling problems.

3.2.2.12. Membrane flushing. Membrane flushing is a simple way of fouling mitigation methods. Forward and backward flushing can be used to eliminate the accumulated particles on membrane surface. The backward flushing is the same process as backwashing that had been explained earlier. During forward membrane flushing, the membrane is flushed with a rinsing solution which can be either feed solution or permeate. The rinsing solution flows through the system more rapidly than during the process itself to create turbulence near membrane surface. In order to produce high turbulence, a high hydraulic pressure gradient is required. Accordingly, the accumulated deposits on membrane surface are released and discharged to the feed solution. However, membrane flushing process can detach the particles from membrane surface only, not from the pores. For a more efficient process, Ramon et al. [237] had suggested a combination of chemical and physical cleaning methods. The chemical cleaning will loosen the fouling layer from membrane surface and extract the foulants from membrane pores, while the physical cleaning will push the particles away by fluid shear force.

Several researchers had covered the physical cleaning of a fouled membrane by membrane flushing. Nghiem et al. [82] had studied membrane flushing as a cleaning method for PTFE flat sheet membrane in DCMD system. The inorganic fouling was examined using synthetic saline water as a feed solution. Scales of CaCO_3 , silicate, and CaSO_4 were found on the surface of the membrane. The most severe type of the three foulants was CaSO_4 . Therefore, more experiments were done related to CaSO_4 foulant. It was found that the precipitation of CaSO_4 particles increased with increasing feed temperature by decreasing the induction period of the scale [34]. If the induction time and nucleation sites at

membrane surface can be controlled and periodically cleaned, then inorganic fouling can be mitigated. Therefore, regular membrane flushing (i.e., every 20 h of working) was used to clean the nucleation sites frequently. Deionized water (DI) was used for rinsing the membrane. After regular membrane flushing, the results showed a constant permeate flux for the whole MD process.

Fig. 8 summarizes different chemical and physical cleaning methods for various types of fouling.

4. Economic feasibility of MD process

The economic feasibility of membrane distillation process is measured by water production cost (WPC). Different models for calculating the water production cost are found in the literature [238,239]. Several researchers have reported various values for the calculated cost of water production through membrane distillation. The procedures found in the literature are not following one standard method of calculation, making the economic comparison between different MD processes challenging.

The cost of produced water from MD process varies from \$ 1.17 m^{-3} to \$ 29.9 m^{-3} depending on several factors. One of the important factors involved in the calculation of water production cost (WPC) in MD is the plant capacity. Usman et al. [240] had calculated the WPC for three different AGMD plants and it was found that water production cost in MD increases with increasing the plant size to reach \$ 1.60 m^{-3} for $100 \text{ m}^3/\text{h}$ plant capacity. Many other factors are involved in the calculation of WPC such as membrane material and MD process configuration. Therefore, the WPC for AGMD process is different from DCMD process. Several researchers had studied the cost of produced water through different MD configurations [238,239,241]. Saffarini et al. [238] had calculated WPC for three different MD configurations; DCMD, AGMD, and VMD. It was found that the highest WPC value accounts for AGMD process. The contradicting results to the previous research work were performed by Histov et al. [239] who compared the price of distillate between DCMD and AGMD configurations through simulated plants with different capacity scenarios. It was found that the price of the produced distillate from DCMD system is higher than the distillate produced from AGMD system. One factor that may explain the differences between the two studies can be the type of feed water and its salinity level.

Although, membrane distillation process is not affected by the salinity level of feed water in terms of water quality. Some research studies had mentioned that water production cost increases with increasing the salinity level of feed solution [241,242].

Most of the previously mentioned research studies have focused on the contribution of waste heat and solar energy to reduce the cost of the produced water. An integrated MD system with an alternative source of energy can be a proper solution to achieve the energy requirements without harming the environment. Khalifa et al. [243] mentioned that the combination of MD process with an alternative source of energy can reduce the price of produced water below \$ 2.00 m^{-3} . Water treatment plants are usually allocated to the power plants to benefit from the waste heat that is used as a source of heating. Usman et al. [240] mentioned that increasing heat waste recovery contribution to MD system reduces the cost of produced water. Theoretically, when the optimized use of waste heat reaches 100% contribution, the cost of produced water in MD system can be equivalent to the cost of produced water in RO that does not require a source of heating.

Similarly, the combination of MD process with solar energy can reduce the price of produced water and eliminate environmental pollution. However, it was found that water production cost of a small MD system combined with a solar system could be more expensive than a simple MD process without an alternative source of heating.

While comparing the water production cost of MD process to other water treatment processes, several conclusions are observed. The typical

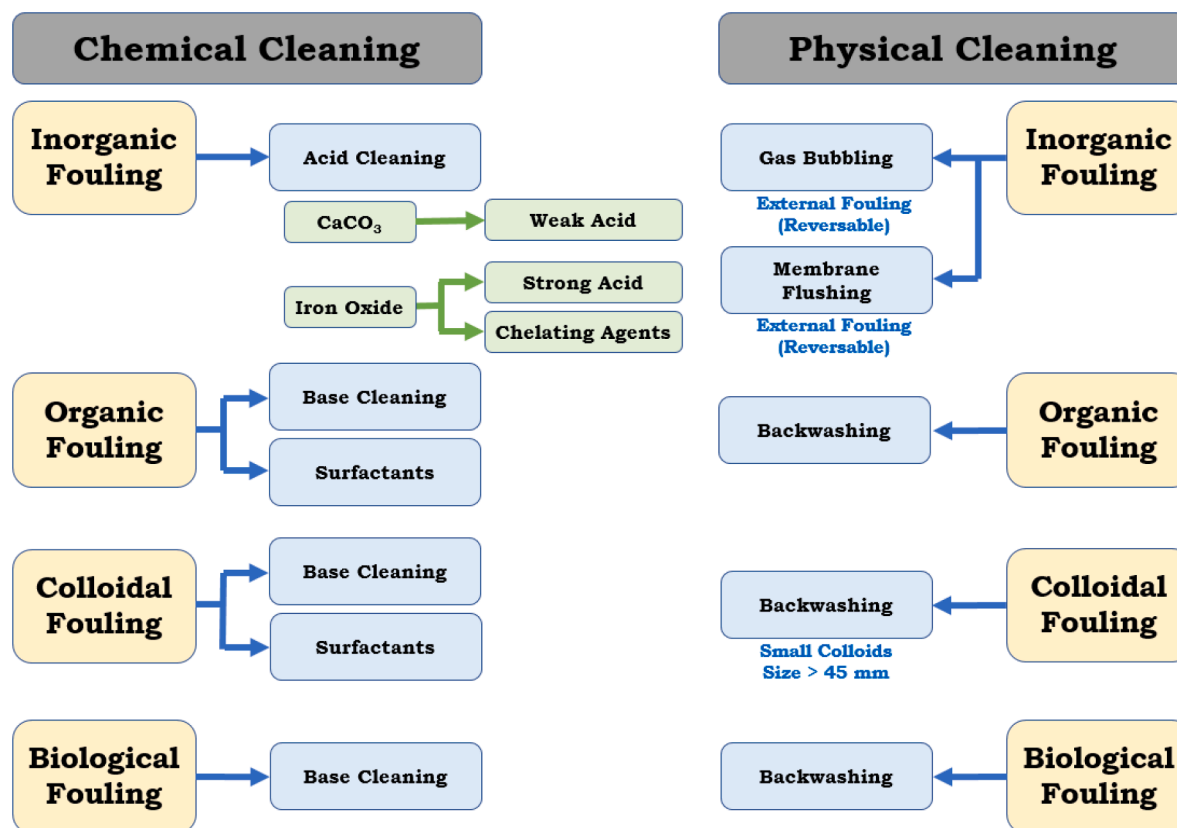


Fig. 8. Suggested different cleaning methods for various types of fouling.

water production cost of conventional thermal processes varies between \$ 1.00 m^{-3} and \$ 1.40 m^{-3} [244]. Approximately similar cost of water production can be achieved by MD process when using waste heat or alternative source of energy. Similarly, when studying the water production cost of RO process, it is found that the values are varying according to the plant capacity and the type of feed water. Piemonte et al. [245] had calculated the water production cost for RO process with different scenarios. The scenarios vary depending on the permeate salinity where the cost of water was approximately € 5.00 m^{-3} . The high cost of water is referred to the high cost of membrane implementation and frequent membrane replacement. Atia et al. [246] mentioned that approximately 20% and 30% of water production cost accounts for membrane implementation and membrane replacement, respectively. Membrane replacement is a frequent procedure in membrane-based technologies due to membrane fouling. Here comes the importance of fouling mitigation that can increase the lifetime of the membrane. Consequently, reduce water production cost.

Some research work studied the RO desalination process powered by different renewable energy sources such as solar cells or wind turbines to reduce energy consumption [247,248]. Mohamed et al. [247] showed that combining RO process with solar cells can increase water production cost up to € 6.64 m^{-3} . The high cost of water production was linked to the high initial cost of PV system. However, when wind turbines energy was introduced to the RO and solar cells hybrid, the water production cost reduced to vary between € 5.52 m^{-3} and € 5.58 m^{-3} according to different configurations.

Table 6 summarizes the water production cost (WPC) for different water treatment systems available in the literature.

5. Conclusions and future work

In all membrane-based treatment technologies including membrane distillation (MD), membrane fouling is a common concern. However,

research studies are working on improving the performance of membrane distillation process and increasing the lifetime of the membrane. Membrane fouling is a dynamic process that is affected by several factors such as membrane properties, operating conditions, and the quality of feed water. Many research studies are done on improving the flux performance by optimizing the operating conditions and modifying the MD membrane surface.

In this review paper, enhancing MD performance is focusing on mitigating membrane fouling. The core aspect of membrane fouling is the association of membrane surface with various particles available in the feed solution. These interactions are undergoing different mechanisms that will cause different particles to deposit inside the pores, and/or on the surface of the membrane. Consequently, causing different types of membrane fouling; organic fouling, biofouling, inorganic fouling, and colloidal fouling. Although fouling mechanisms for the four types of fouling were discussed in detail in this review, a deep understanding of fouling mechanisms is still lacking. Most of the research studies are investigating each fouling mechanism separately. However, membrane fouling in the real life is a complex phenomenon where all types of membrane fouling can occur simultaneously. Another point that makes membrane fouling hard to understand is that the majority of research studies are using synthetic solutions that do not reflect on the real components of the feed solutions.

In addition, it has been found that there is a lack of mathematical models that can predict the fouling mechanisms in MD system. Therefore, more simulation work should be conducted regarding MD process to understand the thermodynamics and mechanisms of membrane fouling. Computational Fluid Dynamics (CFD) simulation, for example, can predict the performance and the degree of fouling at various parameters including the impact of feed composition, membrane properties, operating conditions, and the duration of the experimental run. Therefore, using different simulation work could contribute to the knowledge of understanding fouling mechanisms in MD.

Table 6
Water Production Cost (WPC) of different water treatment systems.

Treatment Process	Type of feed water	Plant Capacity	Water Production Cost (\$ m ⁻³)	Ref.
MD Process only (without an alternative source of heat)				
DCMD	Synthetic saline water	–	1.23	[244]
DCMD	Synthetic saline water	–	1.50	[249]
MD Process with waste heat recovery				
AGMD	–	3600 L/h	~5.50	[238]
DCMD	–	3600 L/h	~3.20	[238]
DCMD	Synthetic saline water	24,000 m ³ /day	1.17	[244]
MD Process with solar energy				
DCMD	Synthetic saline water	10 m ³ /day	21.0	[241]
DCMD	Seawater	39 m ³ /day	0.314	[250]
DCMD	Seawater	40.7 m ³ /day	0.392	[251]
AGMD	Brackish water	10 m ³ /h	1.30	[240]
AGMD	Brackish water	100 m ³ /h	1.6	[240]
AGMD	–	100 L/day	15.0 – 29.9	[252]
RO Process				
RO	Synthetic saline water	–	0.50	[244]
RO	Synthetic produced water	–	5.0 (€ m ⁻³)	[245]
RO	Simulated brackish water	468 m ³ /day	5.14 – 7.90	[246]
RO Process with solar energy				
RO	Simulated seawater	200 L/day	5.20 – 6.64 (€ m ⁻³)	[247]
RO	Simulated seawater	15 L/h	3.75 – 4.85 (€ m ⁻³)	[248]

After discussing different fouling mechanisms, this review paper investigated the possible membrane fouling mitigation methods and suggested potential approaches for different foulants. The majority of the reviewed research studies are focusing on the inorganic type of fouling. It was found that the best mitigation method for inorganic fouling is to avoid inorganic foulants to reach their supersaturation phase. Therefore, pre-treatment method of adjusting the solubility of these particles by controlling the feed temperature and pH is considered as the optimal mitigation method for inorganic fouling. Moreover, cleaning the membrane from the fine inorganic particles that can infiltrate into membrane pores and block the functionality of the membrane is very challenging. Another possible mitigation method for inorganic fouling can be cleaning the membrane with an acidic solution. However, this practice can harm the membrane and reduce its lifetime.

On the other hand, organic fouling can be easily mitigated by cleaning methods. Humic acid or organic macro-particles available mainly in wastewater solutions can be effectively removed by backwashing or flushing the membrane with 0.1 M NaOH solution. It is interesting to point out that polysaccharide materials show a minimal tendency toward fouling formation due to their hydrophilic nature. Therefore, no mitigation method is required for these particles. Although, organic fouling can be mitigated easily. In reality, organic fouling usually coexists with biological fouling. When these two types of

Table 7
A summary of suggested mitigation methods for different foulants.

Type of Fouling	Foulant	Negative Effect	Suggested Mitigation Method
Organic fouling	Humic Acid (HA)	Pore wetting	Backwashing
	Polysaccharide (AA)	Penetration to permeate side	Flushing (0.1 M NaOH)
	Protein (BSA)	Hydrophilic Minimal fouling	NA
Inorganic fouling	Alkaline scale CaCO ₃ , Mg(OH) ₂	High molecular weight No pore wetting	Flushing
		Gel layer formation	
	Non-alkaline scale	Convert the feed into basic solution	Chemical water softening
Biological fouling	CaSO ₄	Start precipitating at feed temperature of 20C	Membrane Filtration
		More difficult to clean than alkaline scaling	Acidification
	MgCl ₂ , MgSO ₄ Calcium phosphate	When antiscalants are used for CaCO ₃ mitigation	Thermal softening
Colloidal fouling	Biofilm, bacteria, fungi, microorganism	Pore wetting	HCl washing
		Pore blockage	Optimizing feed composition and operating conditions
Colloidal fouling	Silica, silt, clay, corrosion products	Complete exclude by pre-treatment is difficult	Antiscalant
		Low pH of the feed solution	
Colloidal fouling	Silica, silt, clay, corrosion products	Large particles	Chlorination
			Coagulation/ Flocculation

fouling appear together, mitigating biological fouling becomes very difficult. If organic components will not be eliminated in the earlier stages of the process, biofilm formation will grow continuously by feeding on it. Pre-treatment methods failed to provide an adequate solution to mitigate biofouling. Moreover, the lack of data for biofouling is making the prediction of suitable fouling mitigation methods is difficult. Therefore, operating the feed solution at high feed temperatures in addition to the chlorination process can minimize biofouling.

The last type of fouling which is colloidal fouling has a lack in research studies too. It was found that pre-treatment methods such as ultrafiltration or microfiltration can help in controlling the colloids extend in the feed solution. Nevertheless, it was found that the total removal of the colloids from MD feed solution is still hard to achieve. Table 7 summarizes all the suggested fouling mitigation methods for different foulants to reduce fouling in MD. Even though membrane fouling is getting lots of attention in recent years, still there is a need for further investigations of different factors that cause membrane fouling.

Economic feasibility of MD process was investigated by evaluating water production cost (WPC). Operating MD process with an alternative source of heating can reduce water production cost (WPC) and protect the environment. The combination of MD process with waste heat can be very beneficial to reduce the cost of produced water. On the other hand, the combination of MD process with solar energy can increase the water production cost if it is operated with a small plant capacity. It is important to point that membrane fouling can affect negatively on the MD process performance, thus the water production cost. This is due to the fact that replacing a fouled membrane is considered one of the most expensive factors involved in the water production cost calculation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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