A review on sources, types, mechanisms, characteristics, impacts and control strategies of fouling in RO membrane systems

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A B S T R A C T

Reverse osmosis (RO) is the largest promising and popular water treatment technology with a distinguished rank at the top of the list compared with other water treatment methods. Unfortunately, RO technology is adversely impacted by fouling, the most crippling obstacle to its spread use in the water treatment industry. Membrane fouling is known to be the process of undesirable matter accumulation on the membrane surface or inside its pores resulting in the reduction of the membrane permeates flux as well as its overall efficiency. This article comprehensively illustrates fouling sources, impacts, influencing factors, characterization, types of fouling, formation mechanisms, and nature. Furthermore, membrane cleaning strategies, fouling control, prevention, and mitigation are also covered. The article emphasized that membrane fouling is an inevitable issue of RO technology and it must be controlled, minimized and if possible overcome. Despite the big efforts made by researchers towards doing so, they need to further understand the fouling issue and strategies to control and mitigate it is consequently in need of further research and investigation. Additionally, novel membrane materials and innovative manufacturing processes should also be adopted to reduce the fouling potential and to provide radical solutions for fouling. Advantageously, this review has the following distinguished merits (1) comprehensive coverage of RO membrane fouling applied in the desalination industry including types and sources, influencing factors, cleaning methods, and prevention and control strategies, (2) constructing a systematic historical referenced-based record of literature fully dedicated for RO membrane fouling applied for desalination industry, and (3) Selectively indicating recent progress and achievements towards understanding and mitigating membrane fouling effects.

Keywords: Reverse osmosis; Treatment; Fouling; Cleaning strategies; Fouling control; Novel membrane materials; Desalination industry

1. Introduction

Water shortage continues to be a major challenge to humanity across the globe. Modern lifestyle and extreme advancement of technology as well as population growth aggravate this challenge with time. The increasing demand for freshwater requires innovative strategies and plans including but not limited to wastewater reuse and seawater desalination; which have been adopted already in many regions around the world. Among the most favorable methods utilized to produce water of lower impurities level is the membrane technology [1]. Membrane technology is used to produce potable water registering a fast breakthrough in the number and size of plants and is driven by the increasing water demands for domestic, industrial, agricultural activities, economic growth, and urbanization [2,3]. Water treatment technologies depending on membranes have remarkable characteristics, such as the lower size of
occupation, higher volumetric rate, outstanding permeate quality, and excellent disinfection ability. So, recently, they have become a shining star in the fields of wastewater treatment, seawater desalination, and sustainable energy regeneration and optimization [4]. The most popular membrane technologies used for water treatment include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), forward osmosis, membrane distillation, electrodialysis and pervaporation [1].

Recently, RO has become the most promising and popular water treatment technology and rendered as one of the top-best water treatment technologies ever [5,6]. RO membrane technology is extensively utilized to produce high-quality water for safe drinking and domestic purposes as well as treatment of various wastewater effluents. RO is utilized in many countries for producing ultra-pure, drinkable, and process waters as well as water recycling and resource recovery. Additionally, RO membranes have many advantages including the provision of high-water permeability, rejection of dissolved solids, the ability to benefit from energy recovers, and conformity with the strictest public health regulations and environmental protection standards and treatment methods. It is therefore a reliable technology with extended capacities to remove microorganisms, organic contaminants, precursors of disinfection by-products, colloids, and other pollutants. Nowadays and when it comes to the desalination industry, the energy demand for 1 m³ is nearly 1.8 kWh, which is greatly lower than the energy demand of any other known desalination methods [1,7,8].

Problematically, RO technology is adversely impacted by fouling, the most crippling obstacle to its spread use in the water treatment industry [5,9,10]. The term membrane fouling describes the process of unwanted materials accumulation (known as foulants) onto the membrane surface or inside its pores. It results in: reducing the active surface area and permeate flux of the membrane, increasing power consumption, increasing periodical membranes cleaning-in-place (CIP) procedure, degrading membrane solute rejection over the period of membrane operation, and adversely impacting the stability of the operation. Practically, in RO systems, the flow distribution in a vessel is irregular; the first membrane element generally produces about 25% of the total vessel permeate flow while the final element yields about 6%–8% of the total vessel permeate, as shown in Fig. 1. The decrease of permeate production with the length of the membrane vessel is basically resulted from the increase in feedwater salinity and associated osmotic pressure as the permeate is removed from the vessel [11–15].

Despite the rapid advancements and developments RO technology experienced; membrane fouling is and will remain, the major bottleneck for water purification and desalination systems. Membrane fouling is currently considered the most challenging issue that limits the potential of the RO technique. This is due to the impacts of fouling on the permeate water quality [16–19]. Membrane fouling phenomena receive a great concern from manufacturing companies, process designers, plant operators, and researchers mainly due to its main effects on the desalination process efficiency and economics. Membrane fouling is systematically the main hurdle that hinders process effectiveness by lowering membrane permeability, reducing the permeate rate, destroying the membrane selectivity, raising the operational and maintenance costs, increasing the energy requirements to keep the membrane performance constant, demanding additional labor for maintenance, raising the cleaning chemicals cost, and reducing the membrane lifetime. It also results in less membrane permeate compared to the estimated amount of the membrane for a certain driving force using a specific membrane. Therefore, membrane technology applications within the desalination industry as well as other water treatment industries continue to have fouling at the top of the challenges and issues list. Forming an external layer on the membrane surface while water is being filtered is the main cause of the membrane's production capacity loss. Membrane fouling needs powerful and superb techniques for restraining and reduction [16–18,20–23].

Due to the deleterious influence for the whole performance of the desalination process, membrane fouling must be addressed in a suitable and careful manner, taking into consideration the membrane process dedicated to desalination which is basically a pressure-driven process (i.e., RO, NF, etc.) [24]. This would significantly assist in
avoiding potential glitches represented by membrane damage and frequent and rapid replacement of the membrane. In general, fouling is categorized into external and internal. When the rejected materials are accumulating onto the outer membrane surface, external fouling will occur. External fouling points to the build-up layers similar to cake or gel onto the feed side of the membrane surface. It includes three distinct mechanisms: (1) build-up of scale, (2) cake formation, and (3) formation of the biofilm. On the other hand, internal fouling results due to the sedimentation or adsorption of minute solids or macromolecules in the membrane internal pores. Internal fouling causes alterations to the membrane structure, this can be explained by the physical compaction or chemical degradation; these changes will affect the solute and solvent transport within the membrane. Physical compaction of the membrane structure can happen due to the long-term application of feed water at pressures higher than what the membranes are designed to withstand [typical values are 41 and 83 bars for brackish and seawater desalination membranes respectively] and/or from prolonged operation at feedwater temperatures over the limit of safe membrane operation (40°C–45°C). Internal pore-clogging results when unwanted materials or foulants are sedimented within the pores by incomplete clogging (gradual pores diminishing), and then as time passes, by complete pores clogging. External fouling can be reversed and overcome by using certain chemicals, but internal fouling or pore-clogging is irreversible in the majority of cases due to foulants compression and membrane material deterioration [5,11,18].

Fig. 2. Types of foulants with examples.

As membrane fouling has great importance, it is important to present an up-to-date review of RO fouling and its control. This review provides a wide thorough and systematic referenced-based knowledge concerning the comprehensive aspects of the membrane fouling phenomenon. It also provides a new distinguished angle of looking into membrane fouling where not only general or partial perspectives are traced and covered historically but a comprehensive and systematic approach reflecting the weight and importance of fouling issues is followed. It is worth mentioning that this review is dedicated to outlining RO membrane fouling associated with desalination applications where a comprehensive summary of RO membrane fouling, types, sources, impacts, and mechanisms are illustrated. Additionally, state of the art strategies of membrane fouling mitigation and minimization, surface modification techniques; including novel membrane antifouling materials and synthesis process are covered. As well, some of the latest advances, emerging studies, and issues concerning membrane fouling optimization and control are also presented.

Unlike many previous reviews where the focus was either to illustrate membrane fouling in general regardless of membrane-type (not specifically RO or its application in the desalination industry) and/or to fouling issues associated with the membrane characterization or operational conditions and/or membrane control strategies, this review covers RO membrane fouling and control strategies within desalination applications comprehensively in systematic historical order including recent progress made by a large number of researchers supported by results-based data and information.

The advantages of this study can be summarized as follows (1) provision of comprehensive coverage for RO membrane fouling applied in desalination industry including fouling types and sources, influencing factors, cleaning methods, and prevention and control strategies, (2) constructing of systematic historical referenced-based record of literature, and (3) selectively indicating recent progress and achievements towards understanding and mitigating membrane fouling effects.

2. Sources and types of fouling

Sources of fouling (termed as foulants) usually contain colloidal materials, moderately dissolved solids, dissolved organic solvents, micro-organisms, protein molecules, and other particles. Fig. 2 illustrates different types of foulants with examples for each type. Since colloidal materials are accumulated and attached to the membrane surface and the flowing water impedance into the membrane is increased; these particles are believed to be the main source of external fouling. Colloidal materials may contain clay particles, colloidal silica, oxy-hydroxide, aluminum, iron and manganese oxides, organic colloidal matter, large organic macromolecules, colloidal organics, suspended materials, and calcium carbonate resulting from precipitation methods [18].

According to the type of the foulant substance accumulated onto the membrane surface, fouling is categorized into colloidal, organic, inorganic, and bio-fouling. However, membrane fouling usually occurs in a combined
pattern, where the four types of membrane fouling cannot be clearly distinguished. Fig. 3 outlines scanning electron microscopy (SEM) images of different fouling types on membrane surfaces. Colloidal fouling is the colloidal matter accumulation onto the surface of the membrane; which results in forming a cake layer. Organic fouling is the attachment of organic substance onto the membrane surface. Inorganic fouling results due to the sedimentation of inorganic particulates, colloidal matter, and crystallization of solids and salts originally present in the feedwater in the membrane pores. Bio-fouling results due to the adhesion and growth of bacterial cells, viruses, fungi, and algae on the membrane surface [1,18,25,26].

The fouling of RO membranes commonly results from the sedimentation, precipitation, and/or attachment of different substances on the membrane surface. This will lead – as time passes – to the deterioration of the main purposes of the membrane, such as permeate flux, efficient solids removal, and pressure decline through the membrane [1]. The main mechanism describing fouling in RO membranes is usually linked to the surface fouling on the polyamide (PA) layer of thin-film composite (TFC) membrane, this is due to the fact that RO membranes, in comparison with micropores membranes, lack the noticeable internal pores. The coming sections present an overview of the mechanism of each type of fouling, its effects on the membrane characteristics, and the overall membrane functionality through the desalination process [27].

2.1. Organic fouling

Organic fouling describes the deposition or sedimentation of the dissolved and colloidal organic materials onto the external membrane layer. It results from various types of materials that are dissolved within the feedwater with the ability to be attached to the membrane surface.
These materials include oil, macro-molecules, proteic materials, anti-foaming substances, fulvic acid, polysaccharides, and polyacrylic polymers. Fouling becomes more severe with increasing concentrations of humic acid. The previously mentioned materials will enhance forming an organic gel layer onto the membrane surface or inside the pores. Adsorption is responsible for the first accumulation of the foulant onto the surface of the membrane. Organic foulants sedimented onto the membrane are commonly difficult to remove, but possibly easy when using chemical substances [18,32,33].

Organic material molecular size also affects the membrane fouling and the filtration process itself. Organic materials that have larger molecular weight compared to the pore size of the membrane may probably cause clogging to membrane pores, and leading to lower flow through the membrane. Organic materials characterized by a small molecular weight compared to the pores of the membrane will get into these pores, and will also impact the flow through the membrane and result in pore-clogging [34,35].

Another mechanism for organic fouling results as different foulant species interact with each other (electrostatic attraction, hydrophobic effect, and hydrogen bonding) and form aggregations in feeds [36,37]. For example, the aggregation of bovine serum albumin (BSA) and humic acids could be formed by the bond between the amide groups of BSA and the hydroxyl groups of humic acids [38].

2.2. Inorganic fouling

Inorganic fouling is commonly defined as scaling, being the precipitation of the deposited hard salts originally found in the feedwater which encompasses crystallization (of solid salts, oxides, and hydroxides) and transport mechanisms. Calcium carbonate (CaCO₃), calcium sulfate (CaSO₄), calcium phosphate Ca₃(PO₄)₂, sodium chloride (NaCl), magnesium sulfate (MgSO₄), magnesium carbonate (MgCO₃), magnesium bicarbonate Mg(HCO₃)₂, barium sulfate (BaSO₄), iron oxides (Fe₂O₃), aluminum oxide (Al₂O₃), and aluminum silicate in the form of kaolinite (Al₂Si₂O₅(OH)₄) are the main inorganic fouling constituents. Additionally, inorganic colloidal matter and residues including silica, silt, clays, and corrosion causing products, are greatly contributing to inorganic fouling. Moreover, inorganic fouling can also happen when the ionic product of moderately soluble salt overrides the equilibrium solubility product (salts concentration is more than the level of saturation), therefore, the formation of precipitate will occur [39–42]. It is reported that iron and manganese oxidizes can be categorized in a separate fouling type, namely metal fouling because their origin can be linked to popular operational practices; mainly coagulation [23].

Dissolved solids concentration may be raised by 4–10 folds when desalinating water by the RO technology, which could result in crystallization as the limit of their solubility is overridden. Membrane inorganic fouling happens as the ions of the over-saturated solution crystallize on the membrane surface via surface crystallization and bulk crystallization. Surface crystallization occurs basically due to the lateral scale accumulation and is more dominant at higher operating pressures and slower cross-flow velocities. Bulk crystallization is attributed to the consistent particles’ growth within the bulk phase and is much favored at higher pressures and moderately cross-flow velocities. These two mechanisms are responsible for RO membrane flow declining and surface clogging [43]. Fig. 4 outlines the main phases of inorganic fouling in RO membranes.

To minimize the inorganic fouling, it is recommended to lower the solution pH, taking into account that this solution is not always applicable; therefore, the use of antiscalants will be suitable. In this case, the effective ingredient is a mix of different molecular weight poly-carboxylates, polyacrylates, and poly-electrolytes, such as poly-phosphonates and poly-phosphates [18].

(a) Introduction of antiscalants and chelating agents to maintain solubility, (b) use of chemical dispersants that obstruct micro-crystal and/or floc aggregation in suspension,
or that interfere with association of micro-flocs with the membrane surface, and (c) cleaning of established mineral scale by treatment with acids, surfactants, and/or proprietary commercial products.

2.3. Biological fouling

Membrane biological fouling can result from the aerobic bacteria, such as those found in brackish water, seawater, and wastewater systems, and/or anaerobic bacteria found in groundwater systems [45]. Biological fouling occurs when algae, plants, fungi, sludge, yeast, or micro-organisms accumulate on the wet surfaces of the membrane, resulting in forming a glutinous slime layer. This layer is formed when microorganisms, the main culprit of biofouling, grow at appropriate conditions of temperature and nutrients in water treatment utilities. Its formation starts as the free-floating micro-organisms adhere to the membrane surface. Biofouling can be characterized by surface attachment, dissimilar structure, genetic variety, complicated community interactions, and adequate use of extracellular matrixes of polymeric materials. Biofouling has negative impacts on membrane life and permeates flux and quality. It leads to loss of productivity and results in serious operational problems [18,24,46].

Great efforts and research are still being developed to understand biofouling and to suggest new antibiofouling solutions [47]. Unfortunately, biofouling has not been adequately elucidated, since its mechanism is complicated by the interactions between foulant-foulant and foulant-membrane surface [48]. Fig. 5 presents the probable stages of biofouling formation. Firstly, the bio-foulants attach to the membrane by a weak van der Waals force. Once they are irreversibly attached, these bio-foulants tend to link themselves permanently by cell adhesion structures. Secondly, the first colonists will ease the arrival of new cells by keeping much various adhesion locations and building the medium that keeps the biofilm jointly. When colonies are formed, the biofilm may build by combining cell division and recruitment. The last stage is the development; in which biofilm establishment takes place and the cells get much resistant [18].

According to statistics given by Khedr [50], and based on sets of conducted fouling study campaigns, seawater reverse osmosis (SWRO) fouling is caused by 41 biofoulants (48%), inorganic colloids (18%), organic compounds (15%), silicates/silicates (13%), mineral scaling (6%) and coagulants (5%) [50]. Biofouling in a SWRO plant is controlled by the surrounding environment as well as the pretreatment of feed water. The population of bacteria in seawater is dependent on various environmental factors such as light, temperature, tides, currents, turbidity, and nutrients. SWRO module is more vulnerable to biofouling in hot climatic conditions. For example, the degradation of humic acid is much easier and greater at a temperature of 35°C than 18°C. The degraded small molecules are a source of nutrition for bacterial growth, so, the biofouling potential is expected at the increased temperatures. For the case of the Middle East and the Gulf Region, about 70% of the seawater RO plants suffer from biofouling problems which can be resolved by the application of several physical and chemical disinfection techniques. Thus, the main reason for flux decline in RO plants in the Middle East is biofouling [46]. Due to the high influx of microorganisms in the seawater and the build-up of nutrients on the membranes, biofouling is one of the biggest challenges desalination plants face; which is the case of Gaza Strip – Palestine. For the case of the Sorek desalination plant, located in Israel, an innovative chemical-free approach was developed to mitigate against biofouling. The seawater is passed through porous lava stone which functions somewhat like a wastewater trickling filter or biologically active filter, giving the microbes somewhere to settle before reaching the RO unit and protecting the membranes [51].

2.4. Colloidal (particulate) fouling

Colloidal fouling occurs when the colloidal particles accumulate on the surface of the membrane or into its pores throughout the solid removal process. Fig. 6 shows a probable schematic illustration of colloidal fouling. Colloidal fouling negatively impacts the quality (a type of solute) and the quantity (permeate flow and solute concentration) of the permeate. When membranes are utilized for RO, NF, UF,
particulates are accumulated into the surface of the membrane and a cake layer starts to form; leading to an extra hydraulic resistance to water flux, hence, lowering the flow of the produced water. When MF membranes are considered in water treatment, the colloidal matter may clog the pores and deposit onto the surface of the membrane. The range of cake layer formation and pore-clogging depends upon the particle size in comparison with the size of the membrane pores [18].

3. Overall impacts of membrane fouling

Generally, membrane fouling can result in an acute decline of the permeate flow rate; this is fundamentally due to the diminishing of the membrane active area and raising the flow impedance throughout the membrane. Moreover, fouling can result in cake enhanced osmotic pressure impacts where the concentration polarization impacts are aggravated because of the fixed layer above the membrane surface. In general, membrane fouling is considered a significant problem because of its major impacts on the reduction of flow rate, productivity, quality of permeate, and lifespan of membrane. It also results in raising the feed pressure and energy demand, increasing the need for pre-treatment and membrane maintenance, increasing the cost of membrane cleaning and exchange [52,53].

4. Factors influencing fouling

Membrane technology involves complex interactions between the membrane surface, processing conditions, and effluents under treatment. Many factors affect the fouling formation rate, they include: salts nature and concentration, water properties, membrane material and surface properties, the membrane pores size and their distribution, membrane size, operating pressure, membrane selectivity, and the hydrodynamic properties of the membranes. The interaction among these factors will produce multifaceted impacts on membrane fouling. Recognizing the fouling occurrence is very essential to get a suitable tactic to minimize, mitigate, and clean the fouling formation. Membrane fouling – whether it is external or internal – is a complicated process, because it is influenced by various parameters [17,24,54,55]. Cipollina et al. [56], based upon data of many years claimed that intermittent operation results in increasing membrane fouling rates and higher membrane fouling rates have been reported in intermittently operated plants [56]. However, up to date, no one either validated this claim experimentally or evaluated how effective is the simple treatment methods in reducing the resulting membrane fouling [57]. The parameters that affect or speed up to the membrane fouling can be categorized into four groups based on their sources, and they are discussed in the following sections.

4.1. Foulant characteristics

Foulant characteristics comprise the type of the foulant existing in the feedwater as well as its characteristics; including its nature, size of the molecule, solute concentration and its solubility, diffusivity, hydrophobicity, and charge. Moreover, many other parameters enhance the fouling tendency including particle interaction and the interaction between the foulants and the surface of the membrane [18]. According to the current experience concerning membrane fouling and based on the foulant type, fouling may be classified as:

- **Particle fouling**: it is formed by two consecutive classical clogging steps. Firstly, the deposition of bigger particulates on the membrane surface, and the smaller particles stay inside the membrane pores. Secondly, the cake is formed as more and more particulates are sedimented on the first layer to the extent of forming highly resisting membrane flow.
- **Organic fouling**: it occurs due to the presence of natural organic matter (NOM) within the feedwater source. NOMs are commonly found in natural water, and its removal remains a needy issue. Molecular weight (MW) and hydrophobicity properties are usually used to classify the NOM. Regarding the MW, the fouling level due to NOM can be categorized into moderate to low MW fractions of NOM, then high MW fractions deposited onto the membrane surface. Many studies concentrated on the influence of the NOM hydrophobicity on organic fouling; these studies revealed that the mechanisms responsible for the fouling by hydrophobic parts, hydrophilic fractions, and transphilic components were concentration polarization, adsorptive fouling, and cake layer formation, respectively [58,59]. Dissolved organic matter (DOM) – as a whole – will result in very intense fouling than that results from every individual component of the DOM. Other studies tackling the organic fouling concentrate on the methods of fractionation, to figure out the responsible fraction of NOM that cause fouling [60].
4.2. Membrane properties

Membrane properties of concern are type, pore sizes, porosity, distribution of pores, surface morphology, charge, roughness, hydrophobicity, membrane module hydrodynamics, and other physical and chemical characteristics. The fouling level is instantly related to the membrane physiochemical characteristics. Membrane physical properties are the surface roughness, pore size, and structure, while the chemical characteristics are hydrophobicity, hydrophilicity, the surface charge, and surface functional groups [63, 64].

The fouling tendency can be enhanced by the interaction between the surface of the membrane and the foulant type; therefore, the membrane characteristics can dramatically influence the fouling. Membrane surface roughness also influences fouling, this is due to the fact that the rough surface is characterized by slips and peaks where the solutes are carried. Because of depressions, the feed solutes may be accumulated inside the pores and accumulate on the membrane surface, which causes clogging and result in flow reduction [65].

Membrane hydrophobicity may tend to encourage fouling; hence, there is a need to manufacture membranes of lower hydrophobicity [66] by fine-tuning their surface characteristics. Membrane surface charge has a great effect on the fouling mechanism; this is due to the fact that more surface charges will result in a strong bond between the membrane surface and the solutes already exist in the feedwater. Moreover, fouling may be lowered by the effect of the repulsive force between the two components, which tend to hinder the sedimentation or adsorption of the foulant on the surface of the membrane. Membranes characterized by a smooth surface and neutral charge are subjected to minimal organic fouling [67].

4.3. Operational conditions

Operational conditions include the transmembrane pressure, temperature, velocity of the cross-flow, and turbulence producers. Fouling rate is also affected by other factors, like; flow rate, flow velocity, system configuration, and design, system cleaning and shutdown, and the used cleaning methods. Many researchers revealed that higher initial flux will promote severe membrane fouling as a result of increased permeate drag force, enhanced concentration polarization, and result in a denser foulant layer [68]. Severe membrane fouling only takes place when the flux exceeds the critical flux [69]. The membrane fouling rate is also influenced by the rate of the permeate flow. In general, if the rate of flow is small and the cross-flow velocity parallel to the surface of the membrane is high, the fouling rate is low [18]. Fouling rates increase exponentially with flux and require the use of high driving pressures and usual chemical cleaning [70]. It is well known that membranes of high areas will lead to the use of lower pressure and more feed and concentrate flows. Shear actions can be utilized to flush the foulants away from the membrane surface. For better foulants removal, it is advised to perform system flushing on shutdown or at start-up and even sporadically in the standby phase. One cause to perform such a technique is that the rate of biological fouling may speed up rapidly when the system is not operating and no flux is flowing [18].

Generally, a higher temperature is favorable to the membrane fouling because of reducing the feedwater viscosity and concentration polarization [71]. However, this is dependent on the foulant type. For example, a higher temperature can trigger the denaturation of protein and expose its inner hydrophobic portions to the surrounding, which increases the tendency of aggregation or adsorption to the membrane surface [72].

4.4. Feed water characteristics

These characteristics include water chemistry, pH, ionic strength, and the presence of organic and non-organic materials. Membrane fouling is largely dependent on the pH, ionic strength, ionic composition (e.g. Ca\(^{2+}\), Mg\(^{2+}\)), and type and concentration of foulants in the feedwater [73]. Many existing literature proved that fouling was encouraged by low pH, high divalent ion concentration, and high ionic strength [74]. Moreover, the degree of pre-filtration and removal of particles may also influence the fouling process. External fouling occurring onto the surface of the membrane is largely affected by the feedwater chemistry [18]. Belkacem et al. [75], stated that using the RO membrane with 50% brine recycling will lead to membrane fouling. However, despite this disadvantage, it will allow reducing the yearly water consumption by about 25%.

5. Characterization of membrane fouling

Important objectives of characterizing foulant layers and membrane surfaces are quantifying their elemental composition and estimating the thickness of the foulant layer. These objectives will provide us with conclusions to be drawn related to the types of foulants including foulant layers and the severity of fouling [76]. Up to date, plenty of characterization methods have been suggested and/or applied to understand the characteristics of fouling, the mechanisms underlying fouling, and to explain or prove the efficiency of some fouling control mechanisms [4]. To illustrate the fouling mechanism, deposit morphology and composition of foulants have been characterized by many methods [77]. These methods are utilized to optimize the membrane operation and to determine the real causes resulting in membrane fouling. Of these methods, optical microscopy (OM), SEM, energy-dispersive X-ray spectrometer (EDS), and atomic force microscopy (AFM) are utilized to facilitate detailed information about fouling [78].

OM characterization is usually taken as the first step in microscopy observations to provide a low-resolution overview. It is also a convenient method that uses an optical
microscope to characterize the surface of the membrane by indirect observation of its cross-section [79]. OM is able to figure out various foulants by their color, size, crystalline structure, or other features. Famous types of foulants that can be identified by OM are iron oxide and bacteria. One limitation of utilizing OM for membrane examination is the need for a transparent sample. This is usually attained by scratching the foulants from the membrane and setting them on a glass plate. However, the possibility of scratching foulants from the membrane is not usually possible, and the tendency of losing necessary information about the foulant structure is high due to foulant scratching. In addition to that, focus depth and the restricted magnification lower the benefit of OM. Hence, SEM is believed to be a more suitable technology for membrane autopsies [78]. SEM is the most widely utilized electron microscope in the characterization of the membrane surface. It is based on the interactions of the electron beam and the membrane to get the image. It gives deeper focus and larger magnification in comparison with OM. On the other hand, EDS, a chemical microanalysis method, is usually used in conjunction with SEM [79]. SEM can also be coupled with EDS, which gives the elemental composition of the area or particle being imaged by the SEM. One more advantage of SEM is that no need to remove the foulant from the surface of the membrane before analysis. Therefore, SEM-EDS is able to give numerous data about the size, shape, structure, and chemical composition of the foulant [80]. In many cases, SEM-EDS is utilized as a means for membrane failure investigation; for example, damage due to chlorine or biological degradation may be examined by SEM-EDS [81]. It is worth to mention that SEM can be utilized in different fields of RO membrane development [82].

Newly, AFM is utilized to characterize the membrane fouling. With AFM, it is possible to attain the same magnification of SEM level or more with the merit of more suitability to measure the surface roughness. AFM and SEM can be used to obtain the RO membranes surface morphology and can relate the surface roughness to membrane permeability [83,84]. With AFM, membrane surface morphology can be got, and the relation between the surface roughness and colloidal fouling of membrane can be obtained [85]. From the previous discussion, it is obvious that microscopy technology can be used for analyzing foulants and investigating membrane surface. It is always utilized to investigate the cause of fouling but is not a common method to study membrane failure [80]. Table 1 presents a comparison between the different methods of fouling characterization.

6. Fouling mechanism

The fouling mechanisms for permeable MF and UF membranes and semipermeable RO membranes may greatly differ, depending upon the types of foulant present in the feedwater. Fouling of MF and UF membranes always happen because of a combination of micropore clogging and cake formation on the membrane surface. RO membranes are generally fouled by the formation of a cake of deposits on the membrane surface (without pore-clogging). Since small particulates generate significantly higher resistance in the filter cake than big particles, their impact on RO membrane fouling can be much more obvious than that of the large-size particles captured by the SDI test [11]. To realize how fouling occurs, it is important to figure out the interaction forces between the foulant particles and the membrane surface [24].

Although RO membranes have gained much attention from both the academic and industrial sectors, the fouling mechanisms of solutes on RO membranes are complex, interconnected, and still not fully understood [18,86]. Monitoring the formation stages of the conditioning film and the following deposition process is thus very important in order to understand and ultimately control fouling [87]. A better understanding of membrane fouling is not only the key to overcome the fouling problems, but also is one of the major factors driving membrane technology-forward [88]. Membrane fouling is basically governed by the electrostatic interactions between the organic compounds and the membrane surface (initial fouling) and among organic molecules (the development of the fouling layer) [89].

There is no unified statement about the mechanisms of membrane fouling, but from the analysis of the causes of membrane fouling, the most popular mechanisms can be classified as follows:

- Solid material adsorption onto the membrane surface and into its pores.
- Cake layer accumulation onto the outer membrane surface.
- Pore blocking due to the presence of solutes within the brine.
- Biofouling resulted from the presence of micro-organisms [18,90].

Focusing on RO membrane fouling, the four-stage theory is proposed. The first stage is that the organic materials including humic acid, polysaccharide ester, and other large molecules, adsorbed on the surface of the RO membrane result in the incentive conditions for biological growth. In the second stage, the free micro-organisms in water migrate to the surface of the membrane in an unstable reversible state [91].

The third stage is the process of biological accumulation and development which prepare for the formation of an irreversible biological membrane layer. The formation of irreversible biological pollution layer which results in the sharp increase of RO membrane resistance and the decrease of water yield happens in the last stage. However, the majority of the RO membrane surface is so smooth, so, the initial organic matrix is extremely difficult to form [91].

Within RO membranes, fouling can also be governed by the electrostatic force between the charge group of the organics and the charged membrane surface [93]. The increasing electrostatic repulsion force between the negatively charged functional groups and the negatively charged membrane surface leads to the reduction of foulant attachment to the membrane surface. While the attractive force between the positively charged functional groups and the negatively charged membrane surface leads to the increase of the fouling. Moreover, the hydrogen bond also plays an important role in membrane fouling [89,94]. Fig. 7 outlines the possible membrane fouling mechanism [18].

Clogging of membrane pores happens when the solid particle size in the feedwater is greater than that of the
Table 1
Comparison of the different methods of characterizing membrane fouling [76,78–80,82–85,92]

<table>
<thead>
<tr>
<th>Method of characterization</th>
<th>Benefits/features</th>
<th>Limitations</th>
<th>Sensitivity</th>
</tr>
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</table>
| Optical microscopy (OM)    | • Used to determine the fouling causes, membrane surface, and foulants analysis.  
• Can figure out various foulants by their color, size, crystalline structure, or other features.  
• Able to identify iron oxide and bacterial foulants. | • Need for a transparent sample.  
• Focus depth and restricted magnification lower the benefit of OM. | • Can resolve many hundreds of nanometers. |
| Scanning electron microscopy (SEM) | • Images are constructed from the emitted secondary electrons.  
• Used to investigate the fouling causes, membrane surface, and foulants analysis.  
• Gives deeper focus and larger magnification than OM.  
• Can be used in various fields of RO membrane development.  
• Can be coupled with EDS.  
• No need to remove the foulant from the membrane surface prior to analysis.  
• SEM-EDS can be used to investigate membrane failure and can provide numerous data about the size, shape, structure, and chemical composition of the foulant. | • Not a common method to study membrane failure. | • 4 nm spatial resolution.  
• 0.6–3 nm for SEM with field emission.  
• 0.5 nm analysis depth.  
• Magnification up to 100,000, with a resolution of 0.1 μm for regular instruments and 2.5 nm for the most advanced high-resolution instruments. |
| Energy-dispersive X-ray spectrometer (EDS) | • Utilizes the characteristic X-rays.  
• More sensitive toward heavier elements. | • Unable to detect trace foulants.  
• Unable to detect major foulants in the thin membrane or foulant layers. | • Features or phases as small as 1 μm or less can be analyzed. |
| Atomic force microscopy (AFM) | • Used to investigate the fouling causes, membrane surface, and foulants analysis.  
• Can attain the same magnification level of SEM or more.  
• Ability to measure surface roughness.  
• With AFM and SEM, RO membranes surface morphology can be obtained.  
• Ability to relate surface roughness to membrane permeability.  
• With AFM, membrane surface morphology can be got, and the relation between the surface roughness and colloidal fouling of membrane can be obtained. | • Not a common method to study membrane failure. | • 0.1 nm lateral resolution, 0.01 nm vertical resolution; typically, 10−8 to 10−7 N; 10−12 N in the air for non-contact mode.  
• Can have an atomic-scale resolution. |
membrane pore, which leads to a complete pore-clogging. Partial pore-clogging results when solids in the feedwater arrive at the membrane surface and partially clog it or attach onto the inactive membrane areas. Internal pore-clogging happened when solid particles whose size is less than that of pores get into the pores and being either adsorbed or sedimented on the wall of pores. Clogging will restrict the permeate flow and will increase the impedance of the membrane due to pore size depression. When the solid particles neither get into the pores nor seal them; the cake filtration will result and a cake is formed onto the surface of the membrane. Cake formation takes a part in the gross flow impedance, which is the cake impedance and the impedance of the membrane itself [18].

The majority of previous fouling researches had highlighted the impacts of a single type of foulant. However, in many water treatment applications, the feedwater is frequently complex, and contain different foulant types [19]. According to Zhao and Yu [74]; few studies focused on combined fouling by both inorganic colloids and dissolved organic matter. These studies concluded that the combined fouling by organic and inorganic colloidal foulants may be affected by the following mechanism: increased hydraulic resistance, cake-enhanced concentration polarization, and changes in colloid surface properties due to organic adsorption [95,96].

7. Reversible, irreversible and irrecoverable fouling

According to the degree of particle adsorption onto the surface of the membrane and depending upon the efficiency of controlling fouling and technique utilized to clean the membrane, membrane fouling can be categorized into reversible, irreversible, and irrecoverable. The continuous accumulation of the foulants layer when filtering water will result in the accumulation of loosely attached foulants and create reversible fouling, which as time passes, is converted into irreversible fouling that is characterized by forming a strong layer of foulants [97,98]. Irreversible fouling is commonly resulted from highly attached solid particles and enclosed inside the membrane pores [18].

Physical cleaning methods or some specific pretreatment technologies can be utilized to completely overcome the reversible fouling; these methods are not guaranteed to completely overcome the irreversible fouling. Applying a strong shearing action, backwashing, backflushing for porous membranes can also overcome fouling, but these techniques are not applicable for membranes characterized by a non-porous structure. The irreversible fouling may illustrate the slow resistance increase of the membrane after operation for a long time, this increase could happen despite implementing a regular efficient pretreatment and membrane physical cleaning. Irreversible fouling is commonly accompanied by a potent attachment of solid particulates. Hence, it is overcome by common methods of cleaning and pretreatment is unattainable [61]. One way to remove irreversible fouling by using chemical cleaning. Since membrane repetitive chemical cleaning may result in adverse impacts on the membrane lifetime; its recurrence should be kept minimal [99]. Irrecoverable fouling, a type that cannot be removed (recovered) by applying physical or chemical cleaning methods and results from the long-term use of membranes after a series of subsequent physical and chemical cleaning cycles [100].

8. Membrane cleaning methods

Cleaning is the process of removing a material away from another material that is not originally part of it [17]. Great efforts and research are still developing to understand the fouling phenomenon and to propose new antifouling techniques [47]. Identification of the membrane fouling type is necessary before choosing a suitable cleaning technique. Subsequently, data concerning the process type and qualitative and quantitative data of the feedwater source and retained materials is needed so as to give a sign about the fouling type. For example, a high concentration of calcium and magnesium in RO or NF is an indication of inorganic fouling. Historical data about the membranes, their installations, and sometimes the membrane autopsy, are needed to choose the most appropriate cleaning strategy. Depending upon fouling identification and monitoring, a cleaning timetable is proposed [18].
RO membrane cleaning mechanism is yet to be fully understood. This is due to the lack of physical understanding about the interaction between (i) foulants and membrane, (ii) among foulants themselves, (iii) foulants and cleaning chemicals, and (iv) between membrane and cleaning chemicals. The membrane cleaning chemistry and its hydrodynamics are necessary to optimize the membrane cleaning process to reduce both chemical and energy demand [13,101].

The mechanical stability of the fouling layer is disturbed in a two-step process that involves both chemical and physical interactions: (1) chemical reaction between foulants and the cleaning agent, (2) release of the foulants from the membrane surface to the bulk solution by shear forces [102,103]. However, membrane cleaning results in a clean membrane from a physical, chemical, and biological point of view, which will therefore give a suitable flow and solids removal. Different techniques of membrane cleaning can be found in the literature [17,18]. These techniques are grouped into five main sets as shown in Table 2. A brief description of each category is presented in the following sections.

8.1. Chemical methods

When the type of fouling is known, cleaning chemicals can be utilized to expel the foulant from the membrane and to recover the membrane flux. Commonly, membrane manufacturing companies provide the cleaning chemicals to be used with the membranes. Caution is required when using cleaning chemicals including the pH restriction and oxidative effects [18]. Chemical cleaning agents are available in sufficient quantities including acids, alkalis, metal chelating agents, surfactants, enzymes, and oxidizing agents. In chemical cleaning methods, strong or weak acids are commonly utilized for cleaning; specifically fouling due to the presence of calcium carbonate (CaCO₃) [104]. In general, rinsing with acid (usually HCl) is specifically efficient in eliminating inorganic fouling, but rinsing with basic/alkali solution is comparatively efficient in reducing organic fouling. For biofouling, the basic barring technique is the continuous dosing of biocides [105,106]. Considering the fouling locations, rinsing can generally recover the original flow if the scales are only accumulated on the surface. Furthermore, crystal-forming within the membrane pores might be more difficult to remove and may result in pore wetting if rinsed continuously, hence, complete recovery is not possible [24]. Common chemicals utilized for membrane cleaning are:

- **Acids**: citric acid, sulfuric acid, and nitric acid;
- **Bases**: sodium hydroxide;
- **Chelating agents**: citric acid and ethylenediaminetetraacetic acid (EDTA);
- **Oxidizing and disinfecting agents**: sodium hypochlorite (NaOCl), hydrogen peroxide (H₂O₂), and peroxycetic acid;
- **Detergents** [18];

Acids, such as hydrochloric acid, nitric acid, and sulfuric acid are effective in removing membrane scaling while alkaline solutions such as sodium hydroxide are more effective in removing organic fouling and biofouling [1]. The commonly used chelating agent is EDTA [107]. EDTA cleaning efficiency is very sensitive to solution pH (Ang et al. [103]). Operational conditions that may affect cleaning efficiency include cleaning time, crossflow velocity, and temperature [108]. However, the impacts are somewhat limited [109]. Surfactants are usually organic compounds that contain both hydrophobic groups and hydrophilic groups. Sodium dodecyl sulfate is a common surfactant used in cleaning [1].

A study conducted by Guillen-Burrieza et al. [43] on membrane fouling and scaling mainly composed of NaCl and Fe, Mg, and Al oxides revealed that a mixture of acids can be effective in chemical membrane cleaning. In their study, the cleaning was conducted using 5 weight % citric acid, 5 weight % formic acid, 5 weight % sulfuric acid, 0.1 weight % oxalic acid + 0.8 weight % citric acid, and 0.1 weight % detergent agent Na₅P₃O₁₀ + 0.2 weight % EDTA. The best cleaning performance was with using the 0.1 weight % oxalic acid + 0.8 weight % citric acid solutions [18].

Yu et al. [110] proposed a novel method using a thermo-responsive polymer as the chemical cleaning agent and found that it could effectively clean RO membranes that were fouled by BSA. Filloux et al. [111] investigated one-step cleaning using free nitrous acid and found that it could effectively remove biofouling and calcium carbonate scaling. Li et al. [112] developed a new ultrasonic-chemical
cleaning system to control organic and inorganic fouling and found that oxalic acid worked best as the chemical agent. Yu et al. [113] studied the effects of common alkaline and acid cleaning on membrane cleaning. Results have revealed that the use of the common agents has not only removed around 94% and 90% of the total bacteria available on the membranes but also altered the microbial community structure. It should be pointed out that while different chemical agents have different cleaning efficiencies towards different foulants, combining chemical cleaning agents are not effective in certain situations [103]. Membrane cleaning agents should be selected in terms of the specific RO membrane operation situations [1].

8.2. Physical methods

Physical cleaning methods will lower membrane fouling, reduce the repetition of chemical cleaning, hence increasing membrane lifespan, and lessen the operation cost [114]. Many physical and mechanical methods aid the foulants elimination, they are discussed below:

8.2.1. Forward flushing

When forward flushing is done, the barrier responsible for dead-end management is opened. Simultaneously, cross-flow filtration within the membrane is tentatively happening, with no permeate flow. The aim of forward flushing is to expel the deposited layer of foulants on the membrane by creating turbulent actions. The feed-water or permeate goes through the membrane faster than during the production mode. Due to the faster flow and the produced turbulence, solids attaching to the membrane are washed and flushed away. Solids that are absorbed into pores of the membrane are not flushed away; they can only be taken away by backward flushing [115].

8.2.2. Back-pulsing

Back-pulsing is a periodic method of forwarding filtration followed by reverse filtration, it incorporates reversing the flow throughout the membrane by altering the direction of the transmembrane pressure. In back-pulsing, the permeate is pumped in the opposite direction throughout the membrane and this can eliminate the majority of the reversible fouling happening due to pore-clogging. Parameters influencing the effectiveness of the back-pulsing contain feedwater characteristics, membrane characteristics, and operating conditions. In back-pulsing or gas back-pulsing, reverse flow takes place at higher recurrence and for shorter durations (<1 s). Back-pulsing is a favorable physical cleaning technique, it can efficiently reduce the outer and non-sticky fouling and has been applied in different industrial applications. Back-pulsing and high-recurrence back-pulsing result in removing the dirt layer efficiently. This technique is usually utilized for ceramic membranes [116]. It can be done by obliging the permeate back through the membrane via opposite transmembrane pressure [18,114]. Fig. 8 outlines a probable backflushing cleaning method.

8.2.3. Reverse-flow

It is done to eliminate solids reversibly sedimented on the RO membrane surface, so, the solids are washed away by the cross-flow that lowers fouling and enhances the forward flow [114]. RO membrane recovery can be raised and antiscalant usage can be lowered or minimized by applying reverse flow to RO trains [117]. After a certain time of filtration, a flow of clean water is pumped back throughout the membrane from the permeate side, therefore, removing foulants from the membrane surface and lowering the concentration polarization near the membrane surface. Reverse flow can be improved by flushing air within the membrane [114].

Fig. 8. Backflushing cleaning method [18].
8.2.4. Cross-flushing

It is believed to be a simple cleaning technique performed on-site via keeping flow above the membrane while periodically pausing the permeate flow. One merit of this technique; it cancels the pressure decline across the membrane and lets the shear applied by the cross-flow to scour the foulant layer. This technique is efficient as back-pulsing in eliminating the foulants inside the membrane. Hence, an assisting method known as vibration-enhanced membrane separation is deemed to be an efficient technology in membrane cleaning; because the vibratory action will result in taking off the foulant from the surface and the pores [18].

8.2.5. Sponge balls

Sponge balls are utilized in tubular membrane systems with an inner tube of radius greater than 5 mm. In this method, it is needed to utilize sponge balls of radius greater than that of the membrane tube, thus, the foulants are physically removed from the membrane surface [18].

8.3. Gas cleaning/sparging

The air flushing/sparging technique can be utilized to reduce the external fouling and to remove the cake layer accumulated onto the membrane surface [118]. In spite of the availability of different flow schemes, slug flow is the most sufficient scheme to improve the mass flow. This is due to the positive impact of the utilized gas on the whole effectiveness of the cleaning process [119]. Air sparging is always performed either throughout the filtration stage – to lower fouling formation – or periodically to eliminate the already deposited particles. This technique can also be used to clean membranes of variable shapes; including tubular, flat sheet, hollow fiber, and spiral wound [120].

The existence of air bubbles will produce a turbulent flow in the feed side of the membrane, resulting in increasing the permeate flow and the solute separation efficiency [121].

In the gas sparging method, a gas-liquid two phase flow is formed and produces secondary flows; thus, the maximum shear stress applied on the membrane surface is increased. Adopted techniques utilized to control fouling via gas sparging are:

- Secondary flow induced by bubbles;
- Physical removal of the concentration polarization layer;
- Pressure pulsing created by the passage of bubbles;
- Increase in superficial cross-flow velocity [122];

It is recognized that gas sparging can lower temperature polarization and can improve the surface shear rate, and hence delaying the scale’s crystallization at the membrane surface. This concludes that membrane scaling can be reduced by using the gas sparging method [123].

8.4. Non-conventional cleaning methods

In the last decades, the research studies have been concentrated on identifying innovative non-conventional methods for reducing membrane fouling. To this end, combining membrane filtration with different processes such as ultrasound or adsorption has been investigated [124–126]. These methods allow simultaneously, unlike conventional methods, the fouling formation control, and the filtration activity, without their interruption [127]. The following discussion highlights some non-conventional membrane cleaning methods.

8.4.1. Osmotic backwash

It is utilized when the osmotic pressure of the feed-side exceeds the applied hydraulic pressure through the membrane. This method works according to the mechanism of water backflow from the permeate side to the feed side. This flow is induced by osmotic forces or salt (for example NaCl) concentration differences between the membrane’s sides. At the moment the feed begins to flow through the feed channel, the concentration of the polarization layer is reduced and the membrane surface is cleaned. Osmotic backwash with hypersaline solution injection is an effective technique that enhances efficient separation, removes an existing foulant layer, dissolves micro-crystals, and separates biomass from the membrane surface, this is the result of the bio-osmotic shock [18].

8.4.2. Ultrasonic cleaning

Ultrasonic is utilized to enhance penetration in membrane processes, and it can be utilized as a pretreatment step to lower fouling resulting from solid particles and organic matter. In this method, high-frequency sound waves are used to vibrate the aqueous environment; hence they will influence the foulants adsorbed to the membrane surface. The entrance of ultrasound waves into the aqueous medium results in particle dispersion, viscosity reduction, particle surface characteristics variation, and cavitation. The ultrasonic cleaner is composed of an ultrasound generator and a specific device that produces ultrasonic pressure waves. The waves spread within the liquid environment, producing a periodic sequence of compression and expansion stages. Compression produces a positive pressure and pushes the liquid particles to each other, but expansion cycles produce negative pressure and attract the particles away from each other. This method has many advantages including:

- Possibility of cleaning the membrane while it is being used.
- No presence of by-product pollutants and no danger accompanying chemical transport and handling, as for the case of chemical cleaning.
- Hydrogen peroxide and hydroxyl free radical resulted from the ultrasound cleaning can be immediately utilized as disinfectants of potable water networks. This will reduce the dependence on chlorine disinfection that produces hurtful by-products [17,128].

8.4.3. Electrical cleaning

It is utilized as an extra driving force with no increase in the shear stress to minimize membrane fouling and to improve the separation process. Electrical cleaning uses an
electric field produced through the membrane by setting two electrodes on each side of the membrane to improve the permeate flow and eliminate fouling. Occasionally, one electrode may be utilized when the membrane material conducts current, and it can behave as an electrode. The applied electric field induces charged molecules or solids to travel toward the opposite charge electrode. This impact is termed electrophoresis, where an electrostatic force carries the sediments from the membrane surface and removes them away [17,18].

8.4.4. Electrochemical methods

Duan et al. [129] have reported an electrochemical method for the prevention and removal of mineral scales such as CaSO$_4$ and CaCO$_3$ using an electrically conducting CNT-PA RO membrane. They further inferred that a continuous application of an electrical potential (2.5 V) to the membrane surface resulted in pushing CaSO$_4$ crystal formation away from the membrane surface, allowing the dispersal of the formed crystals. In the case of the near-neutral membrane, consequent to the preferential separation of water, the solute species both calcium and sulfate ions accumulate on the surface enabling the precipitation. On the other hand, when the membrane is electrically charged, a layer of counter ions (SO$_4^{2-}$) accumulate near the surface while the Ca$^{2+}$ is away from the surface. Any possibility of the formation of CaSO$_4$ can occur only away from the surface [129,130].

8.4.5. Electrocoagulation

EC has been intensively studied recently as an unconventional pretreatment method [1]. Hakizimanana et al. [131] concluded that EC is highly potential in mitigating organic fouling as well as biofouling due to its capacity to reduce dissolved organic matter and microorganisms from water. Sadeddin et al. [132] suggested that the removal efficiencies of total suspended solids and turbidity by EC could reach nearly 100%. However, EC is not widely used due to its relatively high operation cost.

8.5. Biofilm removal and control

Biofouling can be minimized by (1) dominating the fouling during the operation and stop phases, using an uninterrupted or periodical introduction of biocides, (2) building an efficient sanitization and cleaning system after the biological fouling of the membrane. According to the biofouling type, systematic membrane cleaning is needed [18]. Biofouling reduction is possible due to the inactivation of bacteria or degradation of organics, which may otherwise attach to the membrane surface [133]. Bio-fouling can be reduced or removed via the following methods:

• Uninterrupted or periodical doses of biocide.
• Optimization of the operational conditions, such as pre-treatment of feedwater to lower nutrient availability and cleaning steps.
• Producing new membranes or improving the existing ones to make them more resistant to bio-fouling.

Biofouling may be also mitigated and minimized by chemicals including NaOH solutions, chelating or sequestration agents, surfactants, and disinfectants. Other biocides and biological cleaning chemicals, including chlorine, chloramines, hydrogen peroxide, peracetic acid isothiazolin, and enzyme-based slimicides, may be utilized. Biofilm can also be removed and controlled by ozone while biofilm can be prevented by disinfection using ultraviolet light. It is worth to mention that removing or reducing phosphate from water is important since phosphate is a necessary bacterial nutrient [18].

9. Fouling control, prevention and mitigation

The need for more fouling resisting membranes is generally announced to vindicate developing and using desalination processes with higher energy efficiency, especially when desalinating water sources characterized by high fouling potential [134]. Fouling control and prevention methods are widely discussed over decades to lengthen the lifespan of an existing membrane module with maximum permeate service capacity [135]. The unavoidable fouling requires an extra installation footprint to compensate for the reduced permeate [136]. Many attempts had been done to deeply study the fouling phenomenon. It could be practically possible to prevent fouling prior to its happening by conducting some techniques including feedwater pretreatment, chemical conditioning to modify the anti-fouling characteristics of the membrane, and optimizing the operational conditions. However, cyclic membrane cleaning remains unavoidable. It is required as a part and parcel of all membrane processes in modern industries, and it is ought to be uniformly executed to expel foulants and to recover the initial membrane productivity [17]. In general, and based upon the fouling type, there is a variable difficulty to minimize fouling. Inorganic fouling can be simply minimized via chemical and physical techniques. On the contrary that, organic fouling and biofouling are much hard to overcome and really, these two types of fouling are kinds of synergistic [1].

9.1. Pretreatment

Pretreatment is vastly utilized in RO desalination plants and it has a positive impact on improving the feedwater quality, to guarantee trustworthy RO operation, and to extend the lifetime of the membrane. The type and degree of pretreatment technique needed are dependent upon the feedwater source and quality as well as on the plant size and the allocated budget [1,27]. Pretreatment improves the permeate quality and lowers membrane fouling. Nowadays, there are many popular pretreatment methods: coagulation, flocculation, adsorption, oxidation, magnetic ion exchange, biological treatment, and many other integrated pretreatments. The success of pretreatment in expelling marine pollutants and lowering membrane fouling is highly related to the type of the used treatment agent, dose, dosing style (continuous or intermittent), dosing place, mixing technique, temperature, physical and chemical characteristics (hydrophobicity, charge density, and weight and size of molecules) of the marine pollutants (suspended or dissolved, organic.
or inorganic), water properties (pH and ionic strength), and membrane properties (a charge, hydrophobicity, and surface morphology) [61,137]. Generally, pretreatment techniques for RO membrane desalination plants must be capable of addressing the following issues:

- Membrane scaling caused by colloidal materials, metal oxides, and inorganic salts;
- Biofouling resulted due to the presence of microorganisms;
- Organic fouling resulted due to the presence of organic material;
- Chemical oxidation and halogenation by residual chlorine [27];

Integrating pretreatment methods is considered a key solution for reducing membrane fouling and is always utilized to guarantee the highest RO efficiency [138]. Fig. 9 illustrates many practical pretreatment methods, and the following sections will present a description of some pretreatment methods.

9.1.1. Coagulation and flocculation

Coagulation is an efficient and economic pretreatment technique for membrane separation methods. The coagulants alter the colloid’s stable nature within the feedwater via charge neutralization and permit the minute colloids to collide and agglomerate into larger and heavier particles. It is found that coagulation removes essential parts of NOM, such as total organic carbon (TOC), total phosphorus, and some antiscalant materials. The formation of larger crystals as a result of coagulation will minimize the propensity of membrane partial wetting, since larger crystals will not be able to get into the membrane pores, and just remain on its surface [24]. An experimental study performed by Nam et al. [139], revealed that the membrane fouling loading was reduced by the presence of the iron oxide (coagulant), and the membrane performance was improved. Coagulation is thus expected to raise the recovery rate of the pretreatment processes and to lower maintenance costs. Membrane fouling can be mitigated by adding zero-valent iron (ZVI, Fe⁰) to conventional coagulation (ZVI–coagulation) in combination with a membrane treatment of micro-polluted surface water. The addition of ZVI will result in larger and looser flocs and looser and more permeable cake layers. Therefore, this technique represents a promising approach to improve coagulation and reduce membrane fouling during the treatment of micro-polluted surface waters [140].

Flocculation, a gentle mixing process of the formed micro-flocs to formulate bigger visible particulates and hence these macro-flocs can be eliminated by sedimentation, flotation, or filtration. Coagulation/flocculation is confirmed to be an efficient pretreatment technique to improve the whole water quality and to mitigate membrane organic fouling, colloidal fouling, and biofouling [1].

Coagulation/flocculation is proved to be an effective pretreatment method for improving overall water quality as well as for mitigating membrane organic fouling, colloidal fouling, and biofouling [1]. Using ferric chloride as a chemical coagulant, Tabatabai et al. [141], investigated the

Fig. 9. Combination of different pretreatment technologies [1].
performance of coagulation on the removal of algal organic matter (AOM) in seawater and concluded that coagulation substantially reduced fouling potential as well as the compressibility of the AOM cake/gel layer. Peiris et al. [142], found that polyaluminum chloride as a chemical coagulant could reduce hydraulically irreversible fouling caused by humic substances and protein-like matters.

9.1.2. Granular media filtration

Granular media filtration is a method utilized to eliminate colloidal matter, micro-organisms, and other pollutants via passing the feedwater through a porous granular medium. There are a variety of granular materials, such as activated carbon, anthracite, diatomaceous earth, sponge, and cotton. Amongst the granular materials, activated carbon is commonly utilized in commercial water filters as a pretreatment step for the following RO membrane treatment. Activated carbon will lower the concentration of many pollutants commonly found in water. Activated carbon efficiently removes the residual chloride commonly found in water distribution systems after chlorination [1].

When desalinating seawater, brackish water, or treating wastewater, membrane filtration; specifically, UF/MF, becomes a common pretreatment option to minimize RO membrane fouling. Utilizing these options will reduce the area in comparison with conventional treatment methods and they will produce effluent water of high quality to be treated furtherly in RO membranes. RO efficiency will be raised by using the membrane pretreatment. Moreover, UF/MF pretreatment can be less expensive for long-term operation, this can be gained from energy requirement reduction, less usage of chemicals, periodic cleaning, and RO membrane replacement. It should be kept in mind that UF pre-treatment will delay but will not alleviate fouling formation [1,143].

While membrane pretreatment dramatically enhances the efficiency of RO membranes, the high tendency of fouling and apparent irreversibility remains an issue in many cases. Conventional pretreatment methods including coagulation can be combined with membrane pretreatment, and the result is a reasonable reduction of this problem. This is because much of the foulants can be eliminated during coagulation and hence the remaining foulants entering the following UF/MF will be largely lowered [1]. Fig. 10 outlines the sequence of coagulation, flocculation, and granular media filtration as pretreatment processes.

Herzberg et al. [145] found pretreatment of the secondary effluents with MF can reduce the fouling of RO membranes due to the removal of particulate/colloidal matter and can impact biofilm mechanic properties and cleaning strategies which are in favor of the subsequent RO membranes. Moreover, Jeong et al. [146] used submerged membrane hybrid systems as pretreatment for RO system and found pretreatment by submerged membrane combining with a coagulation-adsorption hybrid system with the low doses of ferric chloride and powder-activated carbon can lead to the best results in terms of organic removal and critical flux.

9.1.3. Adsorption

Adsorption, a pretreatment method will enhance removing of contaminants from the water [147]. It is the adhesion of foulants onto the adsorbent surface. Due to their relatively high porosity, adsorbents have a relatively large specific surface area for absorption or accumulation of absorbable impurities [148]. Many adsorbents may be utilized, such as powdered activated carbon, silica, carbon nanotubes, clays, and alumina. The powdered activated carbon layer formulated onto the membrane surface will also increase the effectiveness of the filtration. Adsorption lowers membrane filtration reluctance and increases filtration flux to a certain amount. This is due to the fact that the powdered activated carbon can adsorb dissolved organics of small molecular weight and macromolecular organics [147]. Gur-Reznik et al. [149] studied the adsorption of DOM onto GAC as a pretreatment for RO system of membrane bioreactor (MBR) effluents in laboratory and pilot scales. The results showed GAC pretreatment in pilot-scale columns can stabilize permeability and increase permeate quality of the RO membrane by removing 80%–90% DOM which is mainly composed of hydrophobic and biodegradable components [149]. Kim et al. [150], investigated granular activated carbon adsorption as a pretreatment for the secondary effluent, in combination with either dual media filtration (sand and anthracite) or dual media filtration and flocculation. Although TOC removal efficiency was
up to 75%–90%, the flux decline of the RO membrane was rapid because the activated carbon could remove the soluble contaminants rather than particulate matters [150].

9.1.4. Oxidation

Another method to lower the membrane fouling is feedwater pretreating with oxidants. Oxidants control membrane fouling by changing the interactions between the membrane surface and components of the solution [148]. Ozone pretreatment is a strong technique that oxidizes electron-rich moieties having a double bond of carbon and aromatic alcohols. In this technique, macro-molecular organics are oxidized into small molecules and then are oxidized into inorganic materials. Hence, the foulants concentration is radically reduced resulting in a lower tendency of membrane fouling. Foulants attached to the membrane surface can be expelled by ozone oxidation, and membrane fouling reduction is obtained [151].

9.1.5. Disinfection

It is a vital pretreatment technique since its application will destroy pathogens which can not only result in health impacts but also contribute to membrane biofouling. There are many popular disinfectants utilized to disinfect water, for example, free chlorine, chloramines, chlorine dioxide, ozone, ultraviolet, and potassium permanganate. Chlorine is a very efficient disinfectant utilized for the deactivation of a wide variety of disease-causing pathogens, so, it is the most widely used disinfectant. The efficiency of chlorination is influenced by the pH (the lower the pH the higher the efficiency). Despite being efficient, removal of chlorine has to be executed prior to RO water treatment due to its negative impacts on the membrane that results in its deterioration and shortening its lifetime [1].

Ozone is also a strong oxidizing agent that is vastly utilized to disinfect water. It is recognized that ozone can efficiently eliminate the microbial organisms, E. coli, and coliforms. The extent and level of elimination rate are largely influenced by the ozonation rate. Different from chlorination, ozone residual is not required to keep a sterilized water medium. On the other hand, compared with chlorine, ozone is useful for the following RO membrane treatment, because ozone residual is not required and will not pose a great issue as chlorine [1].

9.1.6. Scale inhibition

A much efficient technique to reduce membrane fouling is scale inhibition. Using scale inhibitor can lower the membrane inorganic fouling via altering the ions chemical and physical characteristics (for example Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions) which have very low ion products and hence changing the mechanism of scale formation. On the other hand, one disadvantage of utilizing scale inhibitors, it may pose a new scaling risk (for example, the formation of Ca₆(PO₄)₂ scales may take place) [1,152].

Several studies have focused on the development of novel antiscalants and comparing their performance with commercial-scale inhibitors [153]. The effectiveness of a few polyacrylic acids (PAA)-based scale inhibitors with hydrophobic end groups and three different commercial-scale inhibitors (Belgard EV 2030, Albrivap DSB(M), and Sokalan PM 10i) were evaluated in real seawater samples [154]. PAA with mid-length hydrophobic end groups, low molar mass PAA with a long end group, and PAA with mid-length hydrophobic end groups were studied to assess their antiscalping performance. The studies indicated that low molar mass (molecular weight) PAA with end groups of moderate hydrophobicity is most effective in the role of scale inhibitor. A relatively newer class of antiscalants is based on chemicals such as polymaleates (PMA), polyaspartates (PAS), and polyepoxysuccinate (PESA), as well as their various derivatives including copolymers with PA. A comparative study is reported for four phosphorus-free polymers (PAS, PESA, polyacrylic acid sodium salt (PAAS), and a copolymer of maleic and acrylic acid (MA-AA) and three phosphonates (ATMP, HEDP, and PBTC) regarding inhibition of CaSO₄ precipitation [155].

Zhao et al. [156], prepared environmentally friendly and low-cost poly(citric acid) antiscalant by condensation polymerization of citric acid and demonstrated its efficacy in CaSO₄ scaling inhibition. Poly (citric acid) interacts with active sites on the surface of growing CaSO₄ scale crystals and distort crystal polymorphs thus checking their growth. Phosphate-free polysuccinimide (PSI) derived antiscalants were also used for CaSO₄ scaling [156,157].

Although a detailed mechanism of antiscalping behavior of the novel candidates is still to be understood, initial studies have indicated the inhibition in the formation of crystals (to allow the crystal growth) as a contributing factor to scale inhibition [155].

9.1.7. Acid addition

It is an easy and efficient technique to inhibit forming calcium carbonate scale. The most popular acid utilized to reduce the feedwater pH is sulfuric acid (H₂SO₄) [158]. In addition to that, hydrochloric acid (HCl) is utilized when there is a tendency to form sulfate precipitates when adding sulfuric acid to the feedwater. Lai et al. found that HCl was a better acid agent than H₂SO₄ due to the overall lower solubility of sulfate salts as compared to that of chloride salts [159]. On the other hand, adding acids will cause other problems such as corrosion because of the lower pH value of the feedwater, transport and storage problems, and safety problems. Moreover, adding acid has no inhibitory influence against other scaling materials except calcium carbonate [158].

9.2. Surface modification

Surface modification of membranes is an efficient means to not only alleviates membrane fouling but also provide sustainable membrane performance [33]. Membrane fouling in RO desalination plants is strongly linked to the surface properties. Amongst these properties, surface smoothness, charge, and hydrophilicity are considered the key agents influencing fouling. Membranes characterized by a smooth and hydrophilic surface shows lower fouling potential than
those characterized by coarse and hydrophobic surfaces. As outlined in Fig. 11, membranes (a) and (c) have hydrophilic surfaces while (b) and (d) have hydrophobic surfaces. At the same time, membranes (a) and (b) have smooth surfaces while (c) and (d) have coarse surfaces. Therefore, it is predicted that (a) will have the best anti-fouling behavior while (d) is expected to be the worst. A water layer can simply be formulated on hydrophilic surfaces and foulants of hydrophobic nature are bounced to the surface. It is worth stating that, in some conditions, hydrophilic membranes are much inclined to catch hydrophilic foulants and may increase fouling potential [1,100].

The membrane surface charge is also another important factor to be taken into account for minimizing membrane fouling. Generally, it is suitable to use membranes with a charge similar to that of the dominant foulants in water. Therefore, the electrostatic repulsion created between the foulants and the membrane will inhibit foulants accumulation on the membrane, hence mitigating fouling. Introducing charged groups on the membrane surface can also benefit mitigating the membrane fouling, caused by charged organic compounds. In this type of modification, various chemical reactions may be used to create multiple functional groups, such as eSO₃⁻ or eCOOH, on the membrane surface. The number of the created functional groups and the thickness of the modified surface layer depend basically on the treatment time, temperature, and concentration of the modification agent [100].

Many studies revealed that smooth and hydrophilic membrane with favorable electrostatic interaction is preferred since they will improve the anti-fouling membrane properties [85,160–162]. There are various techniques to raise membrane surface smoothness and hydrophilic nature, including surface modification, novel materials, and synthesis process. Surface modification is a widely utilized method to lower membrane fouling. Fig. 12 presents a possible surface modification steps including (a) surface coating (physical modification) and (b) surface grafting (chemical modification).

Depending upon the membrane surface adsorption tendency, the adsorbed coating layer can be stable and this technique is feasible. Many researchers have conducted great works to develop the surface properties by coating a thin layer of hydrophilic or antibacterial polymers from solution by physical adsorption so as to modify the anti-fouling properties of the RO membranes. It was noticed that

![Fig. 11. Illustration of membrane surface smoothness and hydrophilicity [1].](image)

![Fig. 12. Schematic diagram of surface modification [27].](image)
the protective coating layer produced a smooth, neutral, and hydrophilic surface with modified fouling resistance, but a declined flux [163].

Nikolaeva et al. [164] applied hydrophilic material on the membrane surface via spray coating. In their study, they successfully bonded a hydrophilic hyperbranched poly(amidoamine) onto the skin layer of a membrane by spraying it after the interfacial polymerization onto the surface. The result showed that BSA adsorption on modified membrane surfaces reduced significantly (from 6.05% for unmodified to 2.86% for modified membrane). Surface roughness was reduced from 38 to 35 nm after modification. Yu et al. [165] modified membrane surface by using poly(N-isopropyl acrylamide) and poly(acrylic acid) copolymers (P(NIPAm-co-AAc)) by simple surface coating procedure. Membrane topography studies showed that the modified membrane appears to comprise a more nodular structure and exhibits an unevenly distributed surface feature indicative of surface roughness increment. Interestingly, the membrane surface roughness found decreased with a higher coating solution concentration. Membrane surface hydrophilicity decreased from approximately 68° to 48° [166].

Surface grafting has been commonly utilized due to simplicity, low cost, and a wide range of applications. Free radical-, photochemical-, radiation-, redox-, plasma-induced grafting, and chemical crosslinking are still in use to covalently attach different hydrophilic monomers to the RO membrane surfaces [167].

Amongst the two steps of modification, the plasma technique is the highest favorable method for surface coating. A merit of the plasma method is the off use of solvents or any risky material. RO membranes subjected to surface modification give an increase of 20%–25% inflow permeability in comparison with un-modified membranes. Surface grafting is a popular worldwide technique to modify membrane surface via preparing a “tailored” membrane surface with favorable performance. It is accomplished by utilizing a single monomer or a mix of monomers. It can be started chemically via UV irradiation and plasma treatment of the membrane surface [27].

Wu et al. [168] grafted a commercial RO membrane with the positively charged and hydrophilic polyvinylamine (PVAm). The membrane surface became more hydrophilic with reduced surface roughness after the modification. More importantly, the membrane surface charge climbed from negative to positive values when PVAm grafted with still higher concentrations. Fouling behaviors of the membrane were investigated with two different proteins, one cationic surfactant feed water compared to unmodified membranes. Surface rejection, and anti-fouling property [172].

Kang et al. [172] grafted two kinds of poly (ethylene glycol) derivatives with different chains onto the existing carboxylic acid groups on the surface of the commercial TFC RO membrane by a carbodiimide-induced method to improve the anti-fouling property. The modified membranes were more resistant to fouling in protein and cationic surfactant feed water compared to unmodified membrane.

9.3. Membrane modification by nanomaterials

With the fast development of nanotechnology, nanoparticles had been utilized to improve membrane surface characteristics, to modify membrane performance, and to mitigate its fouling. The implementation of nanoparticles in membrane industrialization made it possible to highly control fouling and allowed to manufacture of membranes of suitable structure. Silver (Ag) nanoparticles with good biocidal characteristics, usually utilized to provide antimicrobial coatings, were efficiently attached to the surface of polyamide thin-film composite membranes via covalent bonding with cysteamine with the formula HSCH₂CH₂NH₂ and act as a bridging agent. Membranes modified by the Ag-nanoparticles (NPs) have microbial resisting characteristics. This is because of silver reaction with disulfide and thiol groups of enzymes of DNA and influence on metabolic processes that give reactive oxygen species or interrupt replication of DNA, hence killing the bacteria (anti-bacterial agent). Ag-NPs can hinder the cell’s function by attachment to the cell or getting into the bacteria, which leads to extra bacterial destruction [173–175].

Another different nanomaterial used for modifying the membrane is zinc oxide (ZnO). It is characterized by chemical stability, non-toxicity nature, and antibacterial activity. The incorporation of ZnO will improve the performance of the RO membrane in the terms of water permeability, salt rejection, and anti-fouling property [176].

In general, to perform modification to the membrane surface roughness and hydrophobicity, nanoparticles can be utilized. This can be accomplished via trapping nanoparticles within the membrane pores and depositing the nanoparticles onto the membrane surface as shown in Fig. 13.

Using nanoparticles as a modifier for the membrane will result in many benefits; including:

- Improved flux;
- Higher rejection;
- Better antifouling properties;
- Better anti-biofouling properties enhanced mechanical, physical and chemical stability [18];

Aiming at the breakthrough of biofouling problems, Kwak and Kim [177] fabricated hybrid organic/inorganic RO
membranes composed of aromatic PA thin films underneath titanium dioxide (TiO₂) nanosized particles via a self-assembly process. It was noticed that the membrane possessing inorganic NPs was capable of killing the microbes without forming unwanted by-products as a means of precluding the formation of biofilms and, hence, reducing fouling.

A unique work by Fujioka and Nghiem [178] was simply based on the heat treatment of the PA RO membrane, which reduces the pure water permeability but improves the separation efficiency and fouling resistance. But the membrane surface characteristics (i.e., zeta potential, hydrophilicity, chemistry, and roughness) were not significantly affected by heat treatment. Although heat treatment improved fouling resistance, the impact of heat treatment on the long-term performance and lifetime of membranes is still unknown.

Li et al. [179] prepared a few-layered molybdenum disulfide (MoS₂) sheets via liquid-phase exfoliation from bulk MoS₂ crystals and subsequently incorporated into TFN membrane via interfacial polymerization. It was observed that MoS₂ has successfully decreased the membrane selective layer thickness, improved surface hydrophilicity (90° for neat and 71° for 0.01 wt.% MoS₂-TFN), and increased the surface roughness (58 nm for neat and 80.6 nm for 0.01 wt.% MoS₂-TFN). Fouling test demonstrated that 91% of the normalized water flux was maintained for 0.01 wt.% MoS₂-TFN membrane using 100 ppm BSA as the protein foulant.

9.4. Addition of polymers

In spite of the large benefits provided by RO membranes, fouling occurrence is considered the major drawback towards more uptake of RO desalination technology. Currently, modifying the membrane surface is the highest method of controlling fouling in RO membranes; it is categorized into physical adsorption or coating and covalent attachment of anti-fouling polymer chains to the membrane. Covalent attachment involves different mechanisms, including chemical coupling, free radical graft polymerization, and initiated chemical vapor deposition (iCVD). Hydrophilization of RO membrane with hydrophilic polymers like; polyethylene glycol (PEG) based material, hyperbranched polymer, polydopamine (PDA), and zwitterionic polymers gained wider interest due to its capability to minimize the organic fouling and to lower the attachment of organic matter and bacterial cells. Therefore, the operational expenses added by membrane cleaning are lowered and a constant permeate flow is also maintained [180].

9.5. Antiscalants use

To lower membrane fouling in the RO process, the feed water is continuously treated with fouling control chemicals such as antiscalants [13]. Antiscalants are chemical admixtures interfering with the precipitates from chemical and reduce the attachment of the resulting scales with the membrane surface. Using antiscalants is confirmed to be efficient in preventing scale formation RO, conventional thermal desalination methods (MSF, MED), heat exchange, and cooling water applications. The popularly utilized antiscalants include condensed polyphosphates, organo-phosphonates, and polyelectrolytes. Dosage of a small amount of antiscalants can efficiently reduce scale formation via physical process instead of a chemical process. The antiscalant is adsorbed to the crystal surface and clog the actively growing locations, thus leading to:

- Crystal growth rate hindering;
- Alterations in crystal surfaces characteristics and agglomeration potential;
- Alterations in crystal morphology that leads to disfigured or fragile scales characterized by weak adherence to the membrane surface [24].

In general, utilizing the antiscalants can help in reducing in-organic fouling (scaling). Though antiscalants dissolve the substances deposited near the membrane surface and lower the rate of fouling. The high dose of antiscalants leads to an increase in RO membrane deterioration, therefore, controlling the addition of antiscalants to achieve controlled membrane fouling will lead to minimal membrane degradation and lower chemical consumption [13]. Utilizing antiscalants should be executed with care, because its use has some restriction, including:

- Overdosing of antiscalants may result in fouling formation by themselves, therefore optimizing the dose is necessary;
- Many antiscalants are found to enhance the growth of different micro-organisms, thus causing extra biofouling occurrence;
- Many antiscalants may get into chemical reactions through the pretreatment step, which enhance fouling formation or may reduce the effectiveness of the antiscalants;
- Several metal ions, for example; iron, may react with antiscalants leading to fouling formation [24];
Vrouwenvelder et al. [181] found that biological growth varied with antiscalant type, and some antiscalants can induce biofilm formation in full-scale NF/RO systems by increasing the microbial growth potential up to 4–10 times of their normal growth rate. Sweity et al. [182] investigated the contribution of antiscalants to membrane biofouling during desalination and found polyacrylate-based antiscalant enhance initial cell attachment due to rendering the polyamide surface more hydrophobic and polyphosphonate-based antiscalants increased biofilm formation rate by serving as an additional phosphorous source to microbial population. Therefore, it is very important to conduct a wise selection and to use the minimum dosage of antiscalant for scaling control in order to avoid fouling enhancement.

9.6. New antifouling technologies

9.6.1. Development of electroactive anti-fouling properties

It is a charming track that combines electrochemistry with the membrane. Applying a suitable electric field has demonstrated to be efficient in reducing fouling rates and raising permeate flux in both cross-flow and dead-end filtration systems [183–186]. An electroactive membrane operated in cross-flow mode may give an alternative option to reduce the fouling by multiple foulants. A recent experimental study performed by Ma et al. [187] indicated that electroactive polyethersulfone (PES) membranes have excellent anti-fouling properties by adding electrostatic repulsion into the filtration process; this membrane type may provide a new technology for designing next-generation anti-fouling membranes for water and wastewater treatment.

9.6.2. Carbon nanotubes (CNTs)

They have considerable potential in enhancing membrane surface hydrophilicity and reducing membrane fouling [188]. Farahbaksh et al. [189] synthesized a new type of RO membrane by incorporating CNTs with different concentrations and they found that in comparison with bare RO membranes; CNTs-embedded RO membranes showed better anti-fouling performance. Graphene oxide, a cheaper but more effective graphene source material, is gaining more attention recently. He et al. [190] synthesized novel TFC membranes by incorporating graphene oxide nanosheets into polyamide films through a method of interfacial polymerization, which proved excellent anti-biofouling performance.

9.6.3. New RO membrane materials

Brand-new RO membrane materials as an alternative for polyamide, which is of great importance, because although improvements on conventional polyamide RO membranes have been achieved, they are not revolutionary since membrane fouling, membrane degradation in the presence of chlorine as well as other problems are still there and serious as well [167,191]. Falath et al. [192] synthesized a novel RO thin film membrane using a combination of polyvinyl alcohol (PVA) and Gum Arabic (GA) which proved excellent permeation, salt rejection, chlorine tolerance as well as biofouling resistance. However, developing such membranes is still at the beginning and there are still many problems to be overcome before their commercialization [1].

10. Conclusions

Despite the fact that the RO membrane is considered one of the best desalination technologies, fouling continues to pose serious and unavoidable challenges to the desalination industry as well as other water treatment applications. The variety of fouling types and sources involving various influential parameters complicate fouling treatment and control leading to adopt various methods and strategies to control membrane fouling unlimitedly. The need to further study and understand fouling mechanisms is notably rising and developing with a clear focus on fouling types related to membrane application and operational conditions. The development of fouling control and minimization methods, improvement of membrane filtration performance, and optimization of cleaning approaches for fouled membranes are necessary for the continuous usage of RO in the desalination industry. Novel membrane materials and innovative manufacturing processes should be adopted to lower the fouling tendency and to provide radical solutions for fouling problems, therefore, research should be directed to this issue and to produce fouling resisting membranes. Considerably, proper pre-treatment and the use of antiscalants have proven to be sufficient precautions towards reducing membrane fouling tendency. This is also in line with recent approaches of producing RO membrane with new materials that either has better hydrophilic properties or have electroactive membranes both of which increasing membrane fouling resistance. Similarly, Carbon nanotubes enhanced RO membranes have also proven to have high anti-fouling properties. Such trends can be seen as prevention is better than cure-based approaches attempting to prevent or reduce membrane fouling tendency from the very beginning.

On the other hand, various controlling strategies and mitigation measures have been tested for various types of RO membranes. Yet, cleaning and surface modification seems to be suitable for almost all fouling types as indicated by a large number of researchers and publications.

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