Chapter 5

Polymeric Reverse Osmosis and Forward Osmosis Membranes for Water Desalination

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Abstract

Polymeric reverse osmosis (RO) and forward osmosis (FO) membranes have been predominantly used in membrane applications for water desalination. The membrane science has advanced in the past decades and various efforts have been employed to improve the membrane characteristics for enhanced water flux and impurities rejection capability. In this chapter, the progress of RO and FO membranes has been discussed in three sections: synthesis methods of RO and FO membranes, modification works done on the membranes and the formulation used for the synthesis of RO and FO membranes, with particular interest given to the incorporation of nanoparticles in the synthesis of thin film composite membrane.

Keywords

Reverse Osmosis, Forward Osmosis, Desalination, Polymeric Membrane, Membrane Synthesis and Modification, Thin Film Composite Membrane

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1. Introduction

Desalination has been recognized as one of the most promising technologies to minimize the stress arising from water shortage and water scarcity. The advancement of membrane science has contributed to the widespread acceptance of desalination globally due to its advantageous features over conventional thermal-based desalination processes, such as high productivity (recovery rate), high energy efficiency (lower specific energy consumption), small physical footprint (lower space requirement due to the process and plant compactness), operational simplicity, and ease of process automation [1–3]. Furthermore, the carbon dioxide (CO₂) emission from seawater reverse osmosis plant at 1.7-2.8 kgCO₂/m³ is much lower compared to thermal-based desalination processes (multi-stage flash and multi-effect distillation) at 7-25 kgCO₂/m³ [4]. Currently, membrane-based seawater desalination is dominated by seawater reverse osmosis process, where it acquires a share of 65% global production [5]. Reverse osmosis (RO), being the membrane that leads to the success of membrane-based desalination, utilizes

external pressure to force water permeates through the membrane while leaving the salt and other molecules behind, as shown in Fig. 1(a). Naturally, osmosis process is a process resulted from the movement of the solvent molecules (usually water) across a membrane from low to high solute concentration (usually salt) until osmotic equilibrium state for both sides is achieved. At this state, the system is said to possess a minimum pressure or osmotic pressure that maintains the equilibrium of the system. On the other hand, RO process is a process that reverses the direction of the solvent flow by the assistance of external pressure that is higher than the osmotic pressure of the system [3].

Figure 1. Working mechanism of (a) RO (adapted from [6]) and (b) FO (adapted from [7])

Another interesting membrane process that recently gained tremendous attention from the desalination researchers is forward osmosis (FO). Unlike the typical pressure-driven RO process, FO is a non-pressure driven process that utilizes the osmotic pressure difference between two streams (known as feed and draw solutions as shown in Fig. 1(b)) to allow the permeation of water from feed stream to draw solution of higher osmotic pressure [7]. The feed stream will be concentrated while the draw solution will be diluted. The latter can then be regenerated by extracting the water through additional separation processes [8]. This concentration-dilution concept of FO can be applied to desalinate water albeit indirectly (the need to have additional separation processes to extract the clean water). On another note, innovative design has been undertaken to utilize the concentration-dilution nature of FO membrane to improve the desalination process, where FO has been employed as pre-treatment to dilute the seawater (draw) with reclaimed wastewater (feed) before the seawater is sent to RO desalination process [9,10]. This offers the potential for the RO desalination process to be operated at lower operating pressure due to the reduced osmotic pressure of diluted seawater.

The successful application of RO and FO for water desalination is mainly attributed to the advancement of the membrane itself. However, membrane-based desalination still has room for improvements, such as the potential to lower the energy consumption and unit cost (to be as competitive as treated water from surface water sources) as well as more resistant to fouling (consistent performance for a long period of time with minimal downtime for cleaning and membrane replacement) [11]. To realize these aims, the RO/FO membrane with the desired characteristics such as excellent water permeability with good rejection rate for salt and foulants, and great resistance to fouling or membrane degradation should be synthesized. The minor difference between RO and FO membranes is that the latter is expected to have lower structural parameter (thinner membrane) without compromising the mechanical strength. The membrane science has come a long way with researches on the synthesis/modification approaches and material formulation has been actively conducted by the membrane researchers. These topics will be further elaborated in the following section.

2. Development of RO and FO polymeric membranes

Among the various types of membranes, polymeric membrane acquires the largest share of membrane research and market due to its low material cost, good mechanical strength and chemical stability [11]. Similarly, almost all existing commercial RO and FO are polymeric membranes. The first RO membrane was developed by Loeb-Sourirajan where cellulose acetate (CA) polymer was used to synthesize the membrane [12]. This CA RO membrane was capable of producing potable water from sodium chloride (NaCl) brine at

appreciable water flux and reasonable pressure. The invention of Loeb-Sourirajan membrane fabrication procedure in the 1960s has substantially boosted the application of membranes in the later day [1]. Although the CA RO membrane possesses desalination capability, its relatively weak chemical, thermal and physical resistance has resulted in various membrane modification and synthesis efforts to overcome these weaknesses [13]. Later, Cadotte developed thin film composite (TFC) RO membrane via interfacial polymerization (IP). The typical TFC membrane consists of active skin layer (usually polyamide (PA) layer), support layer (usually polymeric polysulfone (PSf) material) and substrate (non-woven polyester (PET) fabric), as shown in Fig. 2. The emerging of TFC RO membrane in the 1970s is one of the most remarkable advancements in the history of RO membrane [14]. In comparison to CA RO membrane, the TFC RO membrane could perform at lower pressure without compromising the salt rejection and has better physicochemical properties. Following on, biological membrane (biomimetic membrane) has been synthesized for desalination application and the performance of the membrane in term of water permeability is reportedly higher than commercially available RO membrane. However, the commercialization of the biomimetic membrane for desalination market is yet to be seen [15]. Overall, the seek for improvement in RO membrane technology continues to grow and attention has been shifted to resolve the few issues currently faced by membrane science, such as the trade-off between salt rejection and water permeability, membrane scaling, physicochemical properties and fouling.

Figure 2. Typical structure of TFC membrane

RO membrane has been employed for FO application prior to the available of membrane specifically synthesized for FO process. However, the water permeability was unsatisfactorily low due to the thick support layer of RO membrane (to withstand the high operating pressure) that made the diffusion of water and draw solute difficult and

increased the mass transfer resistance [16]. The first commercial FO membrane was developed by Hydration Technology Innovations (HTI) where cellulose triacetate (CTA) was casted on the PET mesh support [16]. This CTA FO membrane displays some attractive features over the TFC RO membrane (only for FO application) such as greater water flux (thinner support layer), lower fouling propensity (attributed to its hydrophilic nature), and stronger chlorine resistance [17–19]. Although the cellulosic FO membrane possesses the criteria for FO application, its relatively low salt rejection (especially reverse solute flux where the draw solutes migrate to the feed side) has resulted in the shifting of interest to the development of TFC FO membrane.

The research and development of TFC FO membrane started in the year 2010 and followed by the available of few commercial TFC FO membranes [20–22]. In comparison with the TFC RO membrane, the TFC FO membrane is thinner and has higher porosity. Today, TFC FO membranes have become one of the most competitive membranes for FO application owing to the high versatility of tuning the characteristics of the membranes. For instance, adjustment of synthesis approach, modification of the membrane surface, and the formulation of the polymeric membrane are the few popular methods to improve the performance of TFC FO membrane, especially in terms of water permeation and reverse solute flux.

Table 1. Desirable features of RO and FO membrane for enhanced performance (summarized from [16,23–26])

RO membranes	FO membranes
<ul style="list-style-type: none"> • High permeate flux • Trade-off between permeability and salt rejection • Withstand the chlorine attack and antifouling (scaling, biofouling, inorganic fouling, colloidal fouling) • High salt rejection • Low energy consumption • Excellent chemical, thermal and mechanical stability • Great antifouling and antibiofouling capability • Low concentration polarization issue • Hydrophilic and porous support layer 	<ul style="list-style-type: none"> • High permeate flux • Compatible with the selected draw solution • Withstand the mechanical stresses generated during operation • High salt rejection • Low reverse solute flux • Chemically stable • Great antifouling and antibiofouling capability • Low concentration polarization (internal and external) issues • Thin and porous support layer for water passage

Table 1 summarizes the desirable features of RO and FO membranes which drive the effort to improve membrane characteristics. A wide range of membranes for both RO and FO have been synthesized and sold at market, with membrane in flat sheet and hollow fibre being the dominant configuration. RO is normally sold in flat sheet and spiral wound modules whereas FO membranes normally appear in flat sheet and hollow fibre configuration [3].

3. Synthesis and modification of RO and FO membranes

One of the most popular strategies to improve the membrane properties and performance is through alteration of synthesis conditions and conduction of modification on the RO and FO membranes. This section will discuss the synthesis and modification works done on the RO and FO membranes separately.

3.1 Synthesis

Currently, TFC RO and FO membranes share the largest market in commercial RO and FO membranes, respectively. Hence, the synthesis and associated synthesis conditions of TFC will be the focus and discussed in this section. The discussion includes the works done on support and active layers of TFC membranes.

3.1.1 RO membranes

a. Phase inversion

Most of the polymeric RO and FO membranes for desalination possess the separation thin film layer casted onto a support layer. The support layer should possess good biological, chemical, mechanical, and thermal stabilities and desirable structure and morphology [27]. The support layer is normally fabricated via phase inversion approach. The key components in preparation of the support layer are solvent, polymer, non-solvent and suitable non-woven fabrics [28]. Proper control of the formulation and synthesis conditions will lead to the synthesis of membrane with desired properties [29]. Generally, there are four major approaches based on the phase inversion concept, namely immersion precipitation (nonsolvent induced phase separation, NIPS), thermally induced phase separation (TIPS), vapour induced phase separation (VIPS) and evaporation induced phase separation (EIPS), as shown in Fig. 3. Basically, in phase inversion, the polymer solution (polymer and solvent) is first prepared followed by casting the solution on the surface of the glass sheet using film applicator. The precipitation/solidification process varied according to the selected solidification technique. Among these four approaches, immersion precipitation is the frequently used method owing to its ease of fabrication and stability of the method. For example, in the early of 1960s, Loeb and Sourirajan

developed a RO membrane via phase inversion method using NIPS technique [30]. In this technique, diffusion process happened whereby solvent diffused from the casting solution to the non-solvent bath while the non-solvent diffuses into the casting solution, which caused rapid precipitation.

Figure 3. Membrane Preparation via Phase Inversion Approaches (adapted from [31])

Apart from NIPS, TIPS technique is also used to prepare the support layer of RO membrane. For instance, Sabir et al. (2016) synthesized the support layer for TFC RO membrane via TIPS technique by mixing polymer cellulose acetate/polyethylene glycol (CA/ PEG3000) and silica nanoparticles (SNPs) prior to solution casting. At this point, the casted solution was quenched at lower temperature (using water ice bath) followed by heat treatment using oven to remove the remaining residual solvent. The reported hydrophilicity was measured via water content analysis technique and the modified membrane improved from 64.2% (without SNPs) to 92.1% (with 0.4wt% of SNPs). The increase in the hydrophilicity of the membrane was due to the driving force induced by the hydrophilic PEG3000 that allowed more sorption of water into the polymer matrix. This improvement resulted into the enhancement of the permeation flux for about 36.78 % (from 1.74 LMH to 2.38 LMH). Besides that, the modified membrane also showed improved salt rejection from 72% to 95% due to the presence of mesoporous SNPs that disrupted the polymer chains by forming microporous defect [32].

On the other hand, Abdelsamad et al. (2018) prepared a TFC RO membrane for desalination application via VIPS technique where the porous support layer was prepared by mixing polyethersulfone (PES) polymer, N-methyl-2-pyrrolidone (NMP) solvent, triethylenglycol and polyvinylpyrrolidone (PVP). Immediately after the casting, the glass sheet was moved to a controlled humidity air chamber to allow VIPS process to happen followed by immersion into water to remove the unwanted solvent [33]. However, there is not much work reported on the preparation of asymmetric RO membrane via phase inversion (without TFC film as an active layer).

b. Electrospinning

Electrospinning is another emerging membrane fabrication technique that attracts the attention of researchers. This method allows the formation of interconnected and uniform pore size that is favourable in producing highly porous membrane structures [34]. It is usually applied to form a nanofibrous porous support layer prior to the non-porous active layer (PA layer) to obtain RO membrane with appreciable performance in salt rejection and water permeability [35]. The advantages of using this nanofibrous material as a support layer for RO membrane are its high surface area to volume ratio, low start-up cost, variety of polymers and materials selection and potential of fiber functionalization [36]. For instance, Wang et al. (2017) developed two thin film nanofibrous composite RO membranes by scaffolding polyacrylonitrile (PAN) nanofibrous on top of PET non-woven mat (PAN/PET) and cellulose nanofibers (CN) on top of a PAN/PET non-woven mat (CN/PAN/PET) prior to the PA thin film formation. Upon addition of the CN, the membrane showed better salt rejection (difference by around 1.0 to 1.5 %) while the flux showed slight improvement of around 0.2 to 0.5% as compared to PA/PAN/PET RO

membrane. The reason for these improvements was due to the uniform thickness of membrane surface (smoother surface) for PA/CN/PAN/PET RO membrane as compared to the ridge valley layer (rougher surface) of PA/PAN/PET RO membrane [37].

c. Interfacial polymerization

The previously discussed phase inversion method usually relies on altering the polymer concentration (>20 wt%) to form an asymmetry RO membrane and this often limits the flux improvement. In the later days of 1970s, the invention of TFC membrane via IP technique has marked another breakthrough for RO membrane. Generally, the preparation of TFC membrane usually started by soaking the support layer with the aqueous solution of m-phenylenediamine (MPD) monomer and organic solution of trimesoyl chloride (TMC) to form a dense PA layer on top of the membrane surface. This method could easily alter both flux and salt rejection by tailoring the synthesis parameters, conditions, materials (monomer and organic solvents), additives and the thin film thickness of the active layer [28,38]. For instance, the used of sulfonated diamine monomer namely 3,3'-(ethane-1,2-diylbis(azanediyl))bis(2,6-dimethylbenzenesulfonic acid) instead of MPD monomer for TFC RO membrane synthesis has increased the pure water permeability by around 10% (from approximately 1.7 LMH to 1.92 LMH) as compare to MPD/TMC TFC membrane due to the created fraction of free volumes that allowed lower water transport resistance [39]. Other commonly used monomers and additives to prepare TFC membrane were also reported [40,41].

d. Layer by layer

Apart from the commonly seen phase inversion, IP and electrospinning techniques used to prepare asymmetric RO membrane, layer by layer (LbL) is another attractive method that can be used to synthesize RO membrane owing to the possibility of tuning the thickness of the layers and various choice of materials selection. For instance, Kovacs et al. (2015) modified a PES UF membrane by spraying oppositely charged poly(allylamine hydrochloride) (PAH), poly(diallyldimethyl-ammonium) (PDAC), poly(acrylic acid) (PAA) and laponite (LAP) clay platelets to produce RO membrane. The study showed that by spraying tetralayers on the surface of the membrane (PAH/PAA/PAH/LAP) at pH 5.0, the membrane permeability and salt rejection were around $4.5 \times 10^{-13} \text{ m}^2/\text{Pa.s}$ and 89% (NaCl 10000 ppm), respectively. This performance was comparable with commercial Koch TFC-HR RO membrane ($7.6 \times 10^{-15} \text{ m}^2/\text{Pa.s}$, 98% NaCl 10000 ppm salt rejection). The reason for the appreciable salt rejection was due to the presence of stacked clay layers and polyelectrolytes that increased the tortuosity of the solute diffusion path, and thus impacted the transport of the solute diffusion across the

membrane. The reason for the achieved permeability was probably due to the presence of preferential water flow channels [42].

Apart from the conventional immersion or dipping the membrane substrate with oppositely charged polyelectrolytes layers, another interesting method to deposit the polyelectrolytes layers on the membrane surface is through spin assisted LbL coating. This technique is similar to the conventional self-assembly LbL that involves sequential deposition of polyelectrolytes on the surface of the membrane followed by drying and rinsing prior to the deposition of another oppositely charged polyelectrolytes. The major difference is the polyelectrolytes that are spun cast on a spinning substrate or surface. The spinning effect helps to boost the drying and rinsing rates that are favourable in forming layer with better uniformities. For example, Fadhilah et al. (2012) used spin assisted LbL assembly technique to assemble the poly (allyl amine hydrochloride) (PAH) and PAA on the surface of the PSf membrane. The experimental runs showed that by depositing 35 layers of PAH/PAA on PSf membrane, the modified membrane achieved 88% of NaCl (15000 ppm) salt rejection. This could be attributed to the high number of bilayers (higher Donnan potential) that favoured the rejection of ions [43].

3.1.2 FO membranes

a. Phase inversion

The morphology of the support layer such as thickness, tortuosity, and porosity has a significant impact on the characteristics of FO membrane. Factors such as the polymer composition, the nature of solvent and non-solvent, the coagulation bath, and the interaction mechanism between polymer and casting layer can affect the morphology of the fabricated membrane [11,44–46]. By properly varying these factors during the synthesis process, the thermodynamic (affinity with solvent, non-solvent, polymer, and solvent-non solvent solubility) and kinetic (viscosity of the casting solution) aspects can be controlled to obtain the desired sub-layer morphology [46,47]. For instance, the use of dimethylformamide (DMF) solvent instead of NMP for PSf sub-layer synthesis has increased the water permeability coefficient from 1.73 to 3.14 LMH due to the formation of bigger pore size and a higher porosity (2% vs 1%) of membrane support layer [48]. However, the DMF-prepared membrane recorded a slightly higher solute permeability coefficient at 0.6 LMH as compared to NMP-prepared membrane at 0.5 LMH.

Liang et al. (2017) innovatively tailored the polyvinylidene fluoride (PVDF) substrate of a TFC membrane by using bidirectional freezing synthesis process to obtain support layer with vertically oriented pores [49]. The newly developed FO support layer possessed a porosity of 74% and pore size of about 1.8 μm . SEM imaging showed that pores have an open shape in the bottom and top sides, as well as a spongy structure in the mid layer.

This structure has an excellent low tortuosity that can be proven by much higher water permeability coefficient (4.7 LMH) than the typical phase inversion method (0.63 LMH).

Co-casting is another technique that can be used to produce favourable structured support to reduce the internal concentration polarization (ICP) effect. Basically, co-casting is the fabrication of hollow fibre membrane by simultaneously casting two layers of polymer solutions using a double-blade [50–53]. Ng et al. (2015) demonstrated that co-casting with two polymer solutions of different concentrations was able to produce permeable substrate, yet still retained the surface morphology for the fabrication of active layer [50,51]. In another reported study, PEI sacrificial layer was co-casted beneath the top PSf layer. The resultant PSf substrate possessed an open bottom structure that significantly reduced the ICP effect especially at a high DS concentration [52].

The support for the casting and formulation of the polymer during phase inversion plays a role in affecting the structure of the membrane. For instance, membrane casted on a glass plate and introduced to an intermediate immersion in NMP/water bath before dipping into tap water reduced the structural parameter to 51 μm , an indicator of lower ICP in FO process [54]. Replacing the glass support with Teflon resulted in the formation of relatively dense top layer supported by a fully porous bottom. The formation of this structure was attributed to unfavourable hydrophilic (polymer)-hydrophobic (substrate) interaction. On the other hand, the inclusion of acetic acid in dioxane/acetone solvent promoted the formation of porosity of sublayer due to the complexation between acetic acid and dioxane and the nature of acetic acid as pore forming agent [55]. The inclusion of acetic acid has increased the water flux from 4 LMH to 20 LMH.

b. Electrospinning

Compared to phase inversion, electrospinning is another synthesis technique that has a better control on the tortuosity structure of the membrane [56,57]. Synthesis conditions such as environment conditions, solution viscosity, flow rate of the solution, and the applied voltage can be fine-tuned to obtain the membrane with desirable structural characteristics [34,58]. For example, Song et al. (2014) adjusted the temperature to control the thickness of nanofibers within 50-150 nm [59]. Consequently, the nanofibers formed a support layer with special porous structure, scaffold-like, and with tight pores amongst single nanofiber. This support structure contributed to high water permeation and salt diffusion resistance, resulting in satisfying results in FO process. In another study, Tian et al. (2015) synthesized a polyethyleneimine (PEI) nanofibers support with fine (top) and coarse (bottom) structure [57]. The fine and thin nanofibers at the top are suitable for forming a rejection layer while the coarse bottom structure provides the necessary mechanical support and promotes mass transfer within the substrate.

c. Interfacial Polymerization

The rejection layer of most TFC FO membranes are synthesized via IP between monomers of MPD and TMC on a microporous support as illustrated in Fig. 4. Various synthesis parameters such as composition of the monomers, reaction time, additives in the MPD/TMC solutions, and the method for removing excess MPD can be varied to fine-tune the resulting PA rejection layer [46,60]. Majority of the IP studies focus on the composition of the monomers and additives in the MPD/TMC solutions and hence will be discussed in the following section.

Figure 4. Interfacial polymerisation for the synthesis of TFC membrane (adapted from [41])

d. Layer by layer

LbL assembly on a microporous support layer is another method to fabricate FO membranes [61]. This LbL method involves the deposition of polyelectrolyte layer on the support layer through electrostatic attraction or hydrophobic interaction [61–63]. For instance, Cui et al. (2013) synthesized a multilayer membranes for FO processes by LbL assembly of positively charged PAH and negatively charged blend of PAA and

poly(sodium 4-styrenesulfonate) (PSS) on top of hyperbranched PEI modified Torlon substrates and then crosslinked by glutaraldehyde [64]. The developed 3-bilayer membrane recorded water flux of 28 LMH and reverse salt flux of 1.97 gMH using 0.5 M magnesium chloride (MgCl_2) as the draw solution. Similar polyelectrolytes formulation has also been deposited on PES support to obtain hollow fibre FO membrane [62]. This indicated the flexibility of LbL method in synthesizing FO membrane of different forms.

Double-skinned LbL polyelectrolyte FO membrane as shown in Fig. 5 has been synthesized to enhance its antifouling property as compared to the commonly adopted single-skinned membrane [65]. Polyanion and polycation were coated LbL alternatively for multiple times on the top and bottom surfaces of PAN substrate to grant the FO membrane a double-skinned structure. The double-skinned FO membrane enjoyed lower fouling propensity since foulant clogging within the porous support has been hindered by the second active layer.

Figure 5. Double-skinned FO membrane fabricated via LbL method (adapted from [65])

Chitosan and polyacrylic acid were used as polycation and polyanion respectively for the LbL synthesis of FO membrane [66]. The membrane achieved a high water flux of 25.5 LMH and low reverse salt flux of 0.051 gMH when tested with 2 M NaCl as the draw solution. Experimental data indicated that the membrane also attained high water flux (22.25 LMH) when tested with synthetic wastewater. It was postulated that the dense nature of the LbL surface coating on substrate prevented salt leakage and led to low reverse solute flux.

3.2 Modification

Membrane modification is mainly done chemically to improve the characteristics of the RO and FO membranes, especially to alter the hydrophilicity and antifouling properties of the membrane [24]. The modification is mostly conducted on the separation layer, albeit some works on the support layer have also been reported.

3.2.1 RO membranes

a. Layer by layer

LbL is one of the versatile techniques used to alter the performance of the membrane by alternately stacking oppositely charged polyelectrolytes, namely polycation and polyanion. Attributed to its versatility, the stacking layer can be placed on the surface of the substrate, porous layer or active layer, depending on the needs of the application. The variation of choices in polyelectrolytes, surface charges and thickness can affect the membrane performance. Therefore, properly varying these parameters could lead to the synthesis of membrane with desirable properties [67]. For example, Ishigami et al. (2012) attempted to improve the hydrophilicity of commercial RO via LbL and the modification was performed by immersing the RO membrane alternately with the PSS and PAH solutions. At optimum layer number, the antifouling property of the RO membrane was improved as the relative permeability increased from around 0.72 to 0.88 while the NaCl (500 ppm) salt rejection reported slight increment from 98.25% to 99.25%. The improved antifouling property was attributed to the increased hydrophilicity and smoother membrane surface (roughness decreased from 54.9 nm to 34.8 nm). The increase of salt rejection was because of the increased hydrodynamic resistance induced by the increased layer thickness [68].

Besides stacking polyelectrolytes, oppositely charge nanomaterials can also be stacked on the surface of the membrane. For instance, Choi et al. (2013) coated GO to the PA-TFC membrane surface via LbL approach and the modified membrane still showed better flux (increased from 12.5 LMH to 14 LMH) while maintaining approximately the same rejection (around 96%) even after 10 GO bilayers. Although the deposition of bilayers was postulated to decrease the flux due to the increase of hydrodynamic resistance, interestingly flux drop was not noticed. The reason for this behaviour was because the multilayers of GO was not a strong function of thickness whereby the impact of hydrophilicity (contact angle reduced from 70.6° to 25.9°) of the GO was stronger than the hydrodynamic resistance. Attributed to this strong hydrophilicity and smoother surface induced by the presence of GO, the modified membrane also had lower fouling propensity where the flux decline was improved for almost 50% (from 34% to 15%). The multilayer of GO also helped to shield the membrane from chlorine attack that often is a

challenge faced by the PA RO membrane [69]. However, the non-uniformities and the time taken for the layers to form on the surface of the membrane remain a challenge for this synthesis technique.

In another study, Ma et al. (2016) used both spray and spin assisted LbL approaches to functionalize the TFC PA RO membrane with copper nanoparticles to improve the biofouling resistance. The membrane was modified with positively charged polyethylenimine coated copper nanoparticles and negatively charged PAA until a desired bilayer formed on the surface of the membrane. The modified membrane showed that the presence of copper nanoparticles significantly improved the antibiofouling property by mitigating the growth of *E. coli* on the surface of the membrane in the range of 94.3%-100% as compared to unmodified membrane at 14% [70]. The three methods of applying LbL on the membrane surface are illustrated in Fig. 6.

Figure 6.(a) Self-assembly (b) Spray coating (c) Spin coating (adapted from [71])

b. Coating

Surface coating is a common membrane modification method used to improve the surface properties of the membrane via immersion of coating solution with or without the

presence of cross-linker. For example, Zhang et al. (2016) successfully modified PA RO membrane through the coating of poly (vinyl alcohol) (PVA) polymer. Associated with the modification, the modified membrane exhibited slight improvement in both water flux and salt rejection at around 7% (from 50.5 LMH to 54 LMH) and 99.4 % to 99.5%, respectively, as compared to virgin RO membrane. The increase in water flux could be related to the hydrophilicity of PVA that overcame the hydraulic resistance caused by adsorbed PVA layer. On the other hand, the slight hydraulic resistance happened to improve the salt rejection. Additionally, the flux recovery ratio for modified membrane (60-69%) was higher than controlled RO membrane (55-60%) [72].

In another study, Shafi et al. (2015) modified a RO membrane by coating zwitterionic to improve the fouling resistance property of the membrane. Zwitterionic materials are commonly used as an antifouling coating attributed to its low protein adsorption. In this study, the zwitterionic copolymers were self-synthesized followed by deposition on a commercial Koch membrane (TFC-HR) to evaluate the improvement of fouling resistance. The modified membrane showed increased salt rejection from 96% to 98 % with a small drop in the permeate flux. The authors claimed that the reasons for the observed increase in salt rejection was most likely due to the decline in permeate flux and increased surface charge. The study also demonstrated strong resistance of modified membrane towards *E. coli* and *P. aeruginosa* cells with the number of attached cells on the surface of the membrane was reduced by 98% (from 9146 to 192 bacteria attachment) and 96.5% (from 1270 to 45 bacteria attachment) respectively attributed to the antifouling property of zwitterionic [73].

Another major challenge for the RO membrane is the vulnerability towards chlorine attack that will cause the salt rejection to deteriorate after exposure to higher chlorine containing wastewater. Associated with this, Ni et al. (2014) attempted to improve the chlorine resistance of the membrane by coating a hydrophilic copolymer poly (methylacryloxyethyl dimethyl benzyl ammonium chloride-r-acryl-amide-r-2-hydroxyethyl methacrylate) followed by chemical crosslinking to covalently link the polymer chains on the commercial TFC RO membranes (LCLE and BW30). The results showed that the modified membrane can tolerate chlorine exposure 7 to 10 times better than the controlled membrane. The reason for such behaviour was because the presence of poly (methylacryloxyethyl dimethyl benzyl ammonium chloride-r-acryl-amide-r-2-hydroxyethyl methacrylate) layer that protected the chlorine sensitive sites in PA film from chlorine attack [74].

Other types of polymers such as polymer sericin [75], sulfochlorinated and sulfonated polysulfone [76], PEG polymers [77], hydrophilic hyperbranched polymer, poly(amino amine) [78] and nanomaterials [79] have also been employed for the surface coating of

RO membrane. Though the modified RO membranes exhibited improved performance in terms of flux and rejection, the weak interaction between the coating layer and membrane surface has been an issue as this caused the coated layer to be easily detached from the membrane surface.

c. Grafting

Surface modification via chemical treatment is another effective approach to alter the surface properties of the membrane to minimize the weaknesses of TFC PA RO membrane (e.g. low resistance towards fouling and chlorine). For instance, Cheng et al. (2013) successfully improved the antifouling behaviour and chlorine resistance of commercial TFC RO membrane by exposing the active layer of the membrane with hydrophilic polymer solution, N-isopropylacrylamide (NIPAm) via redox initiated graft polymerization. As a result, the modified membrane showed higher water flux by 3.5% (from 28.2 LMH to 29.2 LMH) while maintaining high NaCl salt rejection (500 mg/L) at 98.6% as compared to the unmodified membrane. The reason for improved water flux was attributed to the decrease of surface contact angle from 60.5° to 40.2° that indicated the enhancement of membrane surface hydrophilicity while the slight increase in salt rejection was mainly due to the increase of the membrane surface negative charge from -42.5 mV to -48.6 mV, which exerted stronger repulsion towards the ionic salts. Besides that, the modified membrane recorded 20.7% of flux decline as compared to controlled membrane at 45.3% over a 40-hour filtration run. The improvement of the fouling resistance was related to the enhanced hydrophilicity and membrane surface charge as well. As for the chlorine resistance, the modified membrane was able to maintain a high salt rejection of 96.5% even after exposure to high chlorine solution (5000 ppm Cl₂) as compare to controlled membrane at 78.5% salt rejection. The subsided chlorine degradation of the modified membrane was mainly due to the reduce of amine groups that were vulnerable to chlorine attack after grafting [80].

In another study, the surface modification was performed by grafting NIPAm and zinc oxide (ZnO) NPs onto the PA layer of RO membrane via gamma irradiation instead of redox initiated. The study reported on the improvement of hydrophilicity, which was indicated by the drop in the contact angle value from 74.8° to 54.8° due to the presence of active polar hydrophilic groups on the membrane surface. The salt rejection for NaCl solution of modified membrane was increased from approximately 91% to 92% while the water flux increased from around 22 LMH to 24 LMH. Such phenomenon was observed because NIPAm and ZnO improved the surface hydrophilicity and membrane surface negative charge after grafting. On the other hand, the chlorine resistance for the modified membrane was better than unmodified membrane whereby it still maintained higher than 90% salt rejection while the latter experience only 73% salt rejection at chlorine exposure

of 4000 ppm. The enhancement of the chlorine resistance was related to the presence of sacrificial grafting layer [81].

Apart from hydrophilic polymer, the use of hydrophilic nanomaterial for surface grafting is also one of the emerging research areas. For instance, Huang et al. (2016) grafted azide-functionalized graphene oxide (AGO) on the surface of the commercial RO membrane to promote anti-adhesion and antifouling properties of the membrane by dipping the membrane surface with AGO dispersion solution followed by UV light exposure. The study reported a slight decrease in the water flux from 37.8 LMH to 36.3 LMH. This could be due to the increased of the hydraulic resistance after the surface grafting. The slight enhancement in terms of salt selectivity (from 94.1% to 95.3%) and significant enhancement of fouling resistance (from 70% flux decline to 40% flux decline after 7 days of filtration) were also observed. The reason for latter enhancement was due to the improved hydrophilicity, which showed by lower contact angle value (decreased from 85° to 45°) that formed a resistance towards the attachment of foulants on the membrane surface. The presence of the oxygen containing hydrophilic groups within the AGO increased the affinity between the membrane and water molecules, and thus resulted in improvement of fouling resistance. The result was further strengthened with the smoother membrane surface (roughness dropped from 44.3 nm to 29.0 nm) of the modified membrane that allowed the foulants to be easily flushed away from the surface of membrane. Additionally, the presence of GO also improved the antibacterial property to the RO membrane with the increase of seventeen folds from 5.46% *E. coli* cells coverage on the surface of the membrane (unmodified membrane) to 0.32% (modified membrane) attributed to the antimicrobial property of AGO [82].

In another study, a combination of surface coating and grafting was reported by Li et al. (2015) whereby the author coated polydopamine (PDA) on the commercial RO membrane (XLE-4040, Dow Co. Ltd) followed by the grafting of polyethyleimine (PEI). Associated with this, the hydrophilicity of the membrane was improved by 25% (reduction in contact angle value from 65.7° to 49.2°). Although the hydrophilicity of the membrane was improved, there was still a slight drop in normalized water flux value from 1.0 to 0.8. This behaviour was due to the higher resistance towards water diffusion across the membrane as compared to the hydrophilicity effect. As a result of the layer resistance and increased electrostatic repulsion between Na⁺ ions and the membrane, a minor increase (95% to 98%) in NaCl salt rejection at 1000 ppm was observed. On another note, the study reported that the changes in membrane properties in terms of hydrophilicity, roughness, and surface membrane charge resulted in lower flux decline (around 20%) as compared to the controlled membrane at 35% [83].

3.2.2 FO membranes

a. Coating

Surface coating is a simple technique used to alter the membrane surface characteristics for better hydrophilicity, surface charge, and antifouling [84,85]. Nguyen et al. (2013) coated a commercial FO membrane surface with poly amino acid 3-(3,4-Dihydroxyphenyl)-L-alanine (L-DOPA) [86]. It was reported that L-DOPA self-polymerized in aqueous solution and attached firmly to the membrane surface [87]. This additional layer (as shown in Fig. 7) could become intensely hydrated and prevented the accumulation and adsorption of foulants on the membrane surface. The contact angle has observed a reduction from 48° to 44° and 38° for membranes coated in a period of 4 h and 12 h, respectively. Also, the membrane surface became more negatively charged after the coating process, which was useful for rejecting negatively charged foulants.

Figure 7. Schematic diagram of surface adsorption resistance for organic matter after the FO membrane coated with L-DOPA (adapted from [86])

Layered double hydroxides (LDHs) nanoparticles could also be deposited on the TFC membranes by PDA-induced coating process [88]. The pristine TFC membrane could be dip-coated into a LDHs suspension and desiccated at 30°C . The modified membrane displayed the least coverage of *E. coli*, indicating the enhanced antibiofouling capability of the membrane due to improved surface hydrophilicity by LDHs.

In general, the hydrophobicity of the support layer exacerbates the ICP phenomenon in FO membranes. Improving the wettability and hydrophilicity of the support layer would reduce the ICP issue and fouling propensity [89]. Liu et al. (2016) coated the bottom surface of a TFC FO membrane (support layer) with PDA and discovered that the contact angle recorded a reduction from 82.2° to 37.4° after a treatment time of 6 h [90]. The hydrophilicity of the bottom surface was obtained due to the phenolic hydroxyl and amine groups contributed by PDA. Though the water permeability and salt rejection did not observe obvious changes, the modified support layer had a good antifouling property.

Another popularly used coating material is PVA, owing to its ability to retain water molecules, easily available in the market, inexpensive, great chemical and physical stability, hydrophilic and antifouling properties, and remarkable film-forming characteristics [91,92]. In the study conducted by Ahn et al. (2015), CA-based membrane was coated with PVA followed by immersion in 0.01% glutaraldehyde solution for cross-linking process [93]. The hydrophilicity of the CA membrane increased substantially, as supported with the reduction of water contact angle from 73.5° to 39.3°.

Support layer can also be coated with minerals such as calcium carbonate (CaCO_3) to improve wettability of the membrane. The coated CaCO_3 can improve the hydrophilicity by connecting to water through strong ionic hydrogen bonding [94]. The modified FO membrane achieved a high water flux of 52 LMH and salt flux of 16.8 gMH using DI water and 2 M NaCl draw solution.

b. Crosslinking

Chemical cross-linking with polyelectrolytes such as PAH, polyethyleneimine, glutaraldehyde, and *p*-xylylene dichloride is a more straightforward method to obtain NF-like rejection layers for FO membrane [95–98]. For instance, Setiawan et al. (2011) fabricated a positively charged PAI hollow fiber FO membranes by cross-linking with polyethyleneimine under mild conditions [99]. The cross-linked FO membrane possessed tight pore size, narrow pore size distribution, and ion repulsion property from Donnan exclusion effect. Consequently, the membranes exhibited good water flux and low reverse solute flux (especially divalent salts) [100]. However, the degree of cross-linking should be optimized as excessive cross-linking could lead to the loss of mechanical strength of the membrane [101].

PEI cross-linking has also been applied to dual-layer hollow fiber poly(amide-imide) (PAI) membrane, with promising water flux of 27.5 LMH coupled with reverse salt flux of 5.5 gMH [100]. However, the modified membrane surface possessed positive charge, which might exacerbate fouling issue due to the oppositely charge attraction towards negatively charged foulants [102]. To overcome fouling propensity, further modification

with PSS polyelectrolytes has been done to alter the surface charge as well as to shrink the pores of active layer of the PEI-cross-linked membrane. It was reported that the further modified membrane maintained a stable flux of 13 LMH against feed mixture of 1000 ppm bovine serum albumin (BSA) and 2000 ppm sodium sulphate (Na_2SO_4) draw solution.

c. Layer by layer

Phytic acid (PhA) is a nontoxic electrolyte that exhibits high affinity toward water molecules and strong chelation capacity with mono/divalent metal ions. This property has been utilized to incorporate antibacterial metal ions such as silver and copper for membrane surface modification [103]. Xiong et al. (2019) adopted LBL assembly to incorporate PhA and silver/copper nanoparticles on the TFC membranes [103]. As illustrated in Fig. 8, the TFC FO membrane was first modified by immersing it in an inorganic salt aqueous solution to anchor metal ions on the TFC membrane. Afterwards, the treated membrane was soaked in PhA solution and the inorganic salt solution alternatively for several cycles. The modification increased the membrane hydrophilicity with water flux enhanced by up to 57-68% and no compromising of membrane selectivity. The membranes also revealed low metal release owing to the strong attachment on the surface.

Figure 8. Modification of TFC membrane by LbL approach through the incorporation of PhA and metal complexes (adapted from [103])

LBL membrane can also be synthesized by incorporating nanoparticles such as GO and oxidized carbon nanotubes (OCNTs) [104]. In a study where GO and OCNTs with five bilayers on a PES support membrane was synthesized, the contact angle of the membrane was lower than that of GO-LBL membrane due to the presence of hydroxyl groups (supported by X-ray photoelectron spectroscopy (XPS) where the former has 9.5% oxygen-containing groups while the latter only 7.6%). However, such synthesis approach that involved covalent attachment and LBL self-assembly was less appealing to industrial production due to the complexity of multiple steps. To overcome this complex synthesis approach, Hegab et al. (2015) adopted a simpler technique by immobilizing GO onto the TFC FO membrane via PDA (adhesive agent) polymer [105]. The modified membrane presented a smoother surface with improved hydrophilicity and antibiofouling capability as compared to pristine membrane.

d. Grafting

The incomplete crosslinking of the MPD and TMC monomers results in the presence of amine and carboxyl functional groups on the surface of TFC PA membrane. Upon soaked in an aqueous solution, the residual acyl chloride groups from the unreacted TMC monomers would convert to carboxyls [106]. These negatively charged moieties may serve as reactive sites for grafting modification of membrane. For instance, Li et al. (2015) grafted photosensitizer porphyrin molecules (Por) on the TFC PA surface via the reaction between the amine group of Por and the carboxyl groups on the TFC membrane to form a strong covalent bonding [84]. When exposed to sunlight radiation, the Por molecules can produce reactive oxygen species, which is highly toxic to bacteria [107,108]. This surface functionalization offered a promising method to address the biofouling issue.

In another approach, coupling reaction is used to bind functionalizing agents onto the TFC surface through other chemicals. For example, graphene oxide (GO) and carbon nanotubes (CNTs) were bound to the TFC membrane surface through N-ethyl-N'-(3-(dimethylamino)propyl)carbodiimide/N-hydroxysuccinimide (EDC/NHS) coupling reaction, where the carboxylic acids were activated with carbodiimide with the aid of NHS followed by the amine addition [109–111]. The carboxyl (–COOH) groups on GO nanosheets were first activated by EDC/NHS, and then grafted onto amine functionalized membrane through the formation of chemical bonding between the functional groups [109]. The GO-functionalized TFC FO membrane exhibited considerable antibacterial capability, which could be attributed to the physical disruption of the bacterial cell or through the release of reactive oxygen species.

Castrillon et al. (2014) functionalized the TFC FO membrane by conducting a second interfacial reaction between ethylenediamine and free carboxyl groups presence on the membrane surface [112]. The functionalized membrane reportedly possessed better antifouling (alginate) property. Similar functionalization has also been adopted by grafting superhydrophilic 3D hyperbranched polyglycerol, PEI, and polyamidoamine (PAMAM) dendrimers to the TFC surface to enhance the antifouling properties by having better rejection of foulants such as BSA, alginate, and ammonia [113–115]. These highly branched molecules offers a high density of hydrophilic functional groups on the membrane surface that could minimize the adsorption of protein and bacteria [116]. The attachment of foulants has also been prevented by the 3D star-like nanostructure of dendrimers through steric hindrance mechanism [113]. For instance, PAMAM was grafted on the TFC FO membrane through the formation of amide bonds between the unreacted carboxyl groups on the PA surface and amine groups of PAMAM dendrimers [117]. The functionalized FO membrane possessed a highly negative surface charge, which improved the ammonia rejection to 98.2% for domestic wastewater treatment.

PDA has recently emerged as one of the most popular biopolymers used in membrane surface modification to suppress biofouling due to its protonated amine groups that could potentially exert antibacterial activity through cell lysis in contact with the bacteria cell membrane [118,119]. For instance, CTA FO membrane modified with PEG-grafted PDA showed improved anti-biofouling property in a submerged FO membrane bioreactor (MBR) over 61-days testing period. It was reported that the modified membrane displayed enhanced surface hydrophilicity and lower flux decline, an indicator that it has better antifouling ability than that of the pristine CTA membrane.

Activation of polybenzimidazole (PBI) flat sheet membrane with 4-(chloromethyl) benzoic acid and subsequent surface modification with taurine, *p*-phenylene diamine (PD), ethylene diamine, and poly(acrylamide-*co*-acrylic acid)(P(Am-*co*-AA)) have shown to improve the hydrophilicity and surface charge of the membrane [120,121]. The water flux was increased twofold to 5.6 LMH as compared to the unmodified PBI membrane when 0.1 M NaCl solution feed and 2 M NH₄HCO₃ draw solution were used.

4. Materials and formulation of RO and FO membranes

Apart from the synthesis conditions and modification approaches discussed previously, the formulation and materials used for the synthesis of RO and FO membranes (both support and separation layers) also play a significant role in improving the membrane characteristics. In most cases, additives especially nanomaterials and nanoparticles will be added either to the active layer or support layer of RO and FO membranes. The incorporation of additives can generally be done through several approaches, either

embedded into the separation and support layers or on top of the membrane surface, as indicated in Fig. 9. The presence of additives would alter the surface properties (e.g. hydrophilicity, roughness, and charge density) and subsequently the membrane separation performance [122]. The additives must have appropriate size and internal structure, as well as compatible with the polymeric membrane to ensure the benefits associated with the additives could be fully utilized.

Figure 9. Approaches for incorporating additives into the RO and FO membranes

4.1 RO membranes

4.1.1 Substrate

The active layer of the membrane has been considered as the key factor to the membrane performances. Associated with that, the modification of active layer is greatly researched. Although the active layer is seen to be the most important part, the formulation or synthesis conditions of the porous layer also play an important role to the performance of the membrane. Factors such as types of solvent and polymers, polymers concentration, additives and operating temperature should not be taken lightly [123].

In the literature, it was observed that the improvement of support layer water permeability and changes in the pore size can be achieved through the addition of hydrophilic additives such as PEG and PVA. For example, Fathizadeh et al. (2012) prepared a PA RO composite membrane by adding PEG additives in the PES substrate. Associated with this modification, the membrane permeability was enhanced by almost six folds from 1.2 LMH to 7.8 LMH. It was reported that the presence of the PEG

enlarged and increased the macrovoid size, and thus allowing the water molecules to easily pass through the membrane with lower resistance [124]. Other studies also showed that by improving the porosity of the support layer, the water permeability could be greatly enhanced [125,126]. However, the increase of macrovoid size that caused a decrease in the thickness of the substrate might affect the mechanical strength of the RO membrane.

Although porous substrate is desirable in membrane to achieve higher flux, the challenge for porous substrate is the difficulty to withstand higher operating pressures. The compression causes the membrane macrovoid to become smaller and increase the tortuosity. When the tortuosity of the porous substrate increases, the distance of water transportation route across membrane becomes longer due to lack of connectivity between pores [127], and this possibly would lead to flux decline behaviour which is undesirable in membrane. As the high operating pressure is unavoidable especially in desalination process, alternative solutions are required to enhance the mechanical strength of the membrane. Since the introduction of nanomaterials in RO membrane in the early of 2000s, the advancement of nanotechnology in polymeric RO membrane has led to the breakthrough of this undesirable flux decline and weak mechanical strength. Not only that, the incorporation of the nanomaterials in the polymeric matrix or substrate has successfully led to improved RO membrane hydrophilicity without compromising the rejection properties of the membrane [128]. For example, Pendergast et al. (2010) observed that, there was an enhancement in flux decline behaviour between unmodified membrane (PA RO-PSf substrate membrane) and modified membrane (PA RO-PSf incorporated silica membrane & PA RO-PSf incorporated zeolite membrane). At optimal membrane performance, the modified membrane experienced lower flux decline in the range of 20% to 22% as compared to unmodified membrane at around 30%. The reason for enhanced flux decline was due to the added mechanical strength of the support structure [129].

Another interesting study of embedment of nanomaterials was reported by Yan et al. (2015) whereby the author investigated the pore formation of the membrane by assuming nanomaterials as a pore former. In this study, silicon dioxide nanomaterial (SiO_2) was embedded into the PSf supports via immersion precipitation followed by NaOH alkali treatment prior to the TFC formation on the nanocomposite support. During immersion precipitation, the pore formation happened when some of the SiO_2 embedded near the surface of the casting film diffused out to the coagulation bath. Associated with this, the total porosity of the modified membrane (optimal condition) increased by around 14 % (from 63.6 ± 2.0 to 72.3 ± 4.3). Moreover, the flux increased about 55.4% (from 35.4 LMH to 55 LMH) and the NaCl rejection achieved as high as 99.10 % as compared to

98.74% of unmodified membrane. The modified membrane also showed a membrane performance (water permeance of 3.55 LMHbar and salt rejection of 99.1%) that was comparable to some of the commercial membranes such as GE-INDUSTRIAL RO6 4040F35 (4.66 LMHbar, 99%) and DOW-BW30-400 (2.91 LMHbar, 99.5%) [130].

Carbon-based additive is another class of nanomaterials that has been adopted in membrane technology. The addition of this nanomaterial has proven its effectiveness in improving the flux, selectivity, antifouling properties and mechanical strength of the membrane. For instance, Son et al. (2014) modified the PES support layer with functionalized carbon nanotube (fCNT) prior to IP process. The presence of fCNT improved the substrate hydrophilicity level with a contact angle of 51.03° (decline from 54.76°) and increased the water permeability by 44% from 0.84 LMH/bar to 1.21 LMH/bar without sacrificing the salt rejection (maintained at around 95% for both cases). Besides, the presence of fCNT also increased the pore size (from to an average size of 10.32-14.45 nm) by connecting the disconnected pores that allowed easy water passage across the PES support. On another note, the fouling analysis showed that the flux recovery ratio increased from 74.81% to 79.87% (an increase of almost 7 %) which could be attributed to the presence of negatively charged fCNT. The negatively charged fCNT contributed to the loosely attachment of foulants on membrane surface, and thus allowing flux to be restored easily as compared to unmodified membrane [131].

Another family from carbon derivatives, GO was adopted by Chae et al. (2017) to improve the performance of the membrane. The GO was embedded into both support and active layers for RO membrane synthesis. The incorporation of GO into the support layer showed substantial improvement in terms of hydrophilicity, pore size, shifting from positive to negative surface charge property and antimicrobial property owing to the presence of hydrophilic functional groups and surface charge of GO. The support layer hydrophilicity improved as indicated by the contact angle measurement (reduced by 28.81% from 59° to 42°) while the average pore size of modified membrane increased from approximately 20 nm to 27 nm. Besides, there was a shifting of surface charge from 0.6 mV (unmodified, nearly neutral) to -16 mV (modified, negatively charge) which favoured the rejection of negatively charged particles. Associated with the alteration in the support layer properties, the water flux for RO membrane with the support incorporated with GO was increased by 2.6% (from 23 LMH to 29 LMH) while the salt rejection was enhanced approximately 4% (from 90.6 to 94.8%) as compared to unmodified TFC membranes. The observation of the enhanced water flux and salt rejection was due to the increased surface hydrophilicity and alteration of membrane surface charge, respectively. On top of this, the presence of GO in the support layer

successfully reduced the biofilm formation with the attachment of biovolume cell was 70% lesser than unmodified TFC membrane [132].

Apart from carbon derivatives, metal organic framework (MOF) was also adopted in improving the membrane performance. For instance, Park et al. (2017) incorporated HKUST-1 [$\text{Cu}_3(\text{BTC})_2$] MOF treated with sulfuric acid into PSf support layer to enhance the porosity and hydrophilicity of support layer of the TFC RO membrane. Associated with the modification, the modified PSf support layer showed improvement in water flux from 175.0 LMH to 245.8 LMH (increased by 40.46%). This was because the hydrophilicity of the support layer was enhanced, which indicated by the higher value of solid-liquid interfacial free energy ($-\Delta G_{SL}$) 108.5 mJ/m^2 (modified support layer) as compared to 98.6 mJ/m^2 (unmodified support layer). Besides, the increase of porosity of the support layer from 40.9% to 49.4% allowed water molecules to move easily across the membrane, and thus resulting in enhancement of water flux. As a result, the TFC RO membrane with the modified support layer also experienced improved flux from 35.7 LMH to 47.6 LMH (increased by 33.33%) without compromising the salt rejection (96%-modified, 94%-unmodified) [133].

4.1.2 Active layer

The discovery of thin film nanocomposite (TFN) membrane marked the breakthrough for TFC membrane in the route of overcoming its relatively low water flux. The first attempt of combining nanomaterial with TFC RO membrane was introduced by Hoek and co-researchers. In the study, Hoek et al, incorporated zeolite nanomaterial into the hexane-TMC solution prior to membrane's modification process. The pure water permeability of the modified membrane increased almost twofold from 7.56×10^{-4} LMH (neat membrane) to 13.68×10^{-4} LMH (modified membrane) without trading off its salt (NaCl) rejection [134]. The positive impact of the TFN membrane concept led to the exploration of different types of nanomaterials, such as inorganic nanomaterials (TiO_2 , silver, SiO_2 , MOF, etc.), carbon-based nanomaterials (GO, CNTs, etc.) and aquaporin (protein) in the synthesis of TFC membrane [135].

For instance, by depositing titanium dioxide (TiO_2) on the active surface of the membrane, the resistance of the modified RO membrane towards biofouling was enhanced. It was reported that the presence of the photocatalytic bactericidal effect of TiO_2 inhibited the bacteria attachment on the membrane surface. Associated with the TiO_2 layer, the survival rate of *E.coli* cells on the RO membrane surface dropped from 60% to 0% under 4 hours of UV illumination. This subsequently minimized the flux loss from its original permeability to 15% as compared to neat RO membrane at 30% without compromising the salt rejection [136].

Carbon-based additives have shown its notable presence in improving RO membrane for water desalination processes. It has been widely employed to enhance the membrane performance in water flux, rejection, antifouling capability and stability [137]. Out of different types of carbon-based additives, graphene-based nanomaterial has attracted tremendous interest in water desalination. It is attributed to the presence of various hydrophilic functional groups, great physicochemical properties, tuneable properties and various possibilities via functionalization. For instance, Hegab et al. (2015) modified the commercial brackish water TFC membrane (BW30LE) by coating graphene oxide functionalized chitosan (GO/f-Cs) to improve the fouling resistance of the membrane. It was found out that the modified membrane showed superior performance as compared to unmodified membrane in terms of NaCl (1500 ppm) salt rejection, hydrophilicity, water flux and antifouling property. The hydrophilicity of the modified membrane was improved with the decrease of contact angle for about 70% (from 63.68° to 19.13°) due to the presence of abundance hydrophilic functional groups of GO. The membrane water flux increased from 56.14 LMH to 61.47 LMH, which could be attributed to the hydrophilicity induced by the nanomaterial and thus promoting water sorption across the membrane. Besides that, the salt rejection was 7.7% higher than the unmodified membrane due to the GO/f-Cs coated dense layer that produced compact structure on the surface of the membrane. On another note, fouling analysis showed that the modified membrane has better flux recovery ratio at 97% as compared to unmodified membrane at 86% while the flux decline has also been reduced from 18% to 6% [138]. Other improvement of GO-based TFC membrane for desalination were also reported [139,140].

Another member of carbon material, CNTs has also proved its capability to improve the membrane performance. Vatanpour et al. (2016) has successfully grafted multiwalled carbon nanotubes (MWCNTs) on a commercial PA seawater RO membrane (RE4040-SHF, South Korea) for enhanced fouling resistance, flux and rejection. The improvement was attributed to the presence of nanotubes channels for water passing and hydrophilic functional groups of MWCNTs. The channels allowed the passage of water molecules while the hydrophilic functional groups increased the affinity towards water molecule. Both mechanisms promoted the permeability of water molecules and thus increased the water flux from around 23 LMH to 25 LMH at 0.0125 wt% MWCNTs concentration while the salt rejection was slightly increased from 95.5% to 96.5% at low MWCNTs concentration (0.0125-0.05). On another note, the flux decline for modified membrane (0.025 wt% MWCNTs) was lower (around 15%) as compared to the unmodified membrane (around 19%). This proved that the modified membrane has a better fouling resistance. However, RO membrane modified with high concentration of MWCNTs was subjected to the negative impact on flux and salt rejection due to the compression of the

grafting layer that eventually making it very stiff, and thus creating a resistance for water passage (increase mass transfer and decreasing the hydrophilicity effect) [141].

Silver nanomaterial displayed a remarkable antibacterial property that is useful to prevent biofouling issue in membrane process. The presence of silver nanomaterial in membrane indeed has become a great interest to membrane desalination technologies nowadays especially for the saline feed waters that contain high biological activity. Usually, the silver nanomaterials are chemically deposited on the membrane surface to suppress the formation of biofilm. For example, a commercial PA-RO membrane modified with silver nanomaterial was tested in Wukan desalination pilot plant, Penghu. It was reported that the modified membrane could reduce the flux reduction by almost 50% (from 75% to 25%), and thus prolonged the lifespan of the RO membrane performance [142]. This could be attributed to the low microbial growth since the presence of silver inhibited the growth of microbes on the membrane surface. In another study, Ben-Sasson et al, performed an in-situ functionalization of silver nanomaterials on the surface of commercial seawater RO membrane. The presence of silver nanomaterials demonstrated strong antibacterial properties towards *E. coli*, *P. aeruginosa* and *S. aureus* with the decrease of bacteria colonies (CFU) by 78%, 91%, 96% as compared to neat membrane [143]. However, the leaching stability of the nanomaterial from the membrane surface remains a major challenge for surface modification process.

Although the incorporation of nanomaterial has proven its effectiveness in tuning the membrane performance, the key challenge of using single nanomaterial (usually inorganic nanomaterial) is the tendency of forming agglomeration and aggregation that discounts the improvement brought to the membrane. To minimize this impact, Rajakumaran et al. (2019) modified the RO membrane using spherical ZnO-GO hybrid material. In this study, GO served as a platform or interface for ZnO nanomaterial dispersion and promoted better attachment with the TFC membrane due to the presence of the of hydrophilic functional groups. As a result, the modified membrane (at 0.03 wt% GO-ZnO concentration) showed almost 65% of water flux improvement (approximately from 15 LMH to 25 LMH) without compromising the salt rejection. Such improvement was attributed to the improvement in the surface hydrophilicity, as shown in the decline of contact angle value (around 20%) that facilitated the movement of water across the membrane. This decrease in contact angle measurement could be related to the presence of abundance hydrophilic functional group of the ZnO-GO hybrid material. Besides, the modified membrane also showed improved membrane stability with consistent RO membrane performance, as indicated by the enhanced chlorine stability and antifouling properties (retained more than 75% of its original flux as compared to neat membrane at 41%). The reason for this stability was due to the lower surface roughness (due to

enhanced hydrophilicity) that decreased the adhesion of foulant particles on membrane surface [144].

Sulfonated materials or copolymers have also been adopted to improve the hydrophilicity of the membrane and to overcome the weak chlorine resistance of PA layer. For instance, Kim et al. (2013) modified a TFC RO membrane to TFN RO membrane by adding sulfonated poly (acrylene ether sulfone) containing amino group (aPES) material and hyper-branched aromatic PA grafted silica nanomaterial (HBP-g-silica) during the membrane synthesis. The salt rejection after chlorine exposure only dropped by 15% (from 97.7% to 82.5%) as compared to the neat membrane which dropped by 31% (from 98.0% to 67.1%). The strong chlorine resistance property was due to the formation of additional amide groups in the RO membrane from the combination of amino groups in HBP-g-silica and TMC solution. This resulted in the formation of denser membrane active layer that shielded it from chlorine attack. Furthermore, the modified membrane possessed better initial water flux (34.5 LMH) than the neat membrane (22.1 LMH) due to the presence of APES sulfonic group ($-\text{SO}_3\text{H}$) and HBP-g-silica that provided additional hydrophilicity to the membrane (drop in the contact angle value from 61.2° to 50.1°) [145].

Recently, aquaporin, (biological proteins) has emerged as one of the promising additives that can improve RO membrane performance, owing to its effective hourglass shape water transport channel and superior rejection at the same time. For example, Qi et al. (2016) synthesized an aquaporin biomimetic based RO membrane and the study revealed that the water and salt fluxes for aquaporin modified membrane improved by almost 50% (from 2.68 LMH to 4.13 LMH) and 17% (from 1.00 LMH to 1.17 LMH), respectively. The increase of flux was attributed to the improved hydrophilicity. Furthermore, the aquaporin modified membrane also recorded good operation stability by operating at 90% of its original performance even after 100 days of operation. Moreover, the energy requirement of the modified membrane was lower than unmodified membrane. The promising chemical stability (flux and rejection) and operational stability (energy and cost) indicated the great potential of aquaporin biomimetic based RO membrane (4.13 LMH water permeability, 97.2% NaCl rejection, 1.17 LMH solute permeability) in practical applications as the separation properties was comparable to the commercial BW30 RO membrane (2.83 LMH water permeability, 97.3% NaCl rejection, 0.79 LMH solute permeability) [146].

4.2 FO membranes

4.2.1 Substrate

Various materials (e.g. PES, PSf, PEI, PAN, and inorganic materials) have been used to synthesize the FO substrates, each with their own advantages and disadvantages in terms of stability, cost, and hydrophilicity [47]. Since majority of the available FO membranes in the market belong to polymeric membrane group, further discussion on the materials and formulation of FO membrane will be focusing on the polymeric membrane.

Adjusting the polymer composition is one of the most commonly used techniques to obtain porous FO support layer. For instance, decreasing the PSf concentration from 18% to 9% increased the water permeability by almost 50% (from 1.09 to 1.63 LMH/bar) [16]. Associated with this change was an elevation of FO water flux from 7.5 to 21 LMH using 1 M NaCl as draw solution and deionized water as feed solution. However, the use of lower polymer concentration might produce support layer with larger pore size, which might be too large to support the selective layer under a high hydraulic pressure [147]. While the operation of FO does not require high hydraulic pressure, sufficient mechanical strength is still required to endure the cross-flow dynamics in a large module for a long operating lifetime.

Pore forming additives such as lithium chloride (LiCl) and PEG could be utilized to modify the structure of the support layer. The incorporation of LiCl in the synthesis resulted in the collapse of the macrovoid, a reduction in pore size and porosity due to slow phase separation at high content of LiCl [148]. The reduced tortuosity has improved the water flux to 31.8 LMH. On another note, Wu et al. (2016) reported that increasing the PEG concentration from 0 to 6% increased the water permeability coefficient by 50% (1 to 1.55 LMH/bar), translating to doubled flux when the DS concentration increased from 0.5 to 1.5 M (NaCl) [149].

Instead of using single polymer, Bui et al. (2013) prepared a polymer consists of PAN and CA at different ratio for the synthesis of FO support layer [150]. The high viscous polymer solution led to the formation of nanofibers with larger diameter. This subsequently promoted the formation of bigger pore size in the support layer and improved the water permeability coefficient to 2.036 LMH as compared to commercial HTI-CTA membrane at 0.683 LMH.

Sulfonation has been adopted to promote the hydrophilicity (and thus productivity) of the FO support layer by replacing the hydrogen atoms of the membrane polymer matrix with sulfonic acid groups through electrophilic reaction [151]. For instance, when 50 wt% sulfonated polymers composed of PES and polyphenylsulfone (PPSU) was used in the

synthesis of support layer, a more favourable sponge-like structure free of macrovoids was obtained [152]. The slow de-mixing in the phase inversion has produced larger pore size and porosity as compared to support layer fabricated from pure PESU. This structure helped to reduce ICP effects. Another advantage of this modification was the improvement of hydrophilicity which increased the water permeability too. However, FO membrane synthesized from sulfonated polymer is susceptible to swelling, a phenomenon that would reduce the mechanical strength of the support layer and pure water permeability [152–154].

The homogenous dispersion of nanoparticles in the polymer matrix may give rise to higher fractional free volume in mixed matrix membranes leading to high water permeability [155]. Apart from this, the aim of incorporating nanoparticles into the polymeric membranes is to promote the hydrophilicity, mechanical strength, and separation property [156]. A wide range of nanoparticles such as zeolite, silica, calcium carbonate, GO, CNTs, and TiO₂ have been explored by researchers where direct blending method is generally employed for adding the nanoparticles into the support layer polymer [24,157]. Park et al. (2015) incorporated GO nanosheets into the polymeric support layer of TFC-FO membrane [158]. The presence of abundant hydroxyl, carboxyl, and epoxy functional groups of GO increased the membrane hydrophilicity and enhanced the pure water permeation to 1.76 LMH from 0.91 LMH of pristine membrane without GO. Interestingly, the incorporation of different nanomaterials has resulted in different physicochemical properties of the support layer. For instance, the addition of PVA or carbon-TiO₂ resulted in the formation of macrovoid structure while GO and MWCNTs formed finger-like macrovoids [159].

The incorporation of titania in PSf sub-layer improved the membrane properties as in good wettability, the formation of finger-like structures, reduced tortuosity, and low ICP impacts [136]. These alterations in the support layer morphology managed to increase the water permeability to 4.27 LMH with 1.0wt% zeolite. Tang et al. (2013) demonstrated that the inclusion of 0.5% zeolite to the PSf substrate increased the substrate surface porosity and hydrophilicity as well as reduced the tortuosity [160]. Subsequently, the water permeability of the rejection layer was increased by 80% since the hydraulic resistance of the support layer has been reduced.

A more drastic formulation has been shown by Fan et al. (2019) where reduced graphene oxide and carbon nanotube have been adopted as active separation layer and substrate of hollow fibre FO membrane, respectively [161]. The GO layer was chemically reducing electrodeposited on the carbon nanotube fibre substrate. With its ultra-low friction and well-defined interlayer spacing, the FO membrane possessed high rejection rate and water permeability. Meanwhile, the carbon nanotube substrate, with tuneable porosity

and good wettability could weaken the ICP phenomenon, and thus facilitated a high water flux. The improvement was quite obvious as revealed by its outstanding water flux at 22.6 LMH, which was 3 times higher than that of the commercial membrane. Besides, the reverse salt flux was only 1.6 gMH in comparison to 2.2 gMH for the commercial membrane. However, the proposed membrane might be too costly for mass production as the current price of GO and carbon nanotube are quite high. Discovery of competitive mass production approach for these materials might materialize the use of this membrane.

Tian et al. (2015) has embedded functionalized MWCNTs to strengthen the substrate strength [57]. The homogenous dispersion of the functionalized MWCNTs in the polymer solution has increased the tensile strength and stiffness. Besides, the increment of porosity from 59% to 81% indicated the formation of more interconnected pore structure. Subsequently, the water permeability coefficient was higher as compared to TFC-HTI membrane (2.6 LMH vs 1.63 LMH). However, the salt permeability coefficient was higher too (0.7 LMH vs 0.3 LMH). This phenomenon has also been observed by other researchers where the improved (higher) water flux is normally associated with higher reverse salt flux [162].

4.2.2 Active layer

The incorporation of nanoparticles in membrane synthesis has resulted in marked improvement in membrane characteristics such as high flux and rejection capability. Various nanomaterials such as zeolite, CNTs, zwitterions, dendrimers, silver, copper, GO, MOF, and aquaporin have been explored in the synthesis of FO membrane [163]. Tang et al. (2013) reported that FO membrane with 0.1 w/v% zeolite loading (in TMC/hexane) achieved approximately 50% higher flux than that of neat membrane [160]. However, the loading of nanoparticles is critical to the membrane formulation since excessive loading of nanoparticles may lead to defect formation, which might cause a high reverse solute flux [157].

Silver is one of the most extensively used biocides with reported multifold antibacterial mechanism: direction adhesion or infiltration to destroy the bacterial cells and generation of reactive oxygen species to cause defects to bacteria cell structure and prevent the formation of biofilm [164,165]. Normally, silver is incorporated near the membrane surface to maximize the interactions between the nanoparticles and bacteria [166]. For example, Liu et al. (2017) utilized layer-by-layer IP approach to covalently bind the silver nanoparticles on the TFC PA surface [166]. The incorporation of silver nanoparticles resulted in stable filtration performance and excellent antibacterial properties. Another alternative biocide with lower cost is copper-based nanoparticles [167]. The copper nanoparticles could be decorated on the membrane surface by soaking

the membrane in dopamine solution containing copper ions [168]. Though the membrane has lower water flux (by 28%), the antibacterial activity against *S. aureus* was increased by up to 97% with very little copper leakage into the permeate, indicating the capability of the functionalized membrane to perform long-term antibacterial activity against Gram-positive bacteria [169].

Silver nanoparticles can also be easily dip-coated onto the membrane surface through PDA layer [170]. The functionalized membrane displayed long-term silver release behaviour with the capacity to be regenerated multiple times after depletion. The thickness of the PDA layer should be controlled as the additional PDA layer would exert mass transfer resistance to water permeation. The facile regeneration of the silver nanoparticles on the PDA surface could be sustainable approach to provide long-term antibiofouling for the membrane.

GO has been recognized as the most amazing and versatile nanomaterial in this decade. It has been widely employed to improve the membrane properties be it in the form of water flux, rejection, and antifouling capability. For instance, Hegab et al. (2015) grafted GO to the TFC PA surface via poly L-Lysine (PLL) intermediary using LbL approach [171]. The modified membrane attained a higher hydrophilic and smooth surface, on top of 99% reduction in surviving bacteria. Also, the reverse salt flux was reduced too, indicating an improvement of membrane salt selectivity. Another family member of carbon-based nanoparticles is CNTs. The incorporation of 0.1 wt/v% (CNTs in MPD aqueous solution) amine-functionalized MWCNTs achieved water flux of 95.7 LMH and solute flux of 4.8 gMH, which observed an improvement of 160% higher and 30% lower than the pristine membrane [172].

The instability and dissolution of nanoparticles from the membrane are some of the hindrances that restricted the practical application of nanoparticles-functionalized membrane in water and wastewater treatment. This challenge can potentially be solved by decorating the nanoparticles onto larger support or carrier that has better compatibility with the polymer matrix (subsequently lower dissolution rate of nanoparticles) [173]. For instance, Soroush et al. (2015) demonstrated that the nanocomposite (silver nanoparticles immobilized on GO nanosheets) could be covalently bound onto the PA FO surface with enhanced hydrophilicity (contact angle below 25°) and antibacterial activity (> 96% in a static test) [174]. The GO nanosheets not only enhanced the amount of silver nanoparticles incorporated into the membrane but also stabilized the nanoparticles and decreased the ion release rate [175]. The stability was due to the covalent bonds formed between the carboxyl groups on the silver-GO nanocomposite and carboxyl groups of the TFC surface via crosslinking reaction [176].

Highly hydrophilic zwitterionic materials have also been employed as carrier to hold the biocidal silver nanoparticles. This nanocomposite possessed two functionalities, with the silver nanoparticles exert toxicity toward the bacteria while the zwitterionic materials shield the membrane surface from adsorption of organic foulants [177]. The synthesis approach first involved the grafting of zwitterionic poly(sulfobetaine methacrylate) brushes to the membrane surface via an atom transfer radical polymerization reaction. Later on, silver nanoparticles were formed in situ through chemical reduction of silver. The functionalized membrane showed superior antibacterial activity (95%) and inhibited the formation of biofilm.

Recently, MOFs have emerged as a promising additive for membrane synthesis due to their hybrid organic/inorganic structure, high surface area, highly tuneable molecular structure, and adjustable pore size [178]. It has been proposed that MOFs could house biocidal metal ions (antibacterial) for continuous gradual release of the metal ions by degradation of the framework [179]. For instance, the popularly used silver has been combined with MOFs to functionalize TFC PA membranes for FO applications [180]. The fabrication process involved only silver salt and organic ligand where both are covalently bonded to the TFC PA FO membrane at ambient temperature (without the need of additional stabilizing or reducing agent). After functionalized with Ag-MOFs, the membrane surface possessed strong antibacterial activity with more than 99% reduction of live bacteria. However, the capability of the membrane to retain its antibacterial property for long-term operation has been hindered by surface depletion of metals [177]. Apparently, regeneration of metal nanoparticles is required to preserve the antibacterial activity of the membrane surface [181].

A key challenge to FO desalination is the reverse solute flux (permeation of solute from draw to feed solutions) and forward solute flux (permeation of solute from feed to draw solutions) that would lead to several problems such as reduced osmotic driven force, salinity build-up on the feed side, feed contamination, aggravated membrane fouling, and elevated operating costs due to the need to continuously replenish draw solution [182]. To minimize the impact arises from this bidirectional solute flux, Zou et al. (2019) modified the FO membrane surface by coating zwitterion functionalized carbon nanotubes onto a commercial TFC FO membrane [183]. The zwitterion functional groups, tertiary amine group and carboxylate group, provided the necessary charge for electrostatic repulsion forces while the CNTs offered steric hindrance property. The combination of these features helped to significantly reduce reverse solute flux (55-84%) for a range draw solutes such as NaCl and $\text{NH}_4\text{H}_2\text{PO}_4$. At the same time, forward solute flux of several impurities such as Mg^{2+} , NO_2^- -N, and NH_4^+ -N has also been reduced in the range of 30-100% as compared to unmodified FO membrane. The improved

membrane characteristics have also led to consistent FO performance with enhanced fouling resistance.

Song et al. (2015) have synthesized a novel double-skinned TFN membrane for enhanced separation performance and antifouling capability in FO process [184]. CNTs were mixed with PDA which then undergone IP with trimesoylchloride to form active separation layer on both sides of PSf support layer. This resulted in the formation of two active layers sandwiching the support layer in the middle. The double-skinned FO membrane possessed better flux performance as compared to pristine TFC FO membrane or single-skinned TFC FO membrane, with approximately 25% higher water flux and 28% of lower reverse solute flux. This could be attributed to the nanocorridors formed from the CNTs provided extra passage for water transport while the dense active layer facing the draw solution prevented the salt from diffusing to feed side. In addition, the double-skinned membrane also possessed better antifouling performance where the initial water flux and normalized recovery flux were much higher compared to single-skinned TFC FO membrane.

Apart from the carbon-based and inorganic nanoparticles, aquaporin (membrane protein) has also been used to enhance the water permeability and salt rejection of FO membrane, owing to the intrinsic characteristics of the protein as a channel for water transfer and small solutes across the membrane [15]. For instance, the incorporation of aquaporin laden vesicles in the PA selective layer of FO increased the water permeability by twofold (from 3.7 to 7.6 LMH/bar) [185]. The water flux was also improved considerably from 38.5 to 49.1 LMH. The promising improvement has also been supported with the commercialization of FO membrane incorporated with aquaporin by Aquaporin A/S and its Singaporean subsidiary Aquaporin Asia Pte. Ltd. [186,187]. However, the availability of aquaporin FO membrane in the market is limited due to its complicated and difficulty in the fabrication process (high manufacturing cost). Furthermore, the long-term stability and integrity of this biomimetic FO membrane is scarce [11]. Hence, efforts are required to simplify and ease the scale-up fabrication of the membrane (reducing the cost) and more long-term operation study should be explored.

Conclusion and future prospects

In spite of the advancement of membrane science, some shortcomings are still persisting for the applications of RO and FO membranes in desalination processes. For instance, the commercially available TFC membranes are susceptible to chlorine attack and extreme pH conditions that will decompose and degrade the membrane performance. This signifies the need to seek for polymer materials that on the one hand could offer higher tolerance and resistance to chemical and mechanical conditions, but on the other hand

would not sacrifice the flux. Also, membrane fouling such as deposition of organic compounds and microorganism on the membrane surface is still a big issue for long-term operation process. Fouling will shorten the membrane lifespan, which increases the cost of membrane desalination process. For RO, scaling is another challenge that leads to the degradation of membrane performance in desalination. Improper handling of scaling formation on the membrane surface will affect the membrane productivity. Moreover, additional cost is required to remove the scale, depending on the severity of the membrane surface blockage. Although the anti-scaling agents were seen to be effective in minimizing the scaling formation, search for new antiscalant and better alternative to further minimize or prevent the scale formation is still on-going.

Scaling is a lesser issue for FO process though concentration polarization is a bigger obstacle for it. Internal and external concentration polarization will weaken the osmotic pressure difference across FO membrane, which subsequently leads to lower flux performance that is infeasible for FO process as the flux of existing FO process is already low. All these phenomena indicate that fouling is an inevitable issue for membrane processes. Hence, apart from improving the membrane antifouling capability, attention should also be given to the pre-treatment process prior to the RO and FO processes such that the foulant present in feed to RO and FO can be removed to reduce membrane fouling propensity.

Though surface modifications and incorporation of additives in membrane synthesis are frequently employed to alter the membrane characteristics, some undesired side-effects have also been reported. Some modifications will result in the formation of external layer on top of membrane to increase the rejection capability but the water flux is compromised (additional resistance for water permeation). Another side-effect is the incorporation of nanoparticle additives that would induce the formation of rougher membrane surface where this characteristic is usually associated with more severe membrane fouling propensity. Thus, controlling the formulation and synthesis condition is crucial to obtain membrane with desired characteristics while suppressing the undesired side-effects.

Numerous studies have indicated that the incorporation of nanoparticles reportedly positively improving the membrane properties and performance. However, there are several challenges associated with this popular membrane modification approach. Due to its nano-size, the nanoparticle additives tend to agglomerate together and dispersed unevenly in the polymeric matrix. The agglomeration and uneven distribution of nanoparticles normally would result in the formation of defects on the membrane surface or structure, and subsequently adversely affects the membrane integrity (flux and rejection) and mechanical strength of the membrane. Another issue dealing with nanoparticles is the compatibility with the polymeric matrix. Inorganic nanoparticles do

not interact or bound strongly with the organic polymeric matrix. Thus, the risk of nanoparticle leakage is apparent and the membrane will be losing its improved capability over time. This defeats the intention of utilizing the nanoparticles for enhanced membrane performance and causes financial loss as the membrane could not last long and the valuable nanoparticles are lost to environment (potentially harmful to the ecosystems and living organisms). Another challenge is related to feasibility of having large-scale production of TFC membrane incorporated with nanoparticles. Many nanoparticles used in the studies are synthesized through complicated procedures, and this will be the obstacle of commercialization of TFC membrane enhanced with nanoparticles. The nanoparticles agglomeration and leaking issues in lab-scale studies have put a doubt on the commercialization and large-scale application of RO and FO membranes enhanced with nanoparticles too. Hence, it could be seen that the road to mass production of TFC RO and FO membranes (enhanced with nanoparticles) is still quite challenging despite the positive outcomes reported in controlled-experimental conditions.

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