

2021

Recent advancements in the application of new monomers and membrane modification techniques for the fabrication of thin film composite membranes: A review

Javad Farahbakhsh
Edith Cowan University

Vahid Vatanpour

Mahsa Khoshnam

Masoumeh Zargar
Edith Cowan University

Follow this and additional works at: <https://ro.ecu.edu.au/ecuworkspost2013>



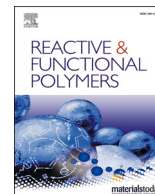
Part of the [Engineering Commons](#)

[10.1016/j.reactfunctpolym.2021.105015](https://doi.org/10.1016/j.reactfunctpolym.2021.105015)

Farahbakhsh, J., Vatanpour, V., Khoshnam, M., & Zargar, M. (2021). Recent advancements in the application of new monomers and membrane modification techniques for the fabrication of thin film composite membranes: A review. *Reactive and Functional Polymers*, 166, article 105015. <https://doi.org/10.1016/j.reactfunctpolym.2021.105015>

This Journal Article is posted at Research Online.

<https://ro.ecu.edu.au/ecuworkspost2013/11031>



Review

Recent advancements in the application of new monomers and membrane modification techniques for the fabrication of thin film composite membranes: A review

Javad Farahbakhsh^a, Vahid Vatanpour^{b,*}, Mahsa Khoshnam^c, Masoumeh Zargar^a

^a School of Engineering, Edith Cowan University, Joondalup, WA 6027, Australia

^b Department of Applied Chemistry, Faculty of Chemistry, Kharazmi University, Tehran 15719-14911, Iran

^c Department of Material Engineering, Isfahan University of Technology, Isfahan, Iran



ARTICLE INFO

Keywords:

TFC membranes
Reverse osmosis
Nanofiltration
Interfacial polymerization
Monomers
Desalination

ABSTRACT

Thin film composite (TFC) membranes have been experiencing significant modifications recently aiming to improve their structure, properties and separation efficiency. One of the promising modifications to tailor the membranes more efficient is changing the materials used. *m*-phenylene diamine (MPD), piperazine (PIP), and trimesoyl chloride (TMC) are the most common monomers used to fabricate TFC membranes. Recent studies have introduced several alternatives to these traditional monomers showing significant contribution of these monomers to the physicochemical properties of the membranes (e.g., surface roughness, hydrophilicity, cross-linking density, chemical structure) as well as membranes' separation efficiency. Emergence of more favorable functional groups such as carboxylic and amine groups due to the new materials integration facilitates the polymerization process and is beneficial to the membrane properties. Here, a critical review on the new interfacial polymerization monomers applied for reverse osmosis (RO) and nanofiltration (NF) membranes fabrication is presented. The membrane molecular structure and fabrication mechanism are investigated in details. This is followed by a review of the recent surface modification methods including grafting, coating and additive incorporating into the thin layer of membranes. The application of alternative monomers to MPD, PIP and TMC are investigated and the benefits of using these monomers or co-monomers are discussed.

1. Introduction

There is an unprecedented demand for drinking water throughout the world [1,2]. The limited freshwater resources and the continuous industrial development increase the concern over the need for more water in the near future. The present water sources can also be polluted by industrial and agricultural activities, exacerbating the issue. Hence, discovering new strategies to produce more drinking water is critical [3]. More than 97% of water on earth is accumulated in the seas and oceans and has a high salinity [1]. Various water treatment techniques including membrane separation processes (ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO)), distillation, and electrochemical processes are applied to produce freshwater [4]. Among all different treatment processes, membrane separation technology is considered the most effective process for desalination of seawater, as well as brackish water, and wastewater effluents treatment due to its

simple operation, low energy consumption, high performance, and relatively lower operational cost [5].

Polymeric membranes used for separation in water treatment are categorized and used through two main processes non-pressure driven and pressure-driven [6]. The main non-pressure driven processes are pervaporation [7], dialysis [8–10], membrane distillation [11,12], and membrane contactors [13,14], in which the separation is based on the concentration gradient. The pressure-driven membrane techniques are typically divided into five main groups depending on the membranes pore size: MF [15], UF [16,17], NF [18–20], RO [21,22], and forward osmosis (FO) membranes [23–25]. RO and NF membranes are commonly used for the desalination of seawater and brackish water respectively [26]. In non-pressure driven membranes such as membrane contactor and membrane distillation, mostly hydrophobic porous structure is used, which usually fabricated by the phase inversion process. For non-pressure driven pervaporation membranes, non-porous

* Corresponding author.

E-mail address: vahidvatanpour@khu.ac.ir (V. Vatanpour).

<https://doi.org/10.1016/j.reactfunctpolym.2021.105015>

Received 20 June 2021; Received in revised form 19 August 2021; Accepted 20 August 2021

Available online 21 August 2021

1381-5148/© 2021 The Authors.

Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

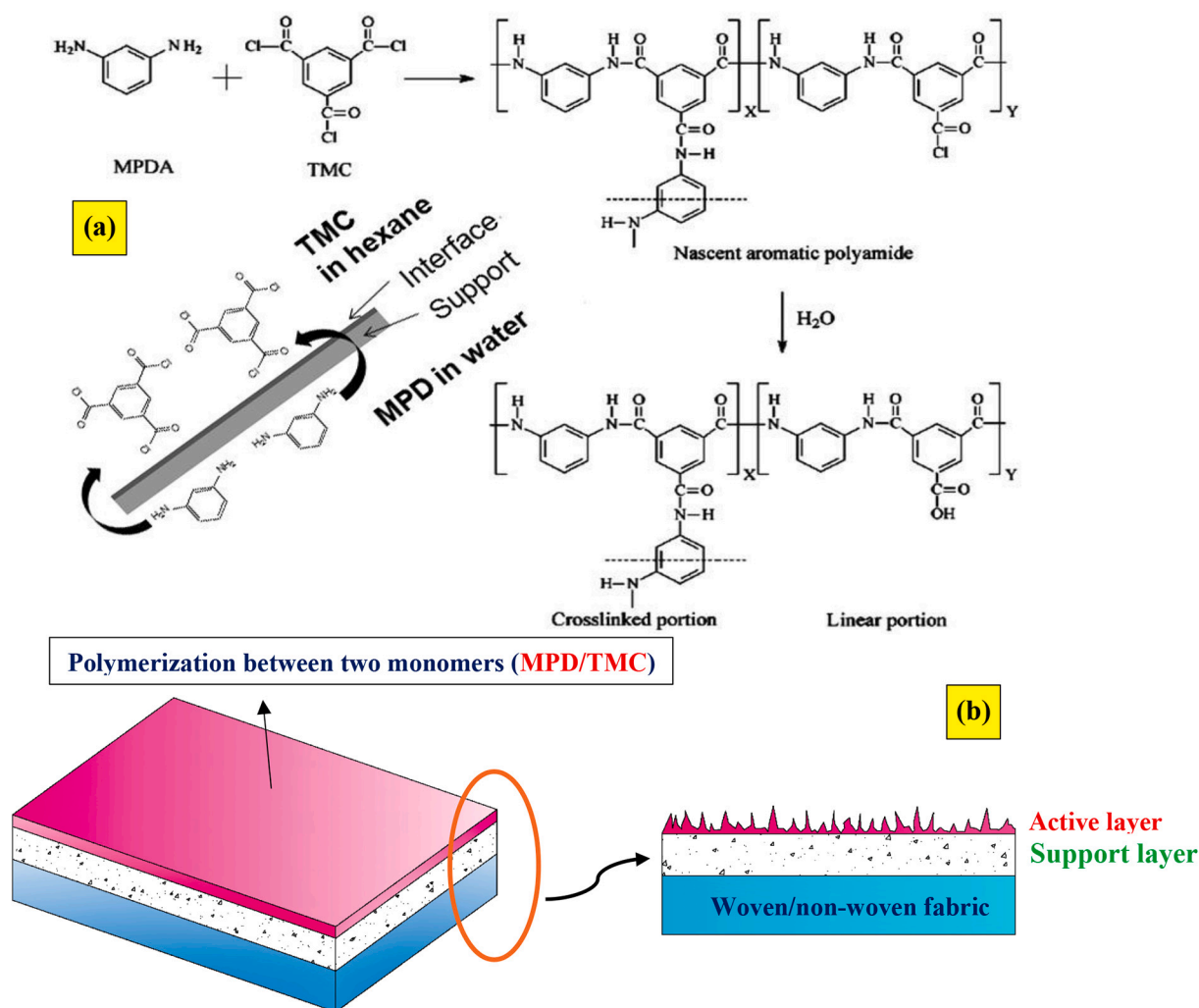


Fig. 1. Schematic illustration of (a) the IP process using MPD and TMC as the PA backbone monomers and (b) TFC membranes.

composite materials are applied. The pressure driven membranes used for water treatment such as UF, RO and NF mostly use hydrophilic materials to increase water permeability in treatment process [27].

Thin film composite (TFC) membranes are the most popular desalination membranes. Nevertheless, there are still many problems in these types of membrane such as fouling, as a result of concentration polarization, and membrane's durability [28,29]. Several modification techniques have been used to improve the TFC membranes performance and properties. The applied modifications are by changing either of physical or chemical properties of the TFC membranes active layer. Coating the membranes with other materials (e.g., nanomaterials, polymers) through weak van der Waals or hydrogen forces is an example of physically based modification of membranes [30,31]. Chemical modification, on the other side, changes the structure of polyamide (PA) layer with covalent bonds and reinforces the stability of membranes. Different methods have been used to chemically modify the active layers including grafting methods, hydrophilization, sol-gel coating, functional nanoparticles incorporation, and chemical coupling [32–35].

Apart from surface modification, the use of different monomers instead of conventional monomers (i.e. MPD, PIP, and TMC) has been under investigation in the past two decades. Monomers in active layer affect the cross-linking density, thickness, surface properties and pore structure of the membranes and consequently alter the membranes filtration performance [36,37]. The presence of hydrophilic monomers can also affect the membrane durability. In general, one of the main factors that considerably impinge on the membrane durability is the

formation of fouling layer on the surface of membrane. Fouling can significantly reduce the lifetime and durability of membrane. Introduction of hydrophilic materials on the surface of membrane can impede fouling and therefore, increase the membrane durability [38,39]. Besides, developing new methods for cleaning membranes can also be very effective in the enhancement of membrane durability. Cleaning processes upon fouling remove foulants from the active layer and increase the membrane's durability. The materials which are selected for the synthesis of membranes especially in active layer during polymerization process can substantially affect the durability as well. The presence of new monomers completely changes the structure of membranes and make them more selective to water molecules and stable against foulants [40]. Research into finding optimum molecular structure with new monomers is on-going. Here, a critical review is conducted on the recent literature considering alternative interfacial polymerization (IP) monomers. The structures of new applied monomers in different studies have been fully investigated and their contribution to the membranes' performance improvement has been discussed. Moreover, all new synthesized monomers and their modification principals are explained in different tables and their impacts on the structure of the developed membranes (e.g., hydrophilicity, thickness, roughness, and surface charge alterations) are discussed in details and compared with each other. In addition, TFC NF and TFC RO membranes and their common synthetic methods are discussed followed by reviewing the alternative monomers for the TFC selective layer formation and their effect on the membrane's performance and properties. The main changes in the

Table 1

The list on newest nanosized materials for modification of NF membranes.

Type of nanosized composite used for modification	Experimental conditions	Method of modification	Key membrane performance and properties after modification	Ref.
Nano-sized aminated graphene quantum dots (GQDs-NH ₂)	Cross-flow system, Pressure: 3 bar, 2000 mg.L ⁻¹ of MgCl ₂ and LiCl solutions	The synthetic process was done by doping nano-sized GQDs-NH ₂ in polyamide layer	-137.8% improvement in permeation -77% rejection of Mg ²⁺ and Li ⁺	[90]
Polymeric polypyrrole (PPy) nanoparticles into graphene oxide-based membrane	Dead-end filtration device, Pressure: 6 bar, 100 mg.L ⁻¹ of different dyes including Methylene blue (MB), Eriochrome black T (EBT), Congo red (CR), Neutral red (NR), Crystal violet (CV), and Trypan Blue (TB)	Nanoparticles deposited on the support layer by vacuum filtration method	-14 times higher water flux -99% rejection rate of all dyes (CV, EBT, CR, and TB) -Enhancement of membrane mechanical strength	[91]
Polydopamine-sulfobetaine methacrylate [P(DA-SBMA)] nanoparticles	Cross-flow NF system, Pressure: 6 bar, 1000 mg.L ⁻¹ of Na ₂ SO ₄ , MgSO ₄ , MgCl ₂ , and NaCl solutions	The nanoparticles were embedded in the organic phase in IP techniques	-Enhancement of membrane hydrophilicity and selectivity -Pure water flux of 73.11 ± 6.78 L.m ⁻² h ⁻¹ -Salt rejections of 98, 95, 54, and 42% for Na ₂ SO ₄ , MgSO ₄ , MgCl ₂ , and NaCl, respectively	[92]
Carbon nanofibers (CNFs) assisted chitosan (CS) nanocomposite	Dead-end filtration device, Pressure: 4.5 bar, 1000 mg.L ⁻¹ Na ₂ SO ₄ solution	Dip-coating method by dissolving chitosan into polymeric solution in acidic condition using 3 wt % of HCl	-Na ₂ SO ₄ rejection of >66% and >88% for unmodified and modified membrane, respectively -Excellent ability in Cu, Cr, Pb removal from water -Great tensile strength for modified membrane	[93]
Graphitic carbon nitride (g-C ₃ N ₄) functionalized with zwitterion (BHC-CN)	Cross-flow system, Pressure: 4 bar, 2000 mg.L ⁻¹ of MgCl ₂ solution	Nanocomposite was immersed into aqueous phase with the help of probe sonicator in IP method	-Salt rejection up to 97.4% -High fouling resistance after during the cyclic protein filtration with 6 h in each cycle -73% flux improvement	[94]
Carbon quantum dots (CQDs) as nanofiller	Dead-end filtration device, Pressure: 6 bar, 1000 mg.L ⁻¹ NaCl, CaCl ₂ , MgCl ₂ , CuSO ₄ , and Na ₃ PO ₄ solutions	Nanofillers were added to aqueous phase through IP technique	-Salt rejection up to 94% -High flux rate of 35 L/m ² h	[95]
FeOOH nanorods	Cross-flow system, Pressure: 4 bar, 2000 mg.L ⁻¹ of NaCl and Na ₂ SO ₄ solutions	Nanorods were coated on the PES-MF membrane by vacuum filtration method	-Pure water permeability of 34.1 L.m ⁻² .h ⁻¹ .bar ⁻¹ -Na ₂ SO ₄ rejection of 95.0%	[96]
Aminated TiO ₂ nanoparticles	Cross-flow system, Pressure: 5 bar, 1000 mg.L ⁻¹ of NaCl and Na ₂ SO ₄ solutions	TiO ₂ nanoparticles applied on the NF membrane through solution casting method by adding nanoparticles to aqueous phase solution (PIP solution)	-Constant rejection rate of Na ₂ SO ₄ up to 95% -Enhancement of water flux from 19.2 to 52 L.m ⁻² .h ⁻¹ (171% flux improvement)	[72]
TiO ₂ @reduced graphene oxide nanohybrids	Cross-flow system, Pressure: 8 bar, 500 mg.L ⁻¹ of Bromothymol blue and Rose Bengal in in organic solvent	TiO ₂ nanoparticles incorporated on the active layer of NF membrane	-The super hydrophilic surface -The formation of a channelization structure -The improvement antifouling properties	[97]
TiO ₂ nanoparticles	Cross-flow system, Pressure: 5 bar, 2000 mg.L ⁻¹ of NaCl solution	Dip coating method by adding dope solution on non-woven polyester	-High rejection result compared to unmodified membrane from 28 to 41%. -62% flux improvement from 27 to 44 L.m ⁻² .h ⁻¹ .	[98]
Polyimide/SiO ₂ nanoparticles (PI/SiO ₂)	Cross-flow system, Pressure: 4 bar, 1000 mg.L ⁻¹ of Na ₂ SO ₄ , MgSO ₄ , NaCl, and MgCl ₂ solutions	PI/SiO ₂ nanoparticles were added to 5, 7, 9, 11, and 13 wt% TEOS in the PI/TEOS solution	-Permeability of 20.4 L.m ⁻² .h ⁻¹ .bar is 4–15 times higher than unmodified membrane -Excellent salt rejection of Na ₂ SO ₄ (87%) > MgSO ₄ (67%) > NaCl (41%) > MgCl ₂ (37%)	[99]
Fe ₃ O ₄ @SiO ₂ -Chitosan (CS) bionanocomposite	Dead-end filtration device, Pressure: 4 bar, 500 mg.L ⁻¹ of Na ₂ SO ₄ , MgSO ₄ , NaCl and MgCl ₂ , 1000 mg.L ⁻¹ of Pb ²⁺ , Cu ²⁺ and Cd ²⁺ solutions	Core-shell of Fe ₃ O ₄ magnetic nanoparticles and amorphous SiO ₂ extracted from wheat straw and functionalized by chitosan groups and then embedding various Fe ₃ O ₄ @SiO ₂ -CS loadings into PES matrix by phase inversion method	-Improvement of water flux from 47.3 to 70.6 L.m ⁻² .h ⁻¹ -Salt rejection for Na ₂ SO ₄ : 90% (increased from 10 to 90%) by addition of nanoparticle -Heavy metal removals from 14.95, 15.45 and 16.11% to 98.11, 98.61 and 98.86% for Pb ²⁺ , Cu ²⁺ and Cd ²⁺	[100]
Beta zeolite nanoparticles	Cross-flow system, Pressure: 2 bar, 2000 mg.L ⁻¹ of Na ₂ SO ₄ , MgSO ₄ , MgCl ₂ and NaCl solutions	A certain amount of β zeolite nanoparticles, 1% TEA and 16% phosphoric acid were added into 1% PIP solution as aqueous phase	-Highest pure water flux: 81.22 L.m ⁻² .h ⁻¹ , 2.5 times more than unmodified membrane	[101]

structure of conventional membranes modified by new monomers are then fully investigated. Finally, some recommendations have been made for the future studies on the TFC membranes to expedite the current studies in this area.

2. Thin film composite (TFC) membranes

TFC membranes generally include three main layers: a woven or non-woven fabric (60–80 μm) on the bottom used as the support for an intermediate layer with micro-sized pores (50–100 μm) and a thin selective layer (100–200 nm) on the top. During filtration process, PA active layer plays as a barrier for the separation of contaminants, while the intermediate micro-porous layer mechanically supports the ultra-thin selective layer from high pressure in RO or NF operation [41,42].

The first ultra-thin TFC RO membrane was fabricated and evaluated by P.S. Francis in 1963 [43]. He made a cellulose acetate ultra-thin film on the surface of membrane by float-casting method and laminated onto the micro-porous cellulose acetate support layer after annealing [44]. This technique never gained commercial attention because of the obtained membranes' low flux and high commercial cost. Some polymeric candidates were then introduced such as polyvinyl methyl ether [45], styrene-acrylonitrile copolymer [46], polyurethanes [47], and alike. However, PA and polysulfone (PSF) or polyethersulfone (PES) are the most common materials for the selective layer and the intermediate substrate, respectively [48,49].

TFC membrane performance is determined through comparing the properties of its influent and effluent. Optimization of each layers' physical characteristics (i.e., thickness, roughness, strength, hydrophilicity, and pore dimension) and chemical properties (i.e., chemical bonds, cross-linking density and structure, surface charge) to improve TFC membranes water flux and salt/contaminant rejection have been the focal research points in recent years.

The PSF or PES micro-porous substrates is fabricated by different techniques (e.g., double-blade casting [50], phase inversion [51], electrospinning [52,53]), with various types of materials (i.e., single polymer, polymer-polymer composite, and polymer-inorganic nanocomposite) [54–57]. Among all techniques for fabrication of micro-porous substrate, phase inversion technique is the most facile and popular method invented by Sidney Loeb and Srinivasa Sourirajan in the 1960s [58]. Non-solvent induced phase separation (NIPS) briefly starts with dissolving about typically 15–20% of PES or PSF polymer into *N*-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF) or dimethylacetamide (DMA) solvents and then, by casting polymer solution using an adjustable doctor blade. The use of polyvinylpyrrolidone (PVP, 0.5–5.0%) can help the increase of porosity of PSF or PES membranes. Polymeric solution is poured on a nonwoven polyester layer over a glass plate. After that, the glass plate with coagulated polymeric film is immersed in non-solvent solution (usually water) to form an intermediate layer by phase inversion method. The hydrophobic properties and limited chemical and thermal ($T < 50\text{ }^\circ\text{C}$) resistance of the support layers synthesized by this approach are their main problems and hence are the focus of research on the TFC support layer modification.

To fabricate the selective PA layer of TFC membranes, MDP and TMC are dissolved separately in aqueous and organic solutions. The polymerization reaction is then performed at the interface of water and organic solvent and a thin PA layer are produced on top of the substrate mainly by IP technique. IP technique which was initially developed by Cadotte et al. [59] is the conventional method for the fabrication of TFC membranes. The chemical structure of PA layer formed through IP process is illustrated in Fig. 1 (a). Briefly, the mesoporous PSF or PES support layer is soaked with the aqueous monomer (mainly MPD or PIP with concentration in range of 1–3 wt%) solution for specific amount of time (usually between 1 and 10 min). The excess monomer solution is then removed and the substrate is dried by an air knife or soft rubber roller for the water-immiscible solvent like *n*-hexane monomer such as TMC (usually 0.1–0.4 wt%) solution to be soaked initiating the

polycondensation reaction between the two monomers on the membrane surface (interface of the aqueous and organic phase) to form PA barrier layer. To increase the cross-linking density of the PA layer, membranes are then commonly heated over or through wet heating by water or other solutions. In addition to IP technique, some other methods (i.e., dip-coating, photo-grafting, plasma-initiated polymerization, and electron beam irradiation) are also used for the synthesis of active layer. This top layer determines antifouling resistance and rate of rejection with its dense, ridge-and-valley structure. However, the PA layer gradually deteriorates due to sequential chemical cleaning, aging, defects in its inner structure (pin holes) or chlorine attack which can significantly reduce the rejection rate of the membranes. Fig. 1 (b) shows the schematic illustration of TFC membranes.

TFC NF membranes are usually synthesized using amine PIP for the aqueous monomer solution whilst *m*-phenylene diamine (MPD) is the most common monomer for PA TFC RO membranes. PA layer formed through PIP as the aqueous monomer has a lower cross-linking density and linear structure than that of PA made by MPD making the NF membranes more permeable to monovalent salts but more suitable for divalent salts separation.

Although TFC membranes have shown some drawbacks, they offer many benefits such as superb mechanical properties under high pressure, high water permeability, and resistance in a wide range of pH.

2.1. Nanofiltration (NF) membranes

NF membranes pore size can be in the range of 0.5–1 nm ($< 2\text{ nm}$), which is tighter than UF (2–100 nm) and looser than RO ($< 1\text{ nm}$) membranes [60]. The common NF membranes reject over 99% of multivalent ions and over 90% of organic compounds with a molecular weight of above the molecular weight of membranes [molecular weight cutoff (MWCO) 150–2000 Da] [61]. However, the rejection rate of these membranes for monovalent ions is relatively low ($> 30\%$) [62]. Nevertheless, their good properties make this type of membrane a good candidate for the various fields of study such as water and wastewater treatment, food engineering, and pharmaceutical processes.

The mass transfer mechanism in TFC NF membranes is through size exclusion (sieving) where shape, size, the charge of solute molecules, and size of nanopores are the most important factors, which all rely on the PA active layer properties. Many new methods have been applied in the literature to improve the PA selectivity of NF membranes for obtaining higher separation efficiency [63,64]. Nanomaterial integration into the PA layer during the IP process has recently gained significant attention with several porous and non-porous nanomaterials being incorporated into the membranes making a structure known as thin film nanocomposite (TFN) membrane. Some of the nanomaterials used for this purpose include: TiO_2 [65], SiO_2 [66], LiBr nanoparticles [67], mesoporous carbon [68], graphene oxide (GO) [69], carbon nanotubes (CNT) [55], zeolite [70], metal organic frameworks (MOFs) [71], and a like. A list of latest work regarding the modification of NF membranes with nanosized materials has been shown in Table 1. To summarize some of recent efforts in detail, Wei et al. added amine functionalized TiO_2 nanoparticles to PIP during IP [72]. The result showed that membrane with 0.3 (w/v.%) nanoparticles had higher pure water flux and monovalent and divalent ions rejections. Liu et al. increased water flux and antifouling properties by the incorporation of 0.01 wt% graphene oxide-silica (GO- SiO_2)- into the PA layer [73]. The results showed that hydrophilicity (53.7°), smoothness, water flux (43.55 $\text{L m}^{-2}\text{ h}^{-1}$), and salt rejection (NaCl: 40.7%, Na_2SO_4 : 93.2%, and MgSO_4 : 82.4%) were superior. It is assumed that the increase in water flux can be attributed to the new special channels generated by the interaction between nano silver and GO.

Chemical structure alteration of PA layer by using new monomers or additives during IP process has also been proven efficient for TFC NF membranes performance improvement [74,75]. The most common monomers for the fabrication of TFC NF membranes are PIP and TMC

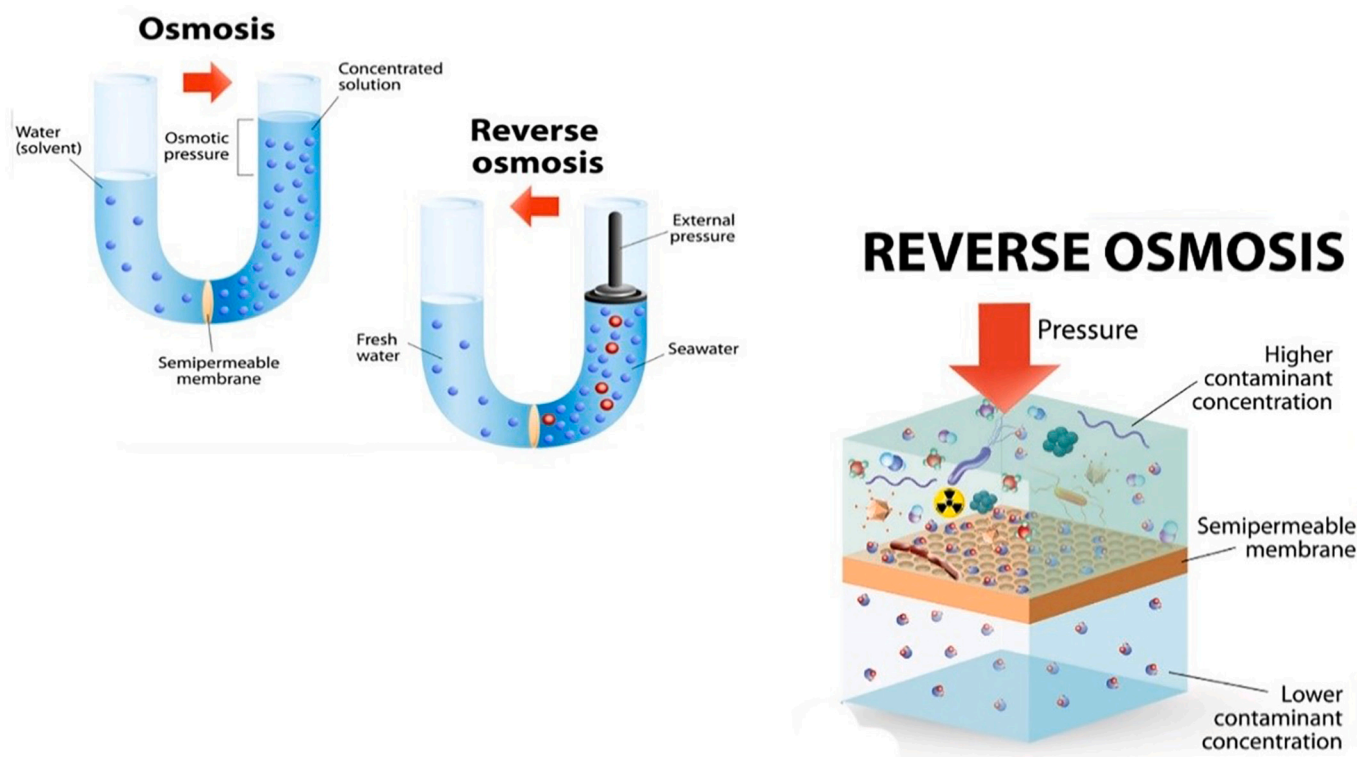


Fig. 2. The normal and RO separation mechanisms through membranes.

where PIP containing amine moieties is responsible for reactivity and solubility of PA, and TMC containing acyl chloride groups influences on the cross-linked network structure of PA, and -COOH groups impacts on the membranes' hydrophilicity and salt rejection by hydrolyzing unreacted acyl chloride groups of TMC. New incorporated materials with the same functionality of the PA monomers (i.e., amine or acyl chloride) that can chemically react with the aqueous and/or organic PA monomers have also shown promising advancements in the TFC membranes performance and properties. For instance, Zargar et al. fabricated SNs with two designed functional groups, epoxy and amine groups which could react with NH_2 groups of aqueous monomer and COCl groups of organic monomer, respectively. The results showed increased stability and durability of the developed TFN membranes [35]. Many studies have examined alternative monomers to obtain optimum performance and properties of the membranes. For instance, alternative acyl chloride monomers (e.g., isomeric biphenyl tetra acyl chloride, 5-chloroformyloxy-isophthaloyl chloride, cyclohexane-1,3,5-tricarbonyl chloride) and alternative amine monomers (e.g., N-aminoethyl piperazine propane sulfonate, 2,5-bis(4-amino-2-trifluoromethyl-phenoxy) benzenesulfonic acid, 4,4-bis(4-amino-2-trifluoromethyl-phenoxy) biphenyl-4,4-disulfonic acid, disulfonated bis[4-(3 aminophenoxy) phenyl] sulfone) have been used in the IP process of TFC NF membranes [76–81], which will be discussed in more details in next sections.

Post-modification technique for improving the TFC NF membranes surface properties is also common (e.g., ion implantation, graft polymerization, surface coating, plasma-induced polymerization). The aim of coating polymers on the top of the interfacially polymerized layer, like grafting method, is to make the membranes more hydrophilic and reduce their surface roughness. Coating may be absorbed on the surface, covalently attached with surface polymer, or cross-linked with itself. It also provides either positive or negative charges on the surface of membrane. Not only could this method increase intrinsic properties of membranes, but also removable coating could physically protect the membrane during fabrication and enhance its antifouling properties.

In graft polymerization, new functional groups are covalently

attached on the surface of substrate [82]. The conventional method used to generate free radicals for grafting is ultraviolet (UV) radiation. Vatanpour et al. [83] used UV-grafting of acrylic acid with the incorporation of carboxylate-MWCNTs (COOH-MWCNTs) for surface modification of commercial PA layer of NF membranes. The results showed improved fouling resistance and permeability by just 5 g.L^{-1} acrylic acid application under 5 min UV exposure. The improved performance was correlated to the enhanced surface hydrophilicity, roughness, and negative charge of the membranes. 30% water flux improvement was obtained by the addition of 0.2 wt% COOH-MWCNTs to the grafting layer. This was, however, the threshold value as adding higher concentration decreased the selectivity, hydrophilicity, and permeability of the membrane. The interrelationship between surface roughness and hydrophilicity is varied for different materials according to the literature [84–86]. For example, some studies have reported that a rougher surface increases the contact angle of the membrane and therefore, reduces the membrane's hydrophilicity [87], while some other studies have reported that rougher surfaces decrease the water contact angle and therefore, increase the membranes' hydrophilicity [84–86]. On the other hand, some researchers have concluded that the variation of surface roughness has no direct impact on the hydrophilicity [70]. Our observations have shown that the surface roughness depends on the new composite materials used in the active layer and rougher surfaces may generally decrease the contact angle and therefore, increase the membranes' hydrophilicity. Focusing on steric effect and electrostatic interaction using ion implantation is considered very effective to increase Donnan exclusion effect and thereby increase its salt rejection. For example, the implantation of F-ions significantly increased salt rejection [88]. Plasma induced polymerization is another promising technique for the modification of membrane. The activation of monomers on the active layer by low energy plasma facilitates the polymerization reactions of active layer. Chen et al. used this technique in plasma-induced polyacrylic acid- TiO_2 coated polyvinylidene fluoride membrane. The results showed that water flux was four times more than unmodified membrane with conventional polymerization technique. Besides, oil rejection rate

Table 2
Modification of different RO and NF membranes in the most recent studies.

Type of material used for modification	Experimental conditions	Method of modification	Key membrane performance and properties after modification	Ref.
Graphene oxide	Cross-flow system, Pressure: 25 bar, 1000 mg.L ⁻¹ of NaCl solution	Functionalization through coating with a solution containing 4 mM of N-(3-Dimethylaminopropyl)-N'-ethyl carbodiimide hydrochloride (EDC, 98%), 10 mM of N105 hydroxysuccinimide (NHS, 98%) and 0.5 M sodium chloride (NaCl) prepared in 10 mM MES 106 mono hydrate (> 99.0%, BioXtra)	-The improvement of surface smoothness and hydrophilicity -7% fouling improvement -81.7% bacteriostasis rate	[115]
Aromatic amine-functionalized multiwalled carbon nanotubes	Cross-flow system, Pressure: 4–22 bar Solution with the mixture of Mg(II), SO ₄ ²⁻ , Na(I), and Cl ⁻ , NH ₄ ⁺ and NO ₃ ⁻	Incorporation with simple amine functionalizing method by applying a reactive intermediate reagent (2,4,6-trichloro-1,3,5-triazine) to improve functionalization efficiency	-The enhancement of chlorine resistance -15% flux improvement -Maximum rejection for sulphate anions (> 79%), and As(V) (> 72%) -48% flux improvement	[116]
Iron nanoparticles (FeNPs)	The feed water was sampled from Sea of Cortez, Mexico (27.917°N, 110.776°W), and El Sol Beach, Chile (33.01°S, 71.553°W)	Coating method, a solution of 1 wt% FeNPs coa48ted with MPD solution via immersion	-48% flux improvement -The reduction of biofilm formation on the surface of membrane	[117]
Ultra-thin polyaminophenylene layer	Cross-flow system, Pressure: 5 bar, 2000 mg.L ⁻¹ salt solution,	Surface grafting of substrate (polysulfone) layer with diazonium-induced anchoring process	Maximum surface and pore wettability -Positive surface charge -Larger cross-linking density and thinner PA active layer -The improvement of permeability and membrane selectivity	[118]
Nitrogen-doped graphene oxide quantum dots (N-GOQDs)	Cross-flow system, Pressure: 15 bar 1000 mg.L ⁻¹ NaCl solution, NaClO solution for chlorine resistance test at pH:7.	Surface grafting of active layer with nitrogen-doped graphene oxide quantum dots grafted onto ethylenediamine (EDA)	-Significant chlorine resistance -The improvement of water flux and NaCl rejection by 11.1% and 2.3% respectively.	[119]
Polyamidoamine dendrimer (PAMAM) containing graphene oxide nanosheets	Cross-flow system, Pressure:15 bar, 2000 mg.L ⁻¹ NaCl solution	Grafting method with 1.5% of PAMAM grafting and 6 min grafting by graphene oxide	-High hydrophilicity, lower fouling, better resistance against chlorine -Excellent salt rejection rate (up to 94% salt rejection and 38% flux improvement)	[109]
Co-Al layered double Hydroxides (LDH) particles	Cross-flow system, Pressure: 20 bar, 2000 mg.L ⁻¹ NaCl solution	Incorporation into the PA layer, LDH was dispersed into the organic phase by ultra-sonication	-Higher hydrophilicity due to intercalated anions -Maximum Water flux and salt rejection up to 55 L.m ⁻² . h ⁻¹ and 99.03%, respectively.	[120]
Deep eutectic solvents and ionic liquids such as choline chloride-urea based DES and a series of commercial ionic liquids (ILs) as additives including 1-hexyl-3-methyl-imidazolium chloride, 3-methyl-1-octyl-imidazolium tetra fluoroborate, N-butyl pyridinium and betaine monohydrate	Cross-flow system, Pressure:15 bar, 2000 mg.L ⁻¹ NaCl solution	Incorporation into PA layer, deep eutectic solvents and ionic liquids were added to MPD solution	-Excellent water flux about 27% higher compared to common membranes -Rejection improvement by 3%.	[121]
β-cyclodextrin-cored star polymers CD-PAH containing multiple linear polymer (polyacryloyl hydrazide)	Cross-flow system, Pressure: 15.5 bar, Flow rate: 1 Lmin ⁻¹ , 2000 mg.L ⁻¹ NaCl solution	PAH arms grafted onto β-CD cores then impregnated on the hydrolyzed PAN support	-Excellent salt rejection because of great density of the cross-linkable amine groups of densely-packed PAH arms -Lower organic fouling	[122]
dialdehyde carboxymethyl cellulose (DACMC)	Cross-flow system, Pressure: 10.3 bar, 1500 mg.L ⁻¹ NaCl solution	Surface grafting using cellulose, cellulose was chemically grafted on the PA layer	-The improvement of hydrophilicity, -Smoother surface -Significant rate of NaCl rejection (up to 98.5%), -Excellent antifouling performance	[123]
graphene oxide and polyacrylic acid	Cross-flow system, Pressure: 25 bar, Flow rate: 1 L.h ⁻¹ ,	Functionalization by graphene oxide nanomaterials, graphene oxide and polyacrylic acid were coated on the active layer through coating solution	-The improvement of anti-bacterial properties -significant enhancement of biofouling properties -Excellent control of mineral scaling, -The prevention of 97% bacterial growth	[124]

(continued on next page)

Table 2 (continued)

Type of material used for modification	Experimental conditions	Method of modification	Key membrane performance and properties after modification	Ref.
Quaternary ammonium salt (2, 3-epoxypropyltrimethylammonium chloride, EPTAC)	Cross-flow system, Pressure: 12 bar, Cross-flow velocity: 0.4 m.s ⁻¹	Surface grafting using 2, 3-epoxypropyltrimethylammonium chloride grafted onto PEI-modified RO membrane	-3% flux reduction compared to conventional membranes -Greater net surface zeta potential values -Excellent removal rate of nuclides -Lower contact angle -Higher hydrophilicity -The improvement of Radioactive treatment for wastewaters.	[125]
Graphitic carbon nitride nanosheets	Cross-flow system, Pressure: 16 bar, Cross-flow velocity: 0.8 m.s ⁻¹ 200 ppm of BSA for fouling test, 2000 mg.L ⁻¹ NaCl salt solution	The nanosheets were incorporated in aqueous phase including MPD solution, SDS and TEA	-30% flux improvement -Significant chlorine resistance due to oxygen containing functional groups -Maximum salt rejection 99.23%.	[126]
Sulfonic groups	Cross-flow system, Pressure: 27.6 bar Feed solution was a mixture of 2.8 mM Na ₂ SiO ₃ , 7.0 mM CaCl ₂ , 3.5 mM MgCl ₂ , and 35 mM NaCl	non-specific grafting of vinyl sulfonic acid (VSA) via redox radical initiation polymerization and (ii) covalent bonding of hydroxylamide- O -sulfonic acid (HOSA) to the native carboxylic groups of the PA layer via carbodiimide mediated reaction	-Higher surface wettability - More negative charge density -Stable water flux because of covalent bonds of hydroxylamide- O -sulfonic acid -97.45% salt rejection -74.52 L.m ⁻² h ⁻¹ water flux	[127]
zwitterionic polymer	Cross-flow system, Pressure: 27.5 bar 27 mM of Na ₂ SO ₄ and CaCl ₂ solutions	First polydopamine fixed an initiator on the surface of active layer then zwitterionic polymer was coated through atom transfer radical polymerization	-Preventing the onset of gypsum scaling -The enhancement of water recovery in RO process, -Formation of super hydrophilic surface	[128]
MCM-41 and SBA-15 nanoparticles	Cross-flow system, Pressure: 15 bar, 2500 mg.L ⁻¹ NaCl solution	Incorporation into the PA layer, through dispersing nanoparticles in organic phase using ultrasonication	-Flux improvement from 40 to 74.17 L.m ⁻² h ⁻¹ for SBA-15 modified membranes -NaCl rejection from 95.1 to 98.5% for SBA-15 modified membranes -Water flux and NaCl rejection enhanced to 60 L.m ⁻² h ⁻¹ and 96.9%, respectively for MCM-41 modified membranes	[129]
Graphene oxide PA composite	Cross-flow system, Pressure: 4 bar 1000 mg.L ⁻¹ of Na ₂ SO ₄ solution	Graphene oxide was coated on nylon substrate through vacuum filtration then coated substrate was immersed in PIP aqueous solution	-Stable membrane -Significant water flux up to 35.14 L.m ⁻² h ⁻¹ bar ⁻¹ -Na ₂ SO ₄ rejection of 93.56%	[130]
UiO-66 nanoparticles	Cross-flow system, Pressure: 15.5 bar, 2000 mg.L ⁻¹ NaCl solution	The nanoparticles incorporated on the surface of membrane through organic phase by adding in n-hexane TMC solution	-50% flux improvement -Excellent salt rejection	[131]
Hierarchical o-hydroxyazo porous organic polymers	Cross-flow system, Pressure: 4 bar, Different salts solutions including NaCl, Na ₂ SO ₄ , MgSO ₄ , and MgCl ₂ (1000 mg.L ⁻¹) and 500 mg.L ⁻¹ reactive dye (RB5)	PIP was first dissolved in Dimethyl sulfoxide solvent using magnetic stirrer, followed by the incorporation of different contents of o-POPs	-The improvement of surface roughness and hydrophilicity, -High water permeance of 29.6 L.m ⁻² h ⁻¹ bar ⁻¹ -Excellent salt Na ₂ SO ₄ rejection of 94.9% -Significant removal of reactive black 5 dye	[132]
Graphene oxide (GO) and amine-functionalized zinc oxide (ZnO)	Cross-flow system, Pressure: 20 bar, 2000 mg.L ⁻¹ NaCl solution	Incorporation into the PA layer. Nanoparticles with specified amount were dispersed in MPD solution	-Higher hydrophilicity, water flux, and permeability -Excellent water flux of 31.41 L.m ⁻² h ⁻¹ compared with conventional membrane with 14.28 L.m ⁻² h ⁻¹	[133]
Zwitterionic sulfobetaine silane compounds	Dead-end filtration device, Pressure: 20 bar, The solution of NaCl, 2250 mg.L ⁻¹ ; CaCl ₂ , 120 mg.L ⁻¹ ;	Coating process by spraying two zwitterionic compounds onto the treated surface of membranes. Membrane surface was treated with 0.01 M potassium metabisulfite and 0.01 M potassium	-Great anti-bacterial effect against the isolated marine biofouling bacteria -Excellent bio-film adhesion	[134]

(continued on next page)

increased up to 92% [89].

2.2. Reverse osmosis membranes

In pressure-driven operations, pressure is applied to overcome the osmotic pressure (chemical potential differences between the two sides of membrane). Another type of membrane used in pressure-driven operation is an RO membrane which is widely used for desalination of brackish and seawater. Pressure gradient between low-pressure permeate and high-pressure feed stream is the driving force for RO process to overcome the osmotic pressure (Fig. 2) [102]. Thus, the RO membrane allows water to permeate and rejects dissolved ions (against the natural osmosis direction). Approximately 80% of liquid contents is recovered by RO membranes. RO membrane's operation temperature is also low (<45 °C at 18–60 atm) [42]. Due to high-pressure requirements

for RO membrane filtration process, it is commonly used as a post-treatment (after filtering by MF and UF to capture the remnant of solute molecules and purify water [103].

There are some obvious differences between TFC NF and TFC RO membranes when considering them for optimizing their properties. The pore size of RO membrane is approximately 0.001 μm and its operating pressure is generally between 10 and 69 bars, however the pore size of TFC NF membranes is larger and its operating pressure is normally between 1 and 10 bars [104]. Furthermore, the RO separation mechanism is based on solution diffusion and capillary flow with greater rejection of all dissolved solids such as sodium and chloride whilst physical separation is the main mechanism of NFs. The major ability of RO membrane is the rejection of multivalent and lesser monovalent dissolved solids by diffusion mechanism [42].

Fouling is a critical issue which may occur for both TFC RO and TFC

Table 2 (continued)

Type of material used for modification	Experimental conditions	Method of modification	Key membrane performance and properties after modification	Ref.
graphitic carbon nitride (g-C ₃ N ₄) nanosheets	KCl, 105 mg.L ⁻¹ ; NaHCO ₃ , 50 mg.L ⁻¹ Cross-flow system, Feed flow rate: 120 L.h ⁻¹ Pressure: 15 bar, 2000 mg.L ⁻¹ NaCl solution	persulfate for 30 min and rinsed with deionized water Incorporated in PA layer with dispersion of nanosheets in MPD solution during the interfacial polymerization process.	resistance -Fouling improvement -Flux improvement -Maximum salt rejection -Lower surface roughness	[135]
Graphene oxide	Cross-flow system, Pressure: 15 bar 1000 mg.L ⁻¹ NaCl aqueous solution	Spin-coating method. Two different solvents, water and 70% ethanol in water, with 0.075 mg.mL ⁻¹ GO were used as coating solutions	- 20% flux improvement - The Improvement of chlorine resistance, - 12% improvement in salt rejection	[136]
monoamines 4-aminobenzoic acid, aniline-2,5-disulfonic acid monosodium salt, and iminodiacetic acid (IDA)	Cross-flow system, Pressure: 11 bar 2000 mg.L ⁻¹ NaCl, Na ₂ SO ₄ , MgCl ₂ and MgSO ₄ solutions	Incorporation through combination of PIP and monoamines solution.	-The production of high negative charges -Flux improvement -Excellent salt rejection.	[137]
Carboxylated multiwalled carbon nanotubes	Cross-flow system, Flow rate: 120 L.h ⁻¹ . Pressure: 15 bar, 2000 mg.L ⁻¹ NaCl solution	grafting by acrylic acid, which nanotubes were dispersed in the grafting solution and deposited on membrane surface	-High hydrophilicity -10% Flux improvement -Maximum salt rejection about 97%	[83]
Boron nitride nanosheets	Cross-flow system, Pressure: 15.5 bar, 2000 mg.L ⁻¹ NaCl solution	Incorporated in PA layer by adding FBNS into the aqueous phase at varying concentrations.	-25% flux improvement -Maximum salt rejection of 96.4%. - High Chlorine resistance and membranes' stability	[138]
Aminophend/formaldehyde resin polymeric nanospheres	Cross-flow system, Flow rate: 1.8 L.min ⁻¹ , Pressure: 16 bar, 2000 mg.L ⁻¹ NaCl solution	Incorporated in PA layer by adding nanoparticles in aqueous phase.	-50% flux improvement -Maximum salt rejection up to 96.0%	[139]
MXene Ti ₃ C ₂ T _x	Cross-flow system, Pressure: 16 bar, 2000 mg.L ⁻¹ NaCl solution	0.005–0.02% Ti ₃ C ₂ T _x was uniformly dispersed into MPD solution via 30 min ultra-sonication	-Maximum salt rejection of 97.1% -High hydrophilicity -45% flux improvement	[140]
Amino-modified hollow mesoporous silica nanospheres (AHMSS)	Cross-flow system, Flow rate: 1.25 L.min ⁻¹ , Pressure: 15.5 bar, 2000 mg.L ⁻¹ NaCl solution	Incorporated in PA layer by adding AHMSS in the organic phase.	-41.5% flux improvement -Maximum salt rejection (97%) -High hydrophilicity	[141]
Tannic acid	Cross-flow system, Flow rate: 2 L.min ⁻¹ , Pressure: 1.5 MPa, 2000 mg.L ⁻¹ NaCl solution	Ethanol/TA solutions were poured onto the polymerized surface of RO membrane and then the membranes were heated at 80 °C for 5 min.	-27.7% flux improvement -Maximum rejection of 98.82 ± 0.18% -Tannic acid enhanced the chlorine resistance of PA RO membrane after 8000 mg.L ⁻¹ h ⁻¹ chlorination exposure	[142]
Sulfonated polyelectrolyte-silver nanoparticle	Cross-flow system, Feed flow rate: 10 mL.min ⁻¹ , Pressure: 15 bar, 2000 mg.L ⁻¹ NaCl solution	Grafting method where the membrane surface was first functionalized by poly(3-sulfopropyl methacrylate potassium salt) (pSM) via atom transfer radical polymerization (ATRP), followed by in situ immobilization of silver nanoparticles (AgNPs)	-High anti-bacterial and anti-fouling properties Because of added nanoparticles -Stable water flux in long-term tests for biofouling	[143]
1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC)	Cross-flow system, Pressure: 5.0 bar, 500 mg.L ⁻¹ aqueous NaCl, NaNO ₃ and glycerol solutions	The EDC solution was poured on the top layer after polymerization process in order to gain a smoother surface	-Less negative charged surface -Excellent salt rejection about 96.4% -Higher stability of the new membranes	[144]

NF membranes. Surface modification and structural changes are very effective to change the membranes antifouling properties and chlorine tolerance. The deposition of foulants on the surface of membrane (cake layer formation) can drastically reduce the performance of membrane during the RO and NF process. Therefore, using chlorine and other cleaning agents (e.g., acids, alkalis, disinfectants, surfactants, metal chelating agents, and enzymes) for membrane cleaning is a common approach in the industry [105]. Extended exposure to chlorine is however detrimental to the PA and hence, needs to be controlled and minimized.

Although a higher surface roughness of membranes is advantageous for the water permeability through the enhanced surface area, rougher surfaces are more prone to foulants deposition [106]. Further, the higher surface charge density of the membranes which is advantageous for their higher hydrophilicity and water permeability can be a drawback for their fouling retention. This is because the contaminants with the opposite charge to that of the membrane surface can get attracted to the membrane much easier through electrostatic attraction and exacerbate the membrane fouling issue. Similar physical or chemical surface modification approaches to those stated for TFC NF membranes can be used on the TFC RO membranes to minimize fouling, and chlorination problems (Section 2.1).

Addition of appropriate amounts of various nanomaterials such as zeolite, silica (SiO₂), silver (Ag), titanium nanotubes (TNTs), halloysite nanotubes (HNTs), aluminosilicate single walled nanotubes (SWNTs), and metal alkoxides into the PA layer during the IP process has shown to provide a preferential flow path and improve intermolecular hydrogen bonding to increase the chlorine and fouling resistance of the membranes [41,107].

In spite of physically embedding nano particles to the PA layers, nanoparticle incorporation into the membranes has shown better results due to the increased mechanical properties by reducing the leaching of nano particles during preparation. This is however more beneficial when functional nanomaterials (with the same PA monomer functionalities) are introduced as they can be chemically bonded to the PA structure and have higher structural stability [35,51,54,108]. For instance, Zargar et al. incorporated amine and epoxy functionalized silica nanoparticles into the PA layer of TFC membranes and showed more sustainable salt rejection efficiency of their membranes as compared to the membranes incorporated with plain nanoparticles [35]. Besides, the negative charge of surface could be reactivated by binding of functional groups of coating surface, which might decrease salt rejection in some cases because of the reduction in the Donnan repulsion effect. For example, Vatanpour et al. [109] considered the negative effects of PA thickness and the decline of Donnan repulsion effect in TFC RO membranes. They introduced hydrophilic polyamidoamine (PAMAM) dendrimer and GO nanosheets to the membranes through grafting technique and could reduce the fouling and chlorine attack propensity of the membranes. The result showed that a considerable improvement in membrane fouling could be attained with the addition of 1.5 wt% PAMAM and 1 wt% GO at the temperature of 30 °C in 6 min. The developed membranes had a contact angle of 44.8° a salt (NaNO₃) rejection of 97% and a relatively high chlorine resistance [109].

3. Strategies to improve the surface properties of TFC membranes

3.1. Nano-integration and surface modification of TFC membranes

The properties of the barrier layer can be changed by varying the reactive monomers (i.e., acyl chloride and amine), the concentration of organic and aqueous solutions, type and surface properties of the substrate membrane, and using other additives (e.g., camphor sulfonic acid (CSA), trimethylamine (TEA), sodium dodecyl sulfate (SDS), trimellitic anhydride chloride (TAC), and alike) [110]. Further, parameters such as reaction time, humidity, temperature, and coating speed can affect the

properties of composite membranes [111].

For instance, Zhang et al. modified PA layer with using trimellitic anhydride chloride (TAC) as co-reactant of TMC in MPD/TMC IP system [112]. They showed that increasing the concentration of TAC from 0.00 to 0.08 wt% increased the charge density, hydrophilicity, and pore size of the PA film from RO to NF range. The results also showed that the lower reactivity of anhydride groups of TAC decreased the PA cross-linking density, enhanced the PA pore size and increased the negative charge density of the membrane [112].

Using an intermediate layer between the PES/PSF substrates and the PA layer has been recently introduced as an efficient modification to reduce the defects in the PA layer structure. For instance, Gong et al. [113] fabricated triple-layered NF TFC membranes with carbon nanotubes (CNT) as the interlayer via IP technique. The results exhibited that both the PA surface pore size and thickness reduced with high selectivity to both mono/divalent salt ions (the rejection of Na₂SO₄ and MgSO₄ solution >98.3%) and dyes (the rejection of methyl violet (MV) >99.5%). The pure water flux was around 21 L.m⁻².h⁻¹.bar⁻¹. This excellent performance was owing to the limited PIP penetrating into the porous PES substrate due to the presence of the CNT interlayer onto the porous substrate, and subsequent formation of ultra-thin, defect-free PA layers [113]. Attempting to find novel IP methods, An et al. proposed combined technique of IP and spin-coating called as dynamic IP process [114]. Support layer made by modified Polyacrylonitrile (PAN) was immersed in 0.1 wt% 1,3-diaminopropane (DAPE) aqueous solution. After 30 s, an organic solution containing 0.2 wt% Succinyl chloride (SCC) in toluene was spin-coated over the surface of the support layer. Due to the centrifugal force, molecular chains were oriented in horizontal direction between the aqueous and the organic phase. Thus, a dense and thin PA active layer with rougher surface, smaller pore sizes (15–30 nm), and higher selectivity and flux rather than the conventional membranes was obtained by dynamic IP process [114]. Other recent surface modifications including grafting, coating, and nanoparticle incorporation have also been used recently which are summarized in Table 2.

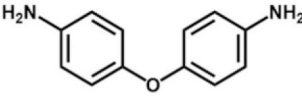
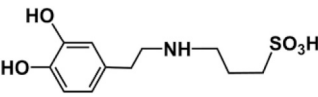
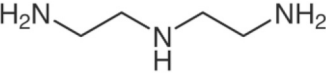
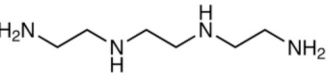
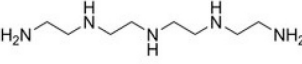
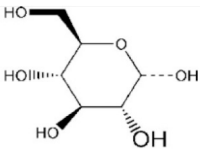
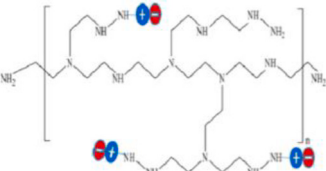
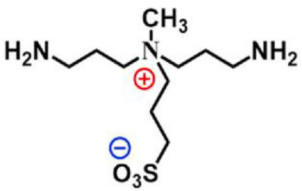
When new membranes/membrane materials/membrane fabrication techniques are introduced, their optimization to meet industry needs and commercial viability as well as upscaling to industrial scale have always been a challenge. As summarized in Table 2, recent studies have proven the efficiency of modifying the conventional IP process evidenced by the promising improvements of the modified membranes' water flux, salt rejection and antifouling properties. Physical or chemical surface modification of the TFC membranes is relatively straightforward and highly influential on the final performance considering that the modification is mainly on the surface layer that is the key selectivity/permeability enhancer in pressure-driven processes. In this regard, new superhydrophilic materials can substantially enhance the membrane structure and improve their permeability and selectivity.

3.2. Tailoring the interfacial polymerization reaction

A common technique to improve TFC membranes' performance is through rising the reactivity between monomers. In fact, using catalysts such as camphor sulfonic acid and triethylamine enhances the reactivity of two monomers in PA layer which effects on the cross-linking density, surface roughness and hydrophilicity of membranes [51]. The density of carboxylic acid groups may also help the improvement of hydrophilicity. Applying more additives can accelerate the hydrolysis of organic phase monomers, which significantly increases the carboxylic acid density [145]. Chemical surface modification of PA layer with different methods such as grafting and coating can considerably enhance membranes' hydrophilicity. Many studies have been done in recent years with grafting [32,146,147] and coating [51,148,149] methods as mentioned earlier in details. Although these methods are so effective for membrane improvement, the thickness of PA becomes larger and therefore it may cause some deterioration in permeability in a long run. Besides, the

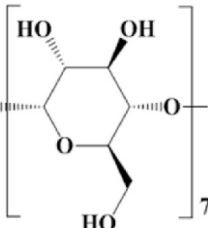
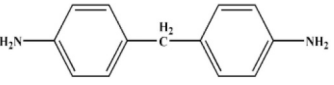
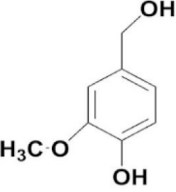
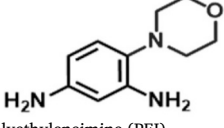
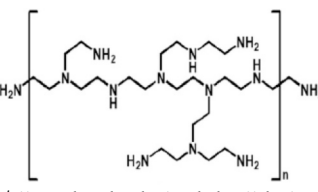
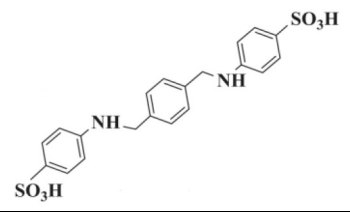
Table 3

Recent studies focusing on new monomers instead of MPD or PIP in TFC RO and TFC NF membranes.

Type of monomer instead of PIP and MPD	Experimental condition	The main change in molecule structure	Membrane performance after modification	Ref.
4,4'-oxydianiline (ODA) 	Dead-end filtration device, Pressure: 6 bar, 10 mg.L ⁻¹ Crystal Violet (CV) dye	-The increase in the intensity of amine and amide groups because of higher concentration of monomer -The presence of carboxylic acid and carboxylic amide carbon groups -The carbon in phenyl rings attached to O molecules and the carbon in aromatic ring attached to amine groups during polymerization	-Faster diffusion -High salt rejection: 96.3% -High water permeance: 4.5 L.m ⁻² .h ⁻¹ .bar ⁻¹	[175]
Mussel-inspired sulfonated dopamine (SDA) 	Cross-flow system, Pressure: 6 bar, 100 mg.L ⁻¹ Congo red, Methyl blue, Methylene blue and Brilliant green	The amine groups of SDA reacted with acyl chloride in organic phase and formed amide groups -The presence of -SO3- groups, -Abundant "volcano" nodular features because of heterogeneous aggregation of DA with TMC	-Five times higher water flux: 62.2 L.m ⁻² .h ⁻¹ -Excellent rejection rate: 99.9% for four representative dyes	[176]
Diethylenetriamine (DETA) 	Dead-end filtration device, Pressure: 2 bar, 1000 mg.L ⁻¹ MgCl ₂ , MgSO ₄ and Na ₂ SO ₄	-The formation of grainy structure -High amount of amines solubility in <i>n</i> -heptane -The molecule structure decrease contact angle to 64° The creation of C=O groups and N-H stretching vibration Zeta potential: -13.7 ± 0.4 mV	-Permeation flux: 3.35 ± 2.0 L.m ⁻² .h ⁻¹ .bar ⁻¹ , -Salt rejection: up to 80% for Na ₂ SO ₄ , -The molecular weight cut-off: 420 Da, -Flux recovery ratio: 87.2 ± 1.2%	[177]
Triethylenetetramine (TETA) 		-The formation of grainy structure -High amount of amines solubility in <i>n</i> -heptane -The molecule structure decrease contact angle to 40° Zeta potential: -18.9 ± 0.6 mV	- Permeation flux: 4.35 ± 0.3 L.m ⁻² .h ⁻¹ .bar ⁻¹ , - Salt rejection over 80% for Na ₂ SO ₄ , - Molecular weight cut-off: 400 Da, FRR = 100 ± 2.0%.	
Tetraethylenepentamine (TEPA) 		-The formation of grainy structure -High amount of amines solubility in <i>n</i> -heptane -The molecule structure decrease contact angle to 34° -Zeta potential: -17.7 ± 0.5 mV	-Permeation flux: 5.10 ± 4.5 L.m ⁻² .h ⁻¹ .bar ⁻¹ , -Salt rejection: over 80% for Na ₂ SO ₄ , -The molecular weight cut-off: 370 Da, -Flux recovery ratio: 98.7 ± 1.8%	
Glucose monomer 	Cross-flow system, Feed flow rate: 7 L.min ⁻¹ , Pressure: 10 bar, 100 mg.L ⁻¹ sodium alginate (NaAlg) aqueous solution	- Finger-like porous structure - The reaction of O-H bonds of G monomers with -COCl bonds in TMC - The formation of hydroxyl-enriched surface because of G monomers resulting in higher hydrophilic property -Lower molecular weight cut-off	-High flux rate: 42.5 L.m ⁻² .h ⁻¹ -Rejection rate: 93.8%, -FRR: 99.4% during 25 h filtration process for 100 mg.L ⁻¹ of NaAlg	[178]
Zwitterionic amine monomer PEI-g-SBMA 	Dead-end filtration device, Low pressure: 2 bar, 0.1 g.L ⁻¹ Methylene blue, Orange GII, Congo red dye solutions at pH: 7.0	-The new peaks at NMR analysis protons (δ=3.36 mg.L ⁻¹), c(δ=3.00 mg.L ⁻¹) and (δ=2.80 mg.L ⁻¹) presenting carbon atoms in α position of the quaternary ammonium ion -The grafting weight percentage = 6.2%, the presence of SO ₃ stretch bonds due to zwitterionic amine monomers	- High water flux: 13.2 L.m ⁻² .h ⁻¹ .bar ⁻¹ , i.e. over 2 times higher than that of the PEI/TMC membranes without new monomer. - Significant improvement in antifouling property against BSA, sodium alginate (SA), and HA	[179]
Zwitterionic N,N-Bis(3-aminopropyl)methylamine, ZDMNA 	Cross-flow system, Pressure: 6 bar 1 g.L ⁻¹ Na ₂ SO ₄ , MgCl ₂ , CaCl ₂ , NaCl solutions 0.5 g.L ⁻¹ Congo Red (CR), Sunset Yellow (SY) and Methyl Blue (MYB) dye aqueous solutions	The introduction of O=S=O bond on the surface of active layer -The increase in cross-linking degree from 38.83% to 95.41% as a result of new molecule structure in top layer -Due to solubility parameter of ZDMNA (14.9 cal ^{1/2} cm ^{3/2}), the diffusion of aqueous monomer toward hexane became tough resulting in smoother surface	-The high-water flux of modified membrane 10.67 L.m ⁻² .h ⁻¹ .bar ⁻¹ . - Modified membrane showed high CR and MYB dyes rejections (99.9%)	[165]
	Dead-end filtration device, Pressure: 2.5 bar 0.1 g.L ⁻¹ Methyl Blue, Alcian Blue, Congo Red and 1 g.L ⁻¹ Na ₂ SO ₄ solution	-The best contact angle 59.3 °C -The existence of three hydroxyl groups in the structure of new monomer which was interacted with acyl chloride groups in organic phase	-The flux increased from 104.6 to 198.7 L.m ⁻² .h ⁻¹ -The rejections of Congo Red and Methyl Blue were 95.6 and 94.4%, respectively	[180]

(continued on next page)

Table 3 (continued)

Type of monomer instead of PIP and MPD	Experimental condition	The main change in molecule structure	Membrane performance after modification	Ref.
<p>β-cyclodextrin (β-CD)</p> 	10,000 mg.L ⁻¹ NaClO solution for 96 h in chlorine resistance test	<p>More electronegative property due to negative behavior of new monomer</p> <p>-The cavity size of β-CD was between 0.6 and 0.78 nm and the diameter of water molecules was 0.27 nm resulted in better water flux</p>	-Significant chlorine resistant property after 96 h without any change in membrane performance	
<p>4,4'-diaminodiphenylmethane and 1,3,5-benzenetricarbonyl trichloride (DADPM)</p> 	Cross-flow system, Pressure: 4 bar Na ₂ SO ₄ salt with different concentrations (5, 10, 20, and 30 g.L ⁻¹) added to congo red dye solution (100 mg.L ⁻¹)	<p>-The existence of NH₂ and CH₂ bonds in new monomer for polymerization process through acyl chloride groups in TMC</p> <p>-The roughness values of the membrane surface are 5.08 nm (R_a) and 8.46 nm (R_q)</p> <p>-The molecular weight cut off: 960 Da</p>	<p>-The dye permeation flux of DADPM-TMC membrane increased from 35.15 to 59.54 L.m⁻².h⁻¹ with specific DADPM concentration,</p> <p>-The pure water flux of DADPM-TMC membrane was 65.52 L.m⁻².h⁻¹ while salt and dye rejection were always above 90%,</p> <p>-The flux recovery rate: 89.85%</p> <p>The water flux increased from 0.97 L.m⁻².h⁻¹.bar⁻¹ to 2.1 L.m⁻².h⁻¹.bar⁻¹,</p> <p>-High rejection rate of 89% for Brilliant Blue R-250 and a rejection of 81% for clindamycin phosphate</p>	[181]
<p>Vanillic alcohol (VA)</p> 	Dead-end filtration device, Pressure:10 bar Dye solution including Brilliant Blue and clindamycin phosphate	<p>-The surface roughness: 12 ± 0.2 nm</p> <p>-The surface become rougher by increasing monomer concentration,</p> <p>-Lower hydrophilicity by increasing monomer concentration</p> <p>-The existence of CH₃, OH and COOH bonds on monomers structure</p>	<p>-The flux recovery rate: 89.85%</p> <p>The water flux increased from 0.97 L.m⁻².h⁻¹.bar⁻¹ to 2.1 L.m⁻².h⁻¹.bar⁻¹,</p> <p>-High rejection rate of 89% for Brilliant Blue R-250 and a rejection of 81% for clindamycin phosphate</p>	[182]
<p>4-morpholino-<i>m</i>-phenylenediamine</p> 	Cross-flow system, Pressure: 15 bar, 2000 mg.L ⁻¹ NaCl solution	<p>-The presence of carbonyl (C=O) asymmetric stretching vibrations of an aliphatic carboxylic acid units</p> <p>-The increase in O content after modification process from 15.92% to 16.98%, better ridge-valley structure with smaller protuberances, leaf-like morphology</p>	<p>-Enhanced hydrophilicity with water contact angle of 28.1° and surface roughness as low as 26.0 nm,</p> <p>-The significant increase in water flux by 24%,</p> <p>-High rejection rate around 98%</p>	[167]
<p>Polyethyleneimine (PEI)</p> 	Cross-flow system, Flow rate: 0.6–0.7 L·min ⁻¹ , Pressure:1 to 7 bar 1000 mg.L ⁻¹ Na ₂ SO ₄ , MgSO ₄ and MgCl ₂ solutions	<p>-The surface looked coarser, resembling that of a corkboard</p> <p>The attractive force between negatively charged surfactant and positively charged PEI would lead to a greater sorption of PEI in the PSf support</p>	<p>-The new monomer with SDS surfactant improved membrane performance resulting from lower the steric hindrance</p> <p>-The new monomer showed maximum flux rate and salt rejection,</p> <p>-Rejection rate: Na₂SO₄: 92.26 ± 3.30%; MgSO₄: 93.83 ± 3.22%; MgCl₂: 94.15 ± 2.52%</p>	[183]
<p>4,4'-((1,4- phenylenebis(methylene) bis(azanediyl)) dibenzenesulfonic acid (PMABSA)</p> 	Cross-flow system, Pressure: 15.5 bar, 2000 mg.L ⁻¹ NaCl solution	<p>-The existence of two specific groups of SO₃H and two NH bonds for polymerization through acyl chloride groups</p> <p>-The PMABSA molecules showed lower solubility and miscibility in the organic phase and therefore diffused slowly through organic phase</p> <p>-The bulky benzene rings also acted as a barrier for further molecular diffusion</p>	<p>-Significant pure water permeability: 1.18 ± 0.03 L.m⁻².h⁻¹.bar⁻¹,</p> <p>-Salt rejection: 98.2 ± 0.4%</p> <p>-The water permeability of the as prepared RO membrane was improved by nearly 63%</p> <p>-The exhibition of considerable desalination performance about 4.00 L.m⁻².h⁻¹.bar⁻¹</p>	[184]

coating of PA layers are normally connected through van der Waals forces, hydrogen bonding and electrostatic interactions which are weaker compared to covalent bonds resulting in the coating deterioration over time [150].

3.3. Application of new monomers in IP

The PA thin film layer is made of two parts including aqueous and organic phase with the cross-linked pores of different monomers synthesized by IP process. A dense sub-layer with ridge and valley shapes is located under PA layer in TFC membranes [151]. For the improvement

of salt rejection and water flux, choosing best structure for these two mentioned layers is imperative. Different structures with different substances can finally change the diffusion rate of membranes [152,153]. Various materials have been used recently to increase the TFC membranes' hydrophilicity. Using new monomers for changing the common structure of TFC membranes can offer new hydrophilic membranes with excellent performances.

3.3.1. New monomers instead of MPD in TFC RO membranes

For decades, *m*-phenylenediamine (MPD) has been used as the aqueous monomer for TFC RO membranes fabrication. Recent studies have shown great improvements of the performance and properties of the membrane by using alternative monomers to MPD [109,154]. The presence of new monomers in PA layer may influence the structure of the membranes creating a more permeable selective layer. When the amine functional groups of MPD react with acyl chloride groups of TMC, pendant carboxylic acid groups are created.

Since the structure and interaction of two monomers in the organic and inorganic phase of PA layer can make a great contribution to the diffusion mechanism of RO membranes, using new monomers can be an efficient way to increase water flux and salt rejection. Further, the density and hydrophilicity of polymer chains in the PA layer are highly dependent on the structure of monomers [155]. The monomers aromatic rings and molecular structure (e.g., carboxylic acid, carbonyl groups and hydrogen bonds) play an important role in solution-diffusion mechanism [156]. The molecular motion of these aromatic rings produced by the interaction between MPD and TMC is also very critical. For example, para-based PAs such as PPD were realized to be less permeable than meta-positioned PA (MPD) because of their less mobile chains [157].

The mechanical strength of interactive monomers is also very effective on the rate of membranes' hydrophilicity. Membranes with higher rupture strength have shown better performance and higher diffusion rates [158,159]. Thus, focusing on monomers and the way they get involved in the active PA layer of TFC membranes can make a considerable change in the future of membranes. Numerous studies have been done in recent years to develop modified recipes involving new monomers instead of MPD for PA layer fabrication [160–165]. For instance, Yong et al. used *m*-phenylenediamine-5-sulfonic acid (SMPD) instead of MPD [159]. The presence of sulfonic acid (SO₃H) in the aromatic ring created a smoother PA surface than the conventional PA synthesis approach (using MPD and TMC). The SMPD created a more hydrophilic surface with higher flux rate while it decreased the salt rejection [159].

Zheng et al. synthesized a new sulfonated diamine monomer and used it instead of MPD to react with TMC and form the PA layer [166]. The molecular analysis of the synthesized monomer showed that the torsion angle of aromatic rings in PA layer was in the range of 60–120°. This angular structure of 3, 3'-(ethane-1, 2-diylbis (azanediyl)) bis (2, 6-dimethylbenzenesulfonic acid) (EDADMBSA) interacting with TMC showed a non-coplanar design with higher rotating state. The presence of methyl groups can interfere the orientation of PA chains which may lead to creating a considerable number of free volumes on the surface of amide layer. This resulted in the improvement of water permeability rate 2.6–2.7 times higher than that of conventional MPD-TMC PA structure. The effect of cross-linking density was also investigated. Since more molecules of EDADMBSA monomers reacted with TMC molecules, because of the smaller differences between the monomers solubility rates, a denser layer with strong cross-linking reactions was created. Although the thickness of the generated PA layer was significantly smaller than the one that is commonly made through conventional MPD-TMC cross-linking, the high density of the developed PA layer significantly increased the salt rejection rate (up to 96%) of the developed TFC RO membranes [166].

Li et al. worked on a new aqueous monomer, 4-morpholinobenzene-1,3-diamine (MpMPD), to react with organic phase (TMC in *n*-hexane) for PA layer fabrication. The morpholino groups in the new monomer

created a smooth area on the surface of membrane with the help of more hydrogen and oxygen bonds. Besides morpholino groups can affect the cross-linking reaction of PA layer by steric hindrance of these molecules at ortho-position. The specific structure of MpMPD helped the membrane permeation rate and increased it by 24% greater than that of the conventional MPD membranes while salt rejection was remained relatively high (97.8%) [167]. Qin et al. used hyperbranched polyester amide as a new aqueous monomer to interact with the PA organic phase [168]. The presence of 4-dimethylaminopyridine as a catalyst not only prevented the steric hindrance of acyl transfer reaction but also helped the phase transfer in the IP step. The cross-section morphology of new synthesized PA layer with new aqueous monomer showed a much thinner PA layer (110 nm) than that of the conventional RO membranes with MPD solution (200–500 nm). This thin, dense, cross-linked and flawless structure can result in a significant improvement of flux rate along with higher salt rejection in RO membranes. The existence of hydrophilic carboxyl groups due to the IP and the presence of unreacted hydroxyl groups of hyperbranched polyester amide increased the hydrophilicity of new RO membranes and decreased the water contact angle from 90° to 54° on the surface of the developed membrane. Thus, water flux reached to 40 L.m⁻².h⁻¹ with a salt rejection of over 92% [168]. The structure of aforementioned monomers used instead of MPD is shown in Table 3. As it is clear from these structures, new monomers increase the membranes hydrophilicity through introducing new functional groups to the developed PA layers.

The introduction of new hydrophilic structures in the aqueous phase of IP process not only increases the performance of membrane but also improves the membrane's stability. For decades, the use of MPD showed consistent results for either RO or NF membranes. Applying new monomers instead of MPD is a promising way to improve the surface structure and properties of TFC membrane and warrants further investigation into the use of these new structures.

3.3.2. New monomers instead of PIP in TFC NF membranes

Since the first introduction of NF membrane by Simpson et al. [169] as a membrane with pore size between RO and UF membranes, the chemical modification of these membranes has been widely studied [170]. As it is clear, the mechanism of NF membranes separation is based on steric effects of molecules and electrostatic interaction between membrane and feed solution, which is noted as Donnan exclusion [171]. Piperazine (PIP) and TMC have been the most common monomers to fabricate TFC NF membranes with nano-sized pores. However, in recent years, many studies have tried to replace PIP with other aqueous monomers [172].

Using more hydrophilic monomers with different structures instead of PIP has a significant effect on the surface behavior especially fouling behavior and flux rate. Zhou et al. used natural polymer sericin instead of PIP together with TMC as the organic phase monomer to fabricate TFC NF membranes [173]. They used sodium dodecyl sulfate (SDS) as a strong surfactant to bolster the reaction of sericin structures with the support layer. The effects of various factors including TMC content, reaction time, pH of aqueous phase and curing temperature showed that the density and molecular position of selective layer changed under different condition. The optimum condition showed a maximum rejection rate of 95.4% to Na₂SO₄ and a water permeability of 11.91 L.m⁻².h⁻¹. The concentration of reactant had a great impact on both water permeation rate and salt rejection. Generally, low reactant concentration leads to weak reaction between organic and aqueous phase and therefore, polymerization remains incomplete. Higher concentration of reaction makes a dense defect-free layer, which improves rejection rate while keeping the water flux high. The ester bonds (COO), COOH, NH₂ and OH bonds are the resulted interaction between hydroxyl and amino groups in sericin with acyl chloride (COCl) which frequently occur in active PA layer and increase the hydrophilic surface properties of the membranes. This was a promising monomer used instead of PIP which improved membrane performance with a significant rate compared to

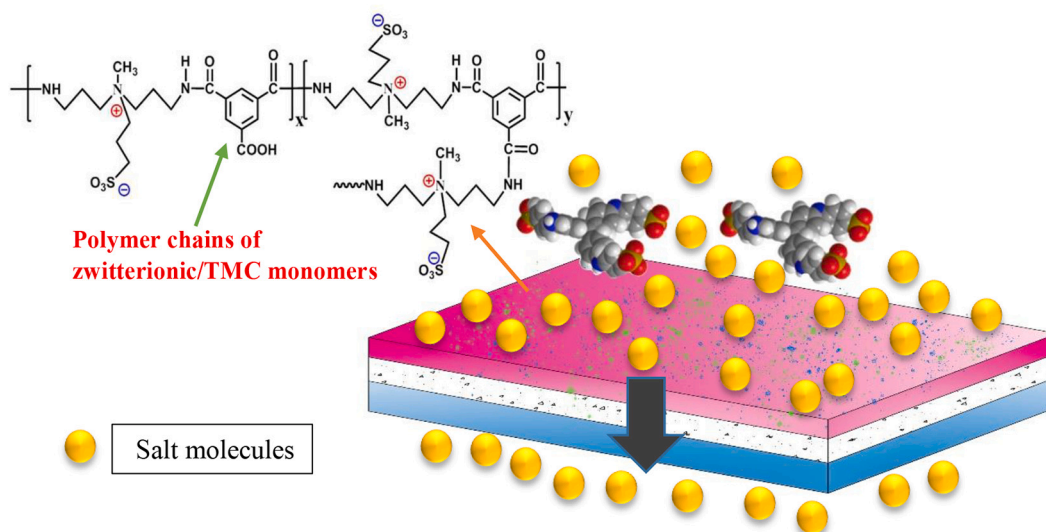


Fig. 3. The mechanism of passing salt molecules from membrane as a result of higher membrane selectivity synthesized by a zwitterion monomer.

conventional NF membranes [173].

Lee et al. used polyethyleneimine as the aqueous monomer to react with TMC on a PES support [174]. The nitrogen bonds of amine groups in polyethyleneimine reacted with acyl chloride bonds. The created amine groups on the top layer formed a denser and smoother surface. Because of higher amount of these amine groups, the surface of membrane was positively charged at natural conditions. Triazine rings were formed as a result of the strong reaction between new monomer and TMC. The developed membrane showed a high resistance against nucleophilic attacks induced by extreme pH conditions [174]. Mi et al. synthesized a NF membrane using zwitterionic *N,N*-Bis(3-aminopropyl) methylamine functionalized monomer as the PA aqueous monomer to separate a combination of dye and salt from solution [165]. The monomer contained amine, sulfonic acid and methylene groups joint by quaternary ammonium (Fig. 3). These new molecular structures changed the morphology, density and shape of the membranes. As the concentration of zwitterionic monomers increased, the pore size and pore size distribution of membranes became lower. The presence of zwitterionic monomers in the PA layer enhanced the chemical properties of the membrane. The high-rate interfacial free energy ($-\Delta G_{SL}$) of ZM3 ($132.61 \text{ mJ}\cdot\text{m}^{-2}$) created a hydrophilic smoother surface which considerably reduced membrane fouling compared to other conventional membranes. These moieties introduce a new hydration layer on the surface of membrane resulting in the change of fouling enthalpy and the prevention of foulants being close to the membrane surface [165]. The mechanism of membrane rejection is illustrated in Fig. 3 where zwitterionic monomers contribute to the perfect separation of dye molecules from salt with high stability.

Overall, the recent application of new aqueous monomers in NF membranes has shown promising results with excellent performance in water permeability and salt rejection rate. The chemical structure of some applied monomers instead of PIP increased membrane stability and reduced membrane thickness. This is a great step in membrane field because new structures are definitely effective and can be readily adopted in industrial scale. Long period tests should be run for these new monomers to fix the errors of these structures in NF membrane for the rejection of bivalent and monovalent ions from water solution and also for other applications.

Table 3 summarizes the results of some other studies on the application of new alternative monomers to MPD, or PIP for both TFC RO and TFC NF membranes.

3.3.3. New monomers instead of TMC

The molecular structure of organic phase in both TFC RO and TFC NF membranes can significantly affect the performance and properties of membranes. The acyl chloride in organic monomers reacts with amine group in aqueous phase and finally forms aliphatic/aromatic rings within the PA layer of TFC membranes. The stability and pore size distribution of both TFC RO and TFC NF membranes depend on the reaction of molecules in the organic and aqueous phases. The solubility and reactivity of organic phase monomers may change the physical and chemical properties of membranes including thickness, chemical morphology, selectivity and permeability [185]. Thus, it is important to know more about different organic monomers and their structures.

Liu et al. investigated the introduction of organic monomer-5-Isocyanato-isophthaloyl chloride (ICIC) in the active layer of TFC RO membranes. As a cross-linking agent, ICIC has trifunctional groups with the structure of $\text{N}=\text{C}=\text{O}$ and $-\text{COCl}$, which reacts with MPD forming the PA layer. The presence of NH_2 , NHCONH and acyl amide ($-\text{CONH}$) groups on the top layer can create higher electronegativity when the surface of membrane is encountering the water molecules. This may finally lead to lower binding energy and higher water flux compared to conventional MPD/TFC membranes. The morphology analysis showed that the synthesized membrane with ridge and valley shape was smoother and thinner than the conventional membrane, which was critical for the improvement of membrane permeability. The presence of new monomer changed the surface structure of the membrane and reduced the membrane thickness to less than $0.2 \mu\text{m}$. The overall surface roughness also decreased and the new modified membrane showed small-scale surface roughness of a typical nodular (ridges and valleys) structure resulting in lower fouling issue on the surface of membrane [186].

Zhang et al. applied dendritic amphiphilic hyperbranched polyester acyl chloride (HPE-COCl) as an organic monomer in the active layer [187]. Because of the structure of HPE-COCl with a high amount of acyl chloride, the reaction of organic phase with aqueous monomer showed higher stability with more hydrophilic bonds. However, the characteristic results showed that new structure of organic phase changed the movement and behavior of PIP in the active layer. In fact, the amphiphilic structure of HPE-COCl affects the diffusion rate of molecules. The hydrophilic side of HPE-COCl reacted with aqueous phase while hydrophobic side stretched into organic part. The nodular crumpled surface was the result of applying HPE-COCl/PIP monomers, which resulted in forming a thicker layer than the conventional membrane. However, the formation of a smoother surface with abundant amine

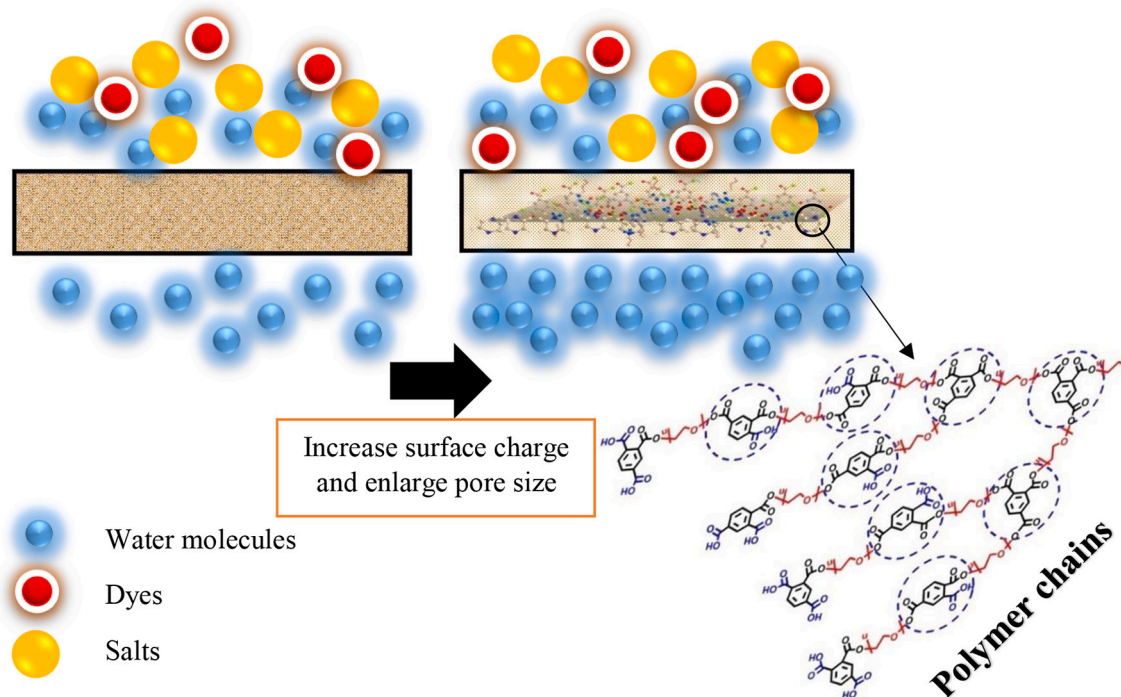


Fig. 4. Water molecule transferring from membrane with the help of new HPE-COCl/PIP monomers.

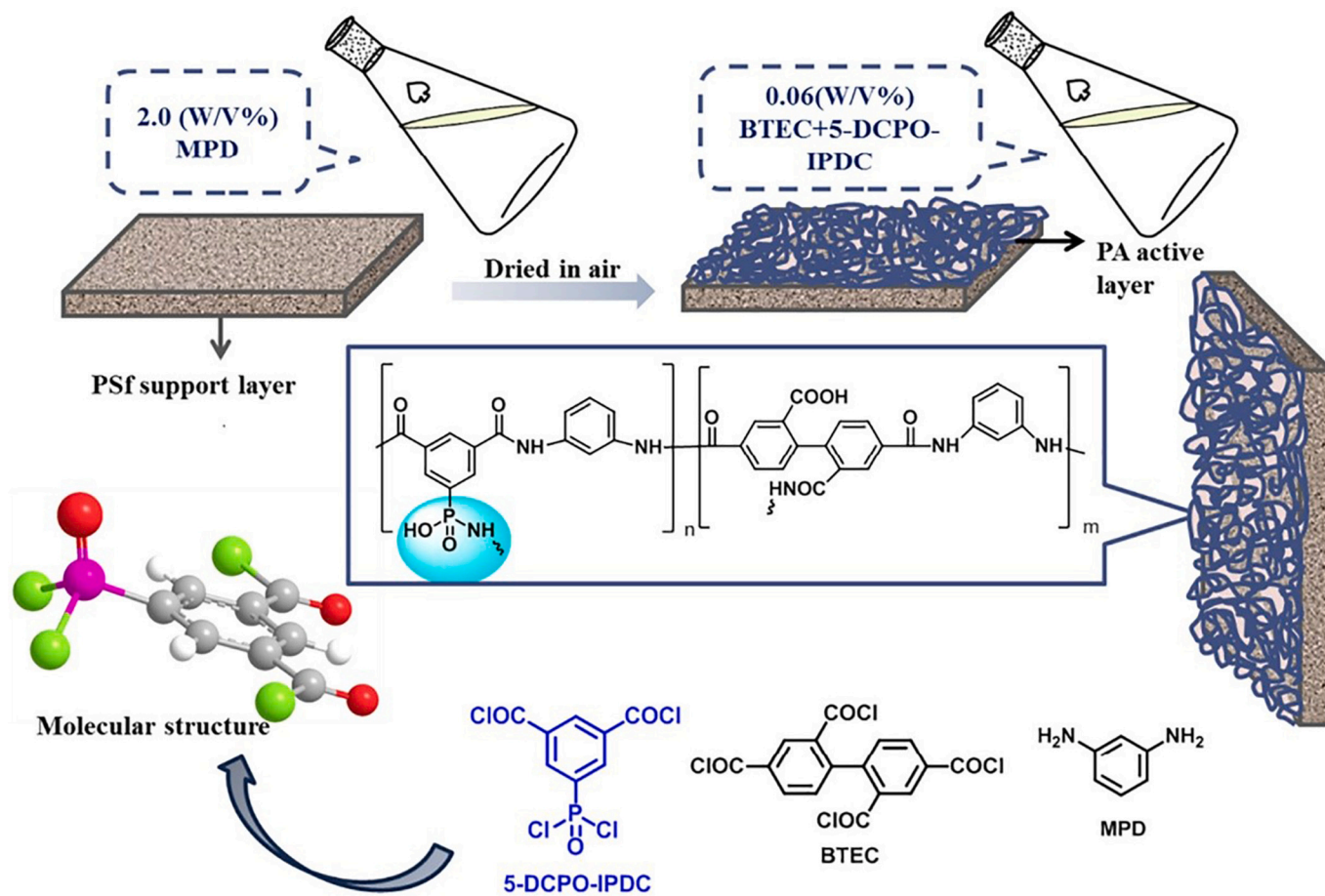
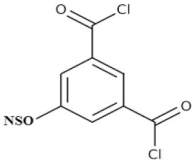
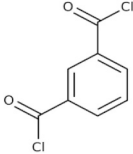
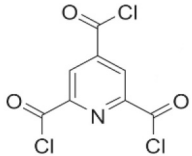
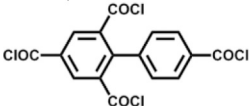
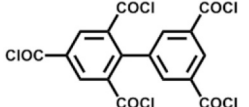
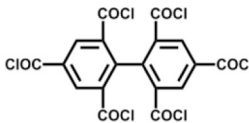


Fig. 5. Synthesis of NF membrane using 5-(dichlorophosphoryl)isophthaloyl dichloride (5-DCPO-IPDC), BTEC and MPD [155].

Table 4
Recent studies using new monomers replacing TMC in organic phase.

Type of monomer instead of TMC	Experimental condition	The main change in molecule structure	Membrane performance after modification	Ref.
Amino group, 5-sulfinyl amino isophthaloyl dichloride (NSO) 	Cross-flow system, Pressure: 10 bar, 2000 mg.L ⁻¹ NaCl, Na ₂ SO ₄ and MgSO ₄ solutions	- The molecules of new monomer are smaller and they are closer compared to TMC monomers. - NSO monomer created a smoother surface - NSO formed thinner surface. - The existence of semi aromatic and aromatic PAs because of NSO monomer	- Significant enhancements of the permeate flux and salt rejections which were ascribed to the -NSO group. - Reductions in the surface -COOH density, surface negative charges, surface roughness and PA layer thickness.	[190]
Isophthaloyl dichloride (IPC) 	Cross-flow system, Pressure: 5 bar, 200 mg.L ⁻¹ humic acid (HA) as a foulant, 7000 mg.L ⁻¹ MgSO ₄	- The presence of acyl chloride groups at 1739.48 cm ⁻¹ because of IPC monomer, – Creating a dense layer with IPC molecules - Cross-linked layer in higher reaction soaking time with PIP	- Higher antifouling behavior in humic acid filtration. - The rejection ability was tested in 8 cycles without losing its characteristics. - The rejection of salts was in order of 99.9, 99, 82, and 72% for Na ₂ SO ₄ , MgSO ₄ , CaCl ₂ and NaCl, respectively.	[191]
hitherto unreported 2,4,6-pyridinetricarboxylic acyl chloride (PTC) 	Cross-flow system, Pressure: 20 bar, 1500 mg.L ⁻¹ NaCl	-The formation of sponge-like or nodular structure - Patchier and non-uniform appearance -The presence of phenyl ring of acyl chloride instead of aromatic N=C (pyridinering) bond	-Higher antimicrobial performance, -Higher water flux: 42.5 L.m ⁻² .h ⁻¹ -Salt rejection: 94%	[192]
2,4,4',6-biphenyltetraacylchloride(BTAC) 	Cross-flow system, Feed flow rate: 100 L.h ⁻¹ , Pressure: 15.5 bar, 2000 mg.L ⁻¹ NaCl solution	-The introduction of four acyl chloride groups onto the surface of the membrane for polymerization -The O/N ratio: 2.248, - The thickness: 205 ± 6 nm	-High average salt rejection above 98% -The higher rate of carboxylic acid groups reduced the permeation rate compared to conventional TMC/MPD interfacial polymerization -The water flux: 43.3 ± 8.1 L.m ⁻² .h ⁻¹	[189]
,3',4,5',6-biphenylpentaacylchloride(BPAC) 		-The introduction of five acyl chloride groups onto the surface of the membrane for polymerization -The O/N ratio: 2.675, -Tightly packed globules with the ear-shaped PA ridges -The thickness: 179 ± 10 nm	-High average salt rejection above 98% -The higher rate of carboxylic acid groups reduced the permeation rate compared to conventional TMC/MPD interfacial polymerization -The water flux: 31.2 ± 0.8	
and 2,2',4,4',6,6'-biphenylhexaacylchloride (BHAC) 		-The introduction of six acyl chloride groups onto the surface of the membrane for polymerization -The highest amount of O/N ratio about 3.219 -Tightly packed globules with the ear-shaped PA ridges -The thickness: 144 ± 8 nm	-High average salt rejection above 98% -The higher rate of carboxylic acid groups reduced the permeation rate compared to conventional TMC/MPD interfacial polymerization -The water flux: 22.1 ± 2.1	

groups created a highly hydrophilic surface which improved the membrane flux compared to conventional PIP/TMC membranes. As shown in Fig. 4, HPE-COCl monomers increased both the surface charge (negative charge) and pore size of membrane resulting in higher water flux with constant salt and dye rejection rate [187].

The position of acyl chloride groups in the organic monomer is also very important for some effective factors in membrane such as solubility and diffusivity of water and salt. In fact, the position of molecules and chemical groups in either aqueous or organic monomer can change both the rate of hydrophilicity and the surface smoothness. The steric effects and cross-linking degree can also be different in monomers with the same chloride bonds but in different positions. Li et al. showed the effect of three tetra-functional biphenyl acyl chloride isomers including mm-BTEC, om-BTEC, and op-BTEC on the membrane properties. The amount of created carboxylic acid groups in mm-BTEC was higher than that obtained by the other two isomers during IP process. Because of this, the hydrophilicity of mm-BTEC was more than that of om-BTEC,

and op-BTEC in the active layer [76]. The functionality of acyl chloride groups in organic phase can also influence on the steric effects and surface charge of membranes. When the functional acyl chloride groups increase in the organic phase, the surface of membrane becomes negatively charged after polymerization process. This can help the solubility of molecules and change the permeability rate of membranes. Moreover, the position of chloride groups in the organic monomer or the amount of acyl chloride groups make a great impact on the surface roughness of membranes [188]. The well-known ridge and valley structure changes during polymerization process under the different structures of organic monomers. Zhao et al. used two types of acyl chloride monomers to fabricate NF membrane [155]. A tetra-functional BTEC partially replaced by an acyl chloride with a -PO(Cl)₂ group (Fig. 5). When the ratio of the concentration of this new monomer to the concentration of BTEC was 60%, an outstanding NF membrane was developed by Na₂SO₄ and NaCl rejection of 99.0% and 48.8%.

Wang et al. investigated on three polyacylchloride monomers

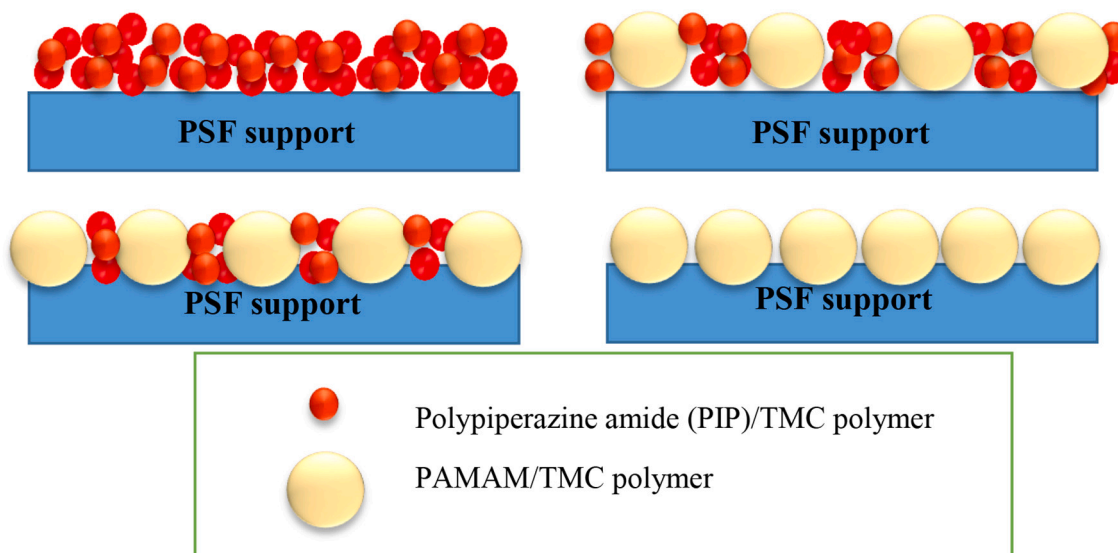


Fig. 6. Two mixed monomers of PIP/PAMAM with TMC for polymerization, one acting as void filler a) PIP and TMC only b) PAMAM/PIP and TMC with low content of PAMAM c) higher content of PAMAM/PIP and TMC d) PAMAM/TMC only.

including 2,4,4',6-biphenyltetraacylchloride (BTAC), 2,3',4,5',6-biphenylpentaacylchloride (BPAC) and 2,2,4,4',6,6'-biphenylhexaacylchloride (BHAC) as promising monomers instead of TMC in RO membranes [189]. The main focus was on the change in chemical properties such as surface charge and hydrophilicity as a result of organic monomer interaction with MPD. The results showed that higher amount of functional chloride groups made a negative surface and the roughness of top layer was lower which improved the membrane resistance against fouling. There was no considerable change in the hydrophilicity due to the cooperative effect between roughness and carboxylic groups [189]. Table 4 summarizes the results of some recent studies on the alternative acyl functional monomers instead of TMC in the PA organic solution of TFC membranes.

Using new monomers in organic phase is very challenging due to their unknown effects on membrane structure and therefore, few studies have been conducted in recent years focusing on the alternative monomers instead of TMC (Table 4). Excellent water flux and salt rejection (up to 94%) of these membranes (Table 4) proves their high efficiency and great promise for further development. However, antibacterial property, chlorine resistance and different dye and salt rejection efficiency of these new membranes have not been fully explored in the literature. These are critical factors to evaluate membrane efficiency in water treatment and need to be investigated in future research. Future research should also consider various operational parameters such as different feed flow rates, pressures and feed concentrations to better analyze the effects of new organic monomers on the membranes overall performance.

3.3.4. Mix of two monomers

Using two different monomers in each phase can significantly enhance the TFC membranes' performance [193]. Different types of monomers act properly when they are blending in active layer. In some cases, they act as a complement and create a strong surface for the separation process. Despite many advantages gained by conventional MPD/TMC or PIP/TMC polymerization process, there are still many problems related to membrane fouling and antibacterial properties. Therefore, finding new ways and materials can be very effective to enhance fouling problems in TFC RO and TFC NF membranes. One of the factors is mixing two monomers in the active layer in order to improve the membranes' surface roughness and surface charge. The improvement of active layer with hydrophilic groups such as carboxylic acid and amine groups is perfectly done with the help of two mixed monomers

[194]. Since one monomer may cause some errors in the structure after polymerization process, using another monomer as a supportive component to fix the defects of active layer has been under investigation in recent literature [195–197]. In fact, the synergistic effects of supportive monomer improve the molecular structure of membranes in terms of molecular shape and chemical position. For example, some monomers act as a void filler of main monomer due to their small molecular size causing the creation of denser and packed active layer and therefore higher salt rejection (Fig. 6).

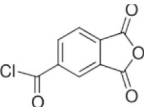
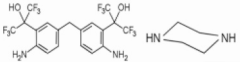
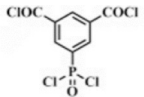
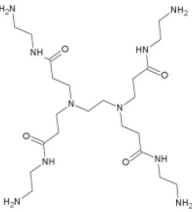
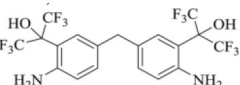
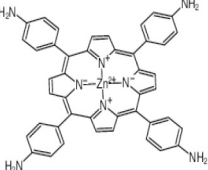
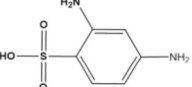
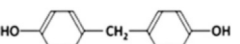
Although PAMAM has higher reactivity than PIP, the diffusivity of this monomer is relatively low due to its larger size. PIP, on the other hand, has higher diffusivity because of its smaller molecular size and hence, diffuses more easily through interface and nascent PA thin film. PIP fills the PA voids and creates a denser layer resulting in a higher salt rejection [193]. Moreover, the hyper-branched polyethylene amine with multiple branches of amine group can somehow improve the membrane permeability and rejection rate as an effective co-monomer. The mobility of polymer chain and polymer-solvent/polymer-solute interaction between two mixing monomers considerably increases membrane permeability. For example, the increasing of acyl chloride groups in organic phase completes the polymerization process through reaction with amine groups or the hydrolysis of unreacted functional acyl chloride groups. By increasing monomer functional bonds, the polymerization process will be completely applied on the surface of membrane and can therefore significantly enhance the membrane performance. The position on co-monomer molecules can help the permeability as they act as a channel for water molecules to easily pass through the active layer while maintaining high rejection rate. Different mixing monomers have been applied in recent years and have shown great ability for the improvement of membrane performance.

A summary of recent studies on the application of mixed monomers for the fabrication of TFC selective layer is presented in Table 5.

The introduction of new structures in membrane surfaces has shown very promising results in recent years. Mixing monomers can create new cross-linked membranes with improved pore sizes and densities. New monomers with various structure not only change the thickness of the membranes but also facilitates the polymerization reaction through their specific groups with unique structure and therefore, improves TFC membrane performance. Based on the results presented in Table 5, the combination of two monomers in one phase or two separated phases (aqueous and organic phase) showed significant improvements in water flux, salt rejection, and antifouling properties of the modified

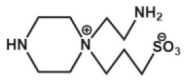
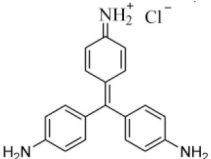
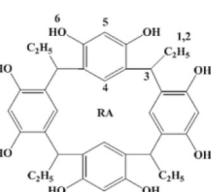
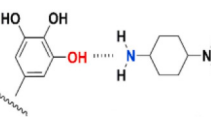
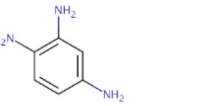
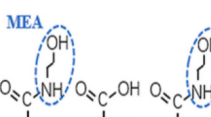
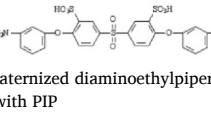
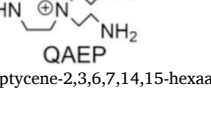
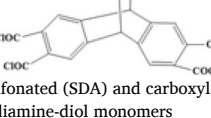
Table 5

Recent studies using a combination of two monomers in each phase for polymerization process of RO and NF membranes.

Type of Monomers	Experimental condition	The main change in molecule structure	Membrane performance after modification	Ref.
Trimellitic anhydride chloride (TAC) 	Cross-flow filtration, Flow rate: 0.6 L. min ⁻¹ , Pressure: 8.0 bar, 1000 mg.L ⁻¹ Na ₂ SO ₄ solution	-The existence of one acyl chloride group in the monomer structure -The rise of carboxylic groups density -The growth of multilayer-ring structure as the TAC content increased	- Pure water permeability: 9.8 L.m ⁻² .h ⁻¹ . bar ⁻¹ , almost 4.2 times higher than the bare membrane (2.3 L.m ⁻² .h ⁻¹ .bar ⁻¹) -Relatively high Na ₂ SO ₄ rejection rate: 83.9%	[112]
(2,2'-bis(1-hydroxyl-1-trifluoromethyl-2,2-trifluoroethyl)-4,4'-methylenedianiline, BHITM) mixed with PIP incorporated with Octadecylamine-grafted GO 	Cross-flow system, Pressure: 6 bar Chlorine resistance test was done with 3000 mg.L ⁻¹ NaClO at pH: 8.0	-The presence of oxygen containing groups including carboxyl, hydroxyl and epoxy groups -The presence of octadecyl amide chain with the content of 11.8% -The formation of CF ₃ and NH ₂ in aqueous solution	-Great chlorine resistance in long period of time with high stability -High Na ₂ SO ₄ rejection above 90% -Pure water flux of 49.6 L.m ⁻² .h ⁻¹ (0.6 MPa), which was 2.5 times than that of pristine PIP TFC membrane and 1.6 times than that of mixed-amine TFC membrane	[164]
Tetra-functional 2,2',4,4'-biphenyl tetraacyl chloride partially replaced with 5-(dichlorophosphoryl) isophthaloyl dichloride (5-DCPO-IPDC) 	Cross-flow system, Pressure: 0.48 MPa, 2000 mg.L ⁻¹ salt solution	- The existence of six acyl chloride groups in two mixture of monomers and a PO (Cl) ₂ group -The a -PO(Cl) ₂ group reacted with MPD or hydrolyzed to a -PO(OH) ₂ -Loose leaf structure with the increase of monomer content -The contact angle decreased to 31°	- Salt rejection of Na ₂ SO ₄ and NaCl: 99.05% and 48.85%, respectively, - Pure water flux increased from 23.63 to 86.49 L.m ⁻² .h ⁻¹	[188]
Ethylenediamine cored polyamidoamine (PAMAM) 	Cross-flow system, Pressure: 7 bar 1000 mg.L ⁻¹ NaCl, Na ₂ SO ₄ , MgCl ₂ and MgSO ₄	-Higher amount of NH stretching bond from the amide group as a result of PAMAM -Higher ratio of amide to amine because of high rate of amide groups in new monomer which leads to strong polymer cross-linking, the creation of compact structures membrane by mixing two monomers -PIP worked as a void filler because of smaller molecule size compared to PAMAM	-The improvement in membrane permeability without affecting solute rejection as a result of mixing monomers -Water permeability increased from 7.79 to 11.75 L.m ⁻² .h ⁻¹	[193]
2,2'-bis(1-hydroxyl-1-trifluoromethyl-2,2-trifluoroethyl)-4,4'-methylenedianiline (BHITM) 	Cross-flow system, Pressure: 6 bar, 2000 mg.L ⁻¹ Na ₂ SO ₄ , MgSO ₄ and NaCl solutions	-New aniline structure, the presence of new molecule structure named 1,1'-carbonylbis-piperazine -The introduction of high amount of O ₂ content due to new added monomer in aqueous phase -The reduction of non-cross-linked nitrogen atoms(-NH) because of new monomer resulted in high hydrophilicity	-The membrane pore size was increased and the electric density of the membrane surface becomes stronger, resulting in a greatly improved flux, an incredible decline in sulfate rejection and an increase in NaCl rejection	[195]
-(tetra-4-aminophenyl)porphyrin 	Dead-end filtration device, Pressure: 2 bar 20 ppm Sudan Blue II and Brilliant Blue R	-The presence of imide rings 1,6-hexanediamine formed by interaction of new monomers support the completion of chemical cross-linking reaction and therefore creation of strong cross-linked membrane -The mixed porphyrin/MPD monomer changed membrane surface color to dark green -The form of defect-free crumpled nodular PA layer with elongated and doughnut-like structures	-Permeation rate was increased from 16.5, 6.7, 8.2, 1.2, and 0.7 to 48.4, 32.5, 36.3, 4.8, and 28.7 L.m ⁻² .h ⁻¹ .bar ⁻¹ , respectively -Up to 90% dye rejection for both Sudan Blue II and Brilliant Blue R	[198]
-diaminobenzene sulfonic acid (2,4-DABSA) 	Dead-end filtration device, Pressure: 3 bar 2000 mg.L ⁻¹ of NaCl, CaCl ₂ , MgSO ₄ and Na ₂ SO ₄ solutions	-The mixing of these two monomers led to the increase in thickness -The surface changed to a cross-linked structure with ridge-and-valley morphology	-Improvements in membrane water flux (30.2 L.m ⁻² .h ⁻¹ .bar ⁻¹) -Monovalent/bivalent salt selectivity (25.0) at low operating pressure of 3 bar with salt rejection of Na ₂ SO ₄ (98.1%), MgSO ₄ (91.4%), and NaCl (54.4%) -Higher fouling resistance against BSA	[199]
monomer-bisphenol F(BPF) 	Cross-flow system, Pressure: 6 bar, 2000 mg.L ⁻¹ Na ₂ SO ₄ , MgSO ₄ and NaCl solutions	-The pore size of membrane changed after modification -The PIP/BPF NF membrane showed the medium cross-linking degree (the amide group+ the ester group content is 8.5%) -The surface was very lumpy	-Significant increase of water flux -The enhancement of the polyester/PA backbone stiffness -Salt rejection for Na ₂ SO ₄ 96.6%, MgSO ₄ 91.7%, and NaCl 55.7%	[200]
Zwitterionic diamine monomer N-aminoethyl piperazine propane sulfonate (AEPPS)	Cross-flow system, Pressure: 15 bar,	-The presence of new groups especially the stretching vibration of sulfonic acid groups due to new monomer	-The hydrophilicity and the water flux of new modified membrane improved from 29.9 ± 1.8 to 54.5 ± 3.2 L.m ⁻² .h ⁻¹ , while	[201]

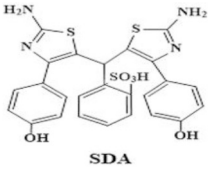
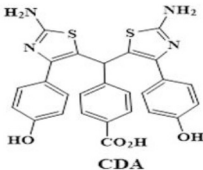
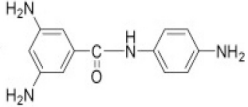
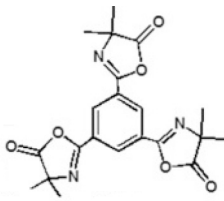
(continued on next page)

Table 5 (continued)

Type of Monomers	Experimental condition	The main change in molecule structure	Membrane performance after modification	Ref.
 trifunctional planar (Pararosaniline, PAR)	2000 mg.L ⁻¹ NaCl solution	-The size of ridge-and-valley structure become larger and looser by increasing AEPPS amount in the membranes	the salt rejection was constant above 98% -Higher stability with the presence of new monomer -Excellent antifouling properties	
 tetra-C-ethyl resorcin[4]arene (RA)	Cross-flow system, Pressure: 15 bar, 1500 mg.L ⁻¹ NaCl solution,	-The presence of conjugated six-membered ring hydrochloride structure of PAR can increase the degree of cross-linking between aqueous and organic phase -The existence of PAR increased the membrane pores on the active layer -The introduction of new monomer formed a three-dimensional structure in top layer	-The high permeable membrane compared to conventional ones -The water permeance of the RO-0.015 was 14.44 L.m ⁻² .h ⁻¹ and salt rejection was over 99.4% compared to conventional membranes -Water permeance: 11.41 L.m ⁻² .h ⁻¹ -Salt rejection: 99.29%	[202]
 Tannic acid (TA), along with cyclohexane-1,4-diamine (CHD)	Cross-flow system, Feed flow rate: 6.5 L.min ⁻¹ , Pressure: 10 bar 2000 mg.L ⁻¹ Na ₂ SO ₄ and NaCl solutions	-The CHD molecules act as a cross-linker and react with TA to form a stable layer -The reaction of these two monomers formed a sphere like structure	-Higher salt rejection above 96% -More hydrophilic surface -The TA1.0-CHD2.5 membrane exhibited relatively higher rejection toward two sulfates, with Na ₂ SO ₄ at 96.96 ± 0.53% and MgSO ₄ at 89.26 ± 0.20%	[204]
 1,2,4-Triaminobenzene (TAB)	Cross-flow system, Pressure: 5 bar, 2000 mg.L ⁻¹ NaCl solution	The formation amide linkage during interfacial polymerization -The decline of membrane surface roughness, the increase in O/N ratio due to new mixing monomer -The release of more free carboxylic acid groups leading to higher hydrophilicity	-Smoother and thinner surface resulting in more water flux -Permeate water flux enhanced from 33 to 55.5 L.m ⁻² .h ⁻¹ , improvement in flux recovery -99.5% NaCl rejection	[205]
 Diethanolamine (DEA) and monoethanolamine (MEA)	Cross-flow system, Flow channel height: 2 mm Pressure: 6, 9, 12, and 15 bar 1800 mg.L ⁻¹ NaCl solution and 50 mg.L ⁻¹ of xylose	-The amidation reaction with amine groups and acyl chloride groups in organic phase -The presence of new alcohol hydroxyl group as a result of two new monomers -The increase in pore size after mixing monomers	-Significant improvement in water permeability -High average rejection for pharmaceuticals above 90% -33.1% NaCl rejection	[206]
 Disodium-3-30 disulfone-4-40 dichlorodiphenylsulfone (S-DADPS)	Dead-end filtration device, Pressures: 6, 9, 12, and 15 bar, 2000 mg.L ⁻¹ MgSO ₄ and NaCl solutions	-The appearance of circular features with large voids on the top layer -Negative surface charge at pH 7 and above	-High flux rate and dye rejection values above 99% rejection for all dyes -Huge amount of water flux for modified membranes with higher amount of S-DADPS monomer (flux rate more than 100 L.m ⁻² .h ⁻¹)	[207]
 Quaternary diaminoethylpiperazine, QAEP mixed with PIP	Cross-flow system, Feed flow rate: 0.5 L.min ⁻¹ , Pressure: 6 bar 1000 mg.L ⁻¹ different salts (Na ₂ SO ₄ , MgSO ₄ , MgCl ₂ and NaCl)	- Blending QAEP increased thickness and roughness of membrane - Significant decrease in contact angle from 62° to 38°, - New monomer had a large number of amines and quaternary ammonium, which improved membrane hydrophilicity	- High salt rejection (Na ₂ SO ₄ : 97.8%, MgSO ₄ : 94.2%), - High permeate flux (96 L.m ⁻² .h ⁻¹) that is 3 times as high as that of the PIP-TMC membranes, - Satisfactory performances against fouling and biofouling	[208]
 Triptycene-2,3,6,7,14,15-hexaacyl chloride (THC)	Dead-end filtration device, Pressure: 2.5–8 bar, 1.0 g.L ⁻¹ Na ₂ SO ₄ , MgSO ₄ and NaCl solutions	-The appearance of C=O stretching vibration of acyl chloride, -COOH was acylated to -COCl entirely and the THC was synthesized successfully -The formation of non-strand hybrid morphology	-Water flux: 21.4 L.m ⁻² .h ⁻¹ .bar ⁻¹ -Na ₂ SO ₄ rejection: 95%, -High divalent to monovalent ions selectivity -Long-term operating stability	[209]
 Sulfonated (SDA) and carboxylated (CDA) aromatic diamine-diol monomers	Cross-flow system, Pressure: 10 bar 2000 mg.L ⁻¹ NaCl,	-The appearance of hydroxyl, sulfonic acid, and amine groups as a mixed band -The presence of symmetric stretching	-The introduction of new monomers resulted in high membrane hydrophilicity,	[210]

(continued on next page)

Table 5 (continued)

Type of Monomers	Experimental condition	The main change in molecule structure	Membrane performance after modification	Ref.
 <p>SDA</p>	Na ₂ SO ₄ , and CaCl ₂ solutions	vibration and the asymmetric stretching vibrations of S=O of SO ₃ H group due to new monomers -Sponge-like structure with high porosity, -The formation of new structures like interconnected strands which have a large number of pores among strands	salt rejection, and flux recovery ratio and water flux	
 <p>CDA</p>	Cross-flow system, Pressure: 20 bar, Cross-flow velocity: 90 L.h ⁻¹ , 2000 mg.L ⁻¹ NaCl solution	-The increase in the intensity of the carboxylic acid band -Higher ratios of O/N on the membrane surface as a result of new monomer which led to having a higher content of free carboxylic acid groups	-The water flux increased from 37.5 to 55.4 L.m ⁻² .h ⁻¹ as the increase of the DABA concentration in amine solution from 0 to 0.25% -Salt rejection above 98%	[211]
 <p>Trimesoyl-[4,4-dimethyl-5(4H)-azlactone] (TMDMA)</p>	Cross-flow system, Cross-flow velocity:7 L.min ⁻¹ , Pressure: 10 bar, 2 g.L ⁻¹ MgCl ₂ , CaCl ₂ , MgSO ₄ , Na ₂ SO ₄ and NaCl solutions	-The monomer contained functional azlactone -The thickness of new membrane with molecule structure of TMDMA was 65 nm -The molecules of TMDMA had no effect on surface roughness -The roughness of membrane was 10.926 nm -Lower carboxyl group content	-The CaCl ₂ rejection rate increased from 71% to 97%, new membrane -Water flux: 19.2 kg.m ⁻² .h ⁻¹ .bar ⁻¹	[212]
 <p>Diacyl chloride monomer dimethyl (3,5-bis(chlorocarbonyl)phenyl)phosphonate (compound I) with a phosphonate group (-PO(OCH₃)₂) blended with 2,2',4,4'-biphenyl tetraacyl chloride (BTEC)</p>	Cross-flow filtration, Pressure: 15.5 bar, 2000 mg.L ⁻¹ NaCl solution	-The existence of six acyl chloride groups in two blended monomers -The presence of -PO(OCH ₃) ₂ group in compound I -The thickness between 100 and 300 nm -The strong hydrophilic structure with contact angle of 38°,	-The salt rejection was still above 99% under a high-water flux -Significant improvement of water flux by increasing monomer content to about 90 L.m ⁻² .h ⁻¹ , while maintaining high salt rejection above 96%, strong stability after 30 days stability test -High antifouling properties	[213]

membranes compared to the conventional TFC membranes. As it is clear in Table 5, the alternative monomers introduce more hydrophilic groups such as NH₂ or OH in aqueous phase or acyl chloride groups in organic phase compared to conventional TFC membranes. For instance, triptycene-2,3,6,7,14,15-hexaacyl chloride (THC) organic monomer introduced 6 acyl chloride groups which can significantly help the polymerization process in IP technique. 5-(dichlorophosphoryl)isophthaloyl dichloride (5-DCPO-IPDC) organic monomers also showed outstanding flux improvement from 23.63 to 86.49 L.m⁻².h⁻¹ in TFC membrane as a result of better structure with new monomer. Overall, the main point that should be considered in the selection of monomers in different pressure driven membranes is the capability of the monomer structure in increasing the hydrophilic groups on the active layer. Moreover, selective monomers should reinforce the polymerization process. In this regard, carboxyl groups, amine groups, and acyl chloride groups (in the case of organic monomers) should be considered. Further, the polymerization reaction mechanism based on the new monomers structure and their reaction with the aqueous and organic phases should be predicted and accounted for.

4. Concluding remarks and future prospects

In this review, the latest TFC RO and TFC NF membranes with different surface modifications (e.g., grafting, coating, incorporating, and applying new monomers instead of conventional MPD and TMC monomers in top layer for polymerization process) are critically analyzed. The goal of using new material on the top layer is to improve membrane surface properties in terms of hydrophilicity, roughness, surface charge and pore structure. The higher quantity of functional groups such as carboxylic acid, amine bonds, hydroxyl bonds, and acyl chloride has shown to improve the interfacial polymerization process and therefore create a more stable membrane with excellent performance. Many studies have been done introducing hydrophilic materials to the surface of membrane for the improvement of membrane hydrophilicity. However, these structures have never fulfilled the optimum requirement to have a defect free membrane with high performance. Many problems are still needed to be solved especially fouling issues resulting from concentration polarization. The use of new monomers was proven to be one of the most effective ways for fouling mitigation and increasing membranes efficiency. Different types of monomers

including diamine monomers, tannic acid, and monomers containing acyl chloride functions have been applied in the interfacial polymerization process instead of conventional monomers (MPD, PIP and TMC). Some monomers create exceeding amounts of functional structures which can hinder the polymerization. Some monomers and modification materials increase membrane thickness, which decrease membrane water permeability. The O/N ratio of selected monomers is very important and should be considered as a key factor for monomer and material selection. Application of specific monomers or mixed monomers can make a balanced surface structure whilst contributing to a complete polymerization reaction, keeping the PA layer thin with high rejection and permeation rates. The data presented here can be a great tool for membrane scientists and industry to tailor the surface and chemical structure of the TFC membranes for higher performance and efficiency.

Despite many recent studies focusing on the development of TFC/TFN membranes with excellent perm-selectivity through surface layer modifications, limited studies have focused on tailoring the membranes properties to industry needs and commercial viability evaluation of their developed structures. That can greatly contribute to the industrial application of the developed membranes.

Previous studies have shown that the application of new monomers with various structures for the fabrication of TFC membranes can play a significant role on the membranes' performance including their fouling retention, permeability and salt rejection rates. However, there are limited studies using new monomers (instead of MPD and PIP in particular). Future studies should focus more on developing TFC membranes with new monomers to modify the polymeric structure and surface properties, and enhance their permselectivity and fouling resistance.

In recent years, mixing of monomers has also shown promise for developing high-efficiency TFC membranes. The presence of additional monomers in the polymerization process acts as a complementary system which helps create strong and hydrophilic TFC membranes. The use of these mixing monomers in future studies can form flawless membranes with high antifouling propensity. In addition, modified TFC membranes with new monomers can be used in other treatment processes such as wastewater treatment, seawater desalination, food processing (as FO membranes), and alike.

Declaration of Competing Interest

None.

Acknowledgments

The authors are grateful for the Kharazmi University for the support from Kharazmi membrane research core (Grant number: H/4/360).

References

- [1] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, *Science* 333 (2011) 712–717.
- [2] M.M. Mekonnen, A.Y. Hoekstra, Four billion people facing severe water scarcity, *Sci. Adv.* 2 (2016), e1500323.
- [3] M. Asadollahi, D. Bastani, S.A. Musavi, Enhancement of surface properties and performance of reverse osmosis membranes after surface modification: a review, *Desalination* 420 (2017) 330–383.
- [4] R.H. Haillemariam, Y.C. Woo, M.M. Damtie, B.C. Kim, K.-D. Park, J.-S. Choi, Reverse osmosis membrane fabrication and modification technologies and future trends: a review, *Adv. Colloid Interf. Sci.* 276 (2020) 102100.
- [5] A. Basile, A. Cassano, N.K. Rastogi, *Advances in Membrane Technologies for Water Treatment: Materials, Processes and Applications*, Elsevier, 2015.
- [6] H. Younas, Z.U.R. Afridi, Y. Zhou, Z. Cui, Progress and perspective of antifouling, pressure driven, flat-sheet nanocomposite, polymeric membranes in water treatment, *J. Membr. Sci. Res.* 6 (2020) 319–332.
- [7] L. Zhen, W. Yingying, L. Shiqing, Y. Bolun, Mass transfer modeling in pervaporation based on multi-fields synergy theory, *Chin. J. Chem. Eng.* 16 (2008) 79–83.
- [8] J.S. Eswari, S. Naik, A critical analysis on various technologies and functionalized materials for manufacturing dialysis membranes, *Mater. Sci. Energy Technol.* 3 (2020) 116–126.
- [9] X. Zhang, F. Zhang, M. Liu, Y. Wang, Z. Xu, N. Li, Quaternized poly (2, 6-dimethyl-1, 4-phenylene oxide)s with zwitterion groups as diffusion dialysis membranes for acid recovery, *Sep. Purif. Technol.* 250 (2020) 117267.
- [10] Z. Qian, H. Miedema, S. Sahin, L.C. de Smet, E.J. Sudhölter, Separation of alkali metal cations by a supported liquid membrane (SLM) operating under electro dialysis (ED) conditions, *Desalination* 495 (2020) 114631.
- [11] A. Bamasag, T. Alqahtani, S. Sinha, N. Ghaffour, P. Phelan, Solar-heated submerged vacuum membrane distillation system with agitation techniques for desalination, *Sep. Purif. Technol.* 256 (2020) 117855.
- [12] F.E. Ahmed, B.S. Lalia, R. Hashaikeh, N. Hilal, Alternative heating techniques in membrane distillation: a review, *Desalination* 496 (2020) 114713.
- [13] Q. Xin, K. An, Y. Zhang, M. Yun, S. Wang, L. Lin, H. Ye, X. Ding, H. Li, Y. Zhang, Metal organic frameworks decorated membrane contactor constructing SO₂-philic channels for efficient flue gas desulphurization, *J. Membr. Sci.* 620 (2021) 118908.
- [14] E. Hosseini, E.S. Miandoab, G.W. Stevens, C.A. Scholes, Absorption of CO₂ from flue gas under oscillating gas flow conditions in gas-solvent hollow fibre membrane contactors, *Sep. Purif. Technol.* 249 (2020) 117151.
- [15] S. Madaeni, R. Pourghorbani, V. Vatanpour, Investigation of parameters affecting the flux of microfiltration poly (vinylidene fluoride) membranes for particulate removal, *Adv. Polym. Technol.* 31 (2012) 29–40.
- [16] G. Chen, Y. Yang, D. Kang, Q. Qin, J. Jin, H. Shao, S. Qin, Enhanced performances of chlorinated polyvinyl chloride (CPVC) ultrafiltration membranes by styrene-maleic anhydride copolymer, *Sep. Purif. Technol.* 258 (2021) 118043.
- [17] B. Diez, A. Sotto, A. Martín, J. Arsuaga, R. Rosal, Poly(vinyl chloride)-hyperbranched polyamidoamine ultrafiltration membranes with antifouling and antibiofouling properties, *React. Funct. Polym.* 154 (2020) 104669.
- [18] H. Kouliavand, A. Shahbazi, V. Vatanpour, M. Rahmandoust, Development of carbon dot-modified polyethersulfone membranes for enhancement of nanofiltration, permeation and antifouling performance, *Sep. Purif. Technol.* 230 (2020) 115895.
- [19] V. Vatanpour, M. Esmaeili, M. Safarpour, A. Ghadimi, J. Adabi, Synergistic effect of carboxylated-MWCNTs on the performance of acrylic acid UV-grafted polyamide nanofiltration membranes, *React. Funct. Polym.* 134 (2019) 74–84.
- [20] M.R. Mahdavi, M. Delnavaz, V. Vatanpour, Fabrication and water desalination performance of piperazine–polyamide nanocomposite nanofiltration membranes embedded with raw and oxidized MWCNTs, *J. Taiwan Inst. Chem. Eng.* 75 (2017) 189–198.
- [21] H. Parschová, E. Mistová, Z. Matějka, L. Jelínek, N. Kabay, P. Kauppinen, Comparison of several polymeric sorbents for selective boron removal from reverse osmosis permeate, *React. Funct. Polym.* 67 (2007) 1622–1627.
- [22] H. Isawi, Development of thin-film composite membranes via radical grafting with methacrylic acid/ ZnO doped TiO₂ nanocomposites, *React. Funct. Polym.* 131 (2018) 400–413.
- [23] W. Wu, Y. Shi, G. Liu, X. Fan, Y. Yu, Recent development of graphene oxide based forward osmosis membrane for water treatment: a critical review, *Desalination* 491 (2020) 114452.
- [24] S. Daly, E. Casey, A.J. Semião, Osmotic backwashing of forward osmosis membranes to detach adhered bacteria and mitigate biofouling, *J. Membr. Sci.* 620 (2021) 118838.
- [25] Y. Hartanto, M. Zargar, X. Cui, B. Jin, S. Dai, Non-ionic copolymer microgels as high-performance draw materials for forward osmosis desalination, *J. Membr. Sci.* 572 (2019) 480–488.
- [26] C. Kaya, Y. Jarma, E. Guler, N. Kabay, M. Arda, M. Yükek, Seawater desalination by using nanofiltration (NF) and brackish water reverse osmosis (BWRO) membranes in sequential mode of operation, *J. Membr. Sci. Res.* 6 (2020) 40–46.
- [27] B.S. Lalia, V. Kochkodan, R. Hashaikeh, N. Hilal, A review on membrane fabrication: structure, properties and performance relationship, *Desalination* 326 (2013) 77–95.
- [28] W. Guo, H.-H. Ngo, J. Li, A mini-review on membrane fouling, *Bioresour. Technol.* 122 (2012) 27–34.
- [29] S.P. Nunes, Can fouling in membranes be ever defeated? *Curr. Opini. Chem. Eng.* 28 (2020) 90–95.
- [30] D. Ankoliya, B. Mehta, H. Raval, Advances in surface modification techniques of reverse osmosis membrane over the years, *Sep. Sci. Technol.* 54 (2019) 293–310.
- [31] F. Wang, J. Li, H. Zhu, H. Zhang, H. Tang, J. Chen, Y. Guo, Physical modification of polytetrafluoroethylene flat membrane by a simple heat setting process and membrane wetting remission in SGMD for desalination, *Desalination* 354 (2014) 143–152.
- [32] X. Shan, S.-L. Li, W. Fu, Y. Hu, G. Gong, Y. Hu, Preparation of high performance TFC RO membranes by surface grafting of small-molecule zwitterions, *J. Membr. Sci.* 608 (2020) 118209.
- [33] H.M. Park, J. Yoo, Y.T. Lee, Improved fouling resistance for RO membranes by a surface modification method, *J. Ind. Eng. Chem.* 76 (2019) 344–354.
- [34] M. Zargar, Y. Hartanto, B. Jin, S. Dai, Polyethylenimine modified silica nanoparticles enhance interfacial interactions and desalination performance of thin film nanocomposite membranes, *J. Membr. Sci.* 541 (2017) 19–28.
- [35] M. Zargar, Y. Hartanto, B. Jin, S. Dai, Understanding functionalized silica nanoparticles incorporation in thin film composite membranes: interactions and desalination performance, *J. Membr. Sci.* 521 (2017) 53–64.
- [36] J. Xue, J. Shen, R. Zhang, F. Wang, S. Liang, X. You, Q. Yu, Y. Hao, Y. Su, Z. Jiang, High-flux nanofiltration membranes prepared with β -cyclodextrin and graphene quantum dots, *J. Membr. Sci.* 612 (2020) 118465.

- [37] S.A. Kumar, N.M. Johanna, V.B. Jenefer, G. Srinivasan, G. Kanimozhi, G. Yuvarani, G. Ridhamsha, K. Prabu, S. Govindaradjane, S. Jayaraman, Influence of monomers involved in the fabrication of a novel PES based nanofiltration thin-film composite membrane and its performance in the treatment of common effluent (CETP) textile industrial wastewater, *J. Environ. Health Sci. Eng.* 19 (2021) 515–529.
- [38] N. Nasrollahi, L. Ghalamchi, V. Vatanpour, A. Khataee, Photocatalytic-membrane technology: a critical review for membrane fouling mitigation, *J. Ind. Eng. Chem.* 93 (2021) 101–116.
- [39] J. Rezaia, V. Vatanpour, A. Shockravi, M. Ehsani, Preparation of novel carboxylated thin-film composite polyamide-polyester nanofiltration membranes with enhanced antifouling property and water flux, *React. Funct. Polym.* 131 (2018) 123–133.
- [40] H. Rezaia, V. Vatanpour, Preparation and modification of thin film composite membrane using a bulky dianhydride monomer, *J. Appl. Polym. Sci.* 134 (2021) 51389.
- [41] M. Zargar, B. Jin, S. Dai, An integrated statistic and systematic approach to study correlation of synthesis condition and desalination performance of thin film composite membranes, *Desalination* 394 (2016) 138–147.
- [42] Z. Yang, Y. Zhou, Z. Feng, X. Rui, T. Zhang, Z. Zhang, A review on reverse osmosis and nanofiltration membranes for water purification, *Polymers* 11 (2019) 1252.
- [43] L. Francis, O. Ogunbiyi, J. Saththasivam, J. Lawler, Z. Liu, A comprehensive review of forward osmosis and niche applications, *Environ. Sci. Water Res. Technol.* 6 (2020) 1986–2015.
- [44] A.-H.M. El-Aassar, Study on polyamide thin film nano-composite membranes using different types of multi-walled carbon nanotubes at different pH feed solutions, *J. Am. Sci.* 12 (2016) 52–63.
- [45] S. Mitrouli, A. Karabelas, N. Isaias, A. Al Rammah, Application of hydrophilic macromolecules on thin film composite polyamide membranes for performance restoration, *Desalination* 278 (2011) 105–116.
- [46] K. Radha, K. Shobana, M. Tarun, D. Mohan, Studies on sulfonated styrene acrylonitrile and cellulose acetate blend ultrafiltration membranes, *Desal. Water Treat.* 52 (2014) 459–469.
- [47] H. Mahdavi, F. Razmi, T. Shahalazade, Polyurethane TFC nanofiltration membranes based on interfacial polymerization of poly (bis-MPA) and MDI on the polyethersulfone support, *Sep. Purif. Technol.* 162 (2016) 37–44.
- [48] M. Son, H.-g. Choi, L. Liu, E. Celik, H. Park, H. Choi, Efficacy of carbon nanotube positioning in the polyethersulfone support layer on the performance of thin-film composite membrane for desalination, *Chem. Eng. J.* 266 (2015) 376–384.
- [49] N. Misdan, W. Lau, A. Ismail, T. Matsuura, Formation of thin film composite nanofiltration membrane: effect of polysulfone substrate characteristics, *Desalination* 329 (2013) 9–18.
- [50] X. Liu, H.Y. Ng, Double-blade casting technique for optimizing substrate membrane in thin-film composite forward osmosis membrane fabrication, *J. Membr. Sci.* 469 (2014) 112–126.
- [51] J. Farahbakhsh, M. Delnavaz, V. Vatanpour, Simulation and characterization of novel reverse osmosis membrane prepared by blending polypyrrole coated multiwalled carbon nanotubes for brackish water desalination and antifouling properties using artificial neural networks, *J. Membr. Sci.* 581 (2019) 123–138.
- [52] R. Gopal, S. Kaur, Z. Ma, C. Chan, S. Ramakrishna, T. Matsuura, Electrospun nanofibrous filtration membrane, *J. Membr. Sci.* 281 (2006) 581–586.
- [53] M. Shibuya, M.J. Park, S. Lim, S. Phuntsho, H. Matsuyama, H.K. Shon, Novel CA/PVDF nanofiber supports strategically designed via coaxial electrospinning for high performance thin-film composite forward osmosis membranes for desalination, *Desalination* 445 (2018) 63–74.
- [54] J. Farahbakhsh, M. Delnavaz, V. Vatanpour, Investigation of raw and oxidized multiwalled carbon nanotubes in fabrication of reverse osmosis polyamide membranes for improvement in desalination and antifouling properties, *Desalination* 410 (2017) 1–9.
- [55] M.R. Mahdavi, M. Delnavaz, V. Vatanpour, J. Farahbakhsh, Effect of blending polypyrrole coated multiwalled carbon nanotube on desalination performance and antifouling property of thin film nanocomposite nanofiltration membranes, *Sep. Purif. Technol.* 184 (2017) 119–127.
- [56] B. Jaleh, E. Zare, S. Azizian, O. Qanati, M. Nasrollahzadeh, R.S. Varma, Preparation and characterization of polyvinylpyrrolidone/polysulfone ultrafiltration membrane modified by graphene oxide and titanium dioxide for enhancing hydrophilicity and antifouling properties, *J. Inorg. Organomet. Polym. Mater.* 30 (2020) 2213–2223.
- [57] M. He, T. Li, M. Hu, C. Chen, B. Liu, J. Crittenden, L.-Y. Chu, H.Y. Ng, Performance improvement for thin-film composite nanofiltration membranes prepared on PSf/PSf-g-PEG blended substrates, *Sep. Purif. Technol.* 230 (2020) 115855.
- [58] S. Loeb, S. Sourirajan, Saline water conversion-II, *Adv. Chem. Ser.* 38 (1963) 117.
- [59] J.E. Cadotte, M.J. Steuck, R.J. Petersen, Research on in situ-formed condensation polymer for reverse osmosis membranes, in: NTIS Report No. PB-288387, loc. cit. 1978 (Mar).
- [60] K. Khulbe, C. Feng, T. Matsuura, Pore size, pore size distribution, and roughness at the membrane surface, in: *Synthetic Polymeric Membranes*, Springer, Berlin, Heidelberg, 2008.
- [61] Z. Yang, W. Fang, Z. Wang, R. Zhang, Y. Zhu, J. Jin, Dual-skin layer nanofiltration membranes for highly selective $\text{Li}^+/\text{Mg}^{2+}$ separation, *J. Membr. Sci.* 620 (2021) 118862.
- [62] B. Van der Bruggen, A. Koninckx, C. Vandecasteele, Separation of monovalent and divalent ions from aqueous solution by electrodialysis and nanofiltration, *Water Res.* 38 (2004) 1347–1353.
- [63] P. Nativ, O. Lahav, Y. Gendel, Separation of divalent and monovalent ions using flow-electrode capacitive deionization with nanofiltration membranes, *Desalination* 425 (2018) 123–129.
- [64] R. Malaissamy, A. Talla-Nwafo, K.L. Jones, Polyelectrolyte modification of nanofiltration membrane for selective removal of monovalent anions, *Sep. Purif. Technol.* 77 (2011) 367–374.
- [65] A.Q. Al-Gamal, W.S. Falath, T.A. Saleh, Enhanced efficiency of polyamide membranes by incorporating TiO_2 -graphene oxide for water purification, *J. Mol. Liq.* 323 (2021) 114922.
- [66] M. Zargar, F. Hartanto, B. Jin, S. Dai, Hollow mesoporous silica nanoparticles: a peculiar structure for thin film nanocomposite membranes, *J. Membr. Sci.* 519 (2016) 1–10.
- [67] N.F.M. Khairuddin, A. Idris, L.W. Hock, Harvesting *Nannochloropsis* sp. using PES/MWCNT/LiBr membrane with good antifouling properties, *Sep. Purif. Technol.* 212 (2019) 1–11.
- [68] E.-S. Kim, B. Deng, Fabrication of polyamide thin-film nano-composite (PA-TFN) membrane with hydrophilized ordered mesoporous carbon (H-OMC) for water purifications, *J. Membr. Sci.* 375 (2011) 46–54.
- [69] Z. Wang, F. He, J. Guo, S. Peng, X.Q. Cheng, Y. Zhang, E. Drioli, A. Figoli, Y. Li, L. Shao, The stability of a graphene oxide (GO) nanofiltration (NF) membrane in an aqueous environment: progress and challenges, *Mater. Adv.* 1 (2020) 554–568.
- [70] L.-x. Dong, X.-c. Huang, Z. Wang, Z. Yang, X.-m. Wang, C.Y. Tang, A thin-film nanocomposite nanofiltration membrane prepared on a support with in situ embedded zeolite nanoparticles, *Sep. Purif. Technol.* 166 (2016) 230–239.
- [71] Z. Rao, K. Feng, B. Tang, P. Wu, Surface decoration of amino-functionalized metal-organic framework/graphene oxide composite onto polydopamine-coated membrane substrate for highly efficient heavy metal removal, *ACS Appl. Mater. Interfaces* 9 (2017) 2594–2605.
- [72] S. Wei, Y. Chen, X. Hu, C. Wang, X. Huang, D. Liu, Y. Zhang, Monovalent/divalent salts separation via thin film nanocomposite nanofiltration membrane containing aminated TiO_2 nanoparticles, *J. Taiwan Inst. Chem. Eng.* 112 (2020) 169–179.
- [73] Y. Liu, J. Liu, Y. Jiang, M. Meng, L. Ni, H. Qiu, R. Yang, Z. Liu, H. Liu, Synthesis of novel high flux thin-film nanocomposite nanofiltration membranes containing GO-SiO_2 via interfacial polymerization, *Ind. Eng. Chem. Res.* 58 (2019) 22324–22333.
- [74] A.F. Ismail, A.R. Hassan, Effect of additive contents on the performances and structural properties of asymmetric polyethersulfone (PES) nanofiltration membranes, *Sep. Purif. Technol.* 55 (2007) 98–109.
- [75] A.R. Hassan, S. Rozali, N.H.M. Safari, B.H. Besar, The roles of polyethersulfone and polyethylene glycol additive on nanofiltration of dyes and membrane morphologies, *Environ. Eng. Res.* 23 (2018) 316–322.
- [76] L. Li, S. Zhang, X. Zhang, G. Zheng, Polyamide thin film composite membranes prepared from isomeric biphenyl tetraacyl chloride and m-phenylenediamine, *J. Membr. Sci.* 315 (2008) 20–27.
- [77] M. Liu, D. Wu, S. Yu, C. Gao, Influence of the polyacyl chloride structure on the reverse osmosis performance, surface properties and chlorine stability of the thin-film composite polyamide membranes, *J. Membr. Sci.* 326 (2009) 205–214.
- [78] S. Yu, M. Liu, Z. Lü, Y. Zhou, C. Gao, Aromatic-cycloaliphatic polyamide thin-film composite membrane with improved chlorine resistance prepared from m-phenylenediamine-4-methyl and cyclohexane-1, 3, 5-tricarboxyl chloride, *J. Membr. Sci.* 344 (2009) 155–164.
- [79] Q.-F. An, W.-D. Sun, Q. Zhao, Y.-L. Ji, C.-J. Gao, Study on a novel nanofiltration membrane prepared by interfacial polymerization with zwitterionic amine monomers, *J. Membr. Sci.* 431 (2013) 171–179.
- [80] Y. Liu, S. Zhang, Z. Zhou, J. Ren, Z. Geng, J. Luan, G. Wang, Novel sulfonated thin-film composite nanofiltration membranes with improved water flux for treatment of dye solutions, *J. Membr. Sci.* 394 (2012) 218–229.
- [81] W. Xie, G.M. Geise, B.D. Freeman, H.-S. Lee, G. Byun, J.E. McGrath, Polyamide interfacial composite membranes prepared from m-phenylene diamine, trimesoyl chloride and a new disulfonated diamine, *J. Membr. Sci.* 403 (2012) 152–161.
- [82] I.V. Korolkov, Y.G. Gorin, A.B. Yeszhanov, A.L. Kozlovskiy, M.V. Zdorovets, Preparation of PET track-etched membranes for membrane distillation by photo-induced graft polymerization, *Mater. Chem. Phys.* 205 (2018) 55–63.
- [83] V. Vatanpour, N. Zoqi, Surface modification of commercial seawater reverse osmosis membranes by grafting of hydrophilic monomer blended with carboxylated multiwalled carbon nanotubes, *Appl. Surf. Sci.* 396 (2017) 1478–1489.
- [84] D. Emadzadeh, W.J. Lau, T. Matsuura, A.F. Ismail, M. Rahbari-Sisakht, Synthesis and characterization of thin film nanocomposite forward osmosis membrane with hydrophilic nanocomposite support to reduce internal concentration polarization, *J. Membr. Sci.* 449 (2014) 74–85.
- [85] A.S. Lashkenrai, M. Najafi, M. Peyravi, M. Jahanshahi, M.T.H. Mosavian, A. Amiri, M.H. Shahavi, Direct filtration procedure to attain antibacterial TFC membrane: a facile developing route of membrane surface properties and fouling resistance, *Chem. Eng. Res. Des.* 149 (2019) 158–168.
- [86] B.J.A. Tarboush, D. Rana, T. Matsuura, H. Arafat, R. Narbaitz, Preparation of thin-film-composite polyamide membranes for desalination using novel hydrophilic surface modifying macromolecules, *J. Membr. Sci.* 325 (2008) 166–175.
- [87] H.-R. Chae, J. Lee, C.-H. Lee, I.-C. Kim, P.-K. Park, Graphene oxide-embedded thin-film composite reverse osmosis membrane with high flux, anti-biofouling, and chlorine resistance, *J. Membr. Sci.* 483 (2015) 128–135.
- [88] P. Mukherjee, K.L. Jones, J.O. Abitoye, Surface modification of nanofiltration membranes by ion implantation, *J. Membr. Sci.* 254 (2005) 303–310.
- [89] X. Chen, G. Huang, C. An, R. Feng, Y. Yao, S. Zhao, C. Huang, Y. Wu, Plasma-induced poly (acrylic acid)- TiO_2 coated polyvinylidene fluoride membrane for

- produced water treatment: synchrotron X-ray, optimization, and insight studies, *J. Clean. Prod.* 227 (2019) 772–783.
- [90] P. Xu, J. Hong, Z. Xu, H. Xia, Q.-Q. Ni, Novel aminated graphene quantum dots (GQDs-NH₂)-engineered nanofiltration membrane with high Mg²⁺/Li⁺ separation efficiency, *Sep. Purif. Technol.* 258 (2021) 118042.
- [91] H. Yu, Y. He, G. Xiao, H. Li, X. Mei, Y. Cheng, F. Zhong, L. Zhou, J.Z. Ou, Intercalation of soft PPy polymeric nanoparticles in graphene oxide membrane for enhancing nanofiltration performances, *Sep. Purif. Technol.* 272 (2021) 118933.
- [92] C.K.S. Haresco, M.B.M.Y. Ang, B.T. Doma Jr., S.-H. Huang, K.-R. Lee, Performance enhancement of thin-film nanocomposite nanofiltration membranes via embedment of novel polydopamine-sulfobetaine methacrylate nanoparticles, *Sep. Purif. Technol.* 274 (2021) 119022.
- [93] S.M. Hosseini, F. Moradi, S.K. Farahani, S. Bandehali, F. Parviziyan, M. Ebrahimi, J. Shen, Carbon nanofibers/chitosan nanocomposite thin film for surface modification of poly (ether sulphone) nanofiltration membrane, *Mater. Chem. Phys.* 269 (2021) 124720.
- [94] Q. Bi, C. Zhang, J. Liu, X. Liu, S. Xu, Positively charged zwitterion-carbon nitride functionalized nanofiltration membranes with excellent separation performance of Mg²⁺/Li⁺ and good antifouling properties, *Sep. Purif. Technol.* 257 (2021) 117959.
- [95] N.H.Z. Abidin, S.N.A. Shafie, H. Suhaimi, N.S. Sambudi, N.A.H.S.M. Nordin, Incorporation of carboxyl and amino functionalized carbon quantum dots in thin film membrane for nanofiltration, *Polym. Test.* 100 (2021) 107270.
- [96] H.-Z. Zhang, Z.-L. Xu, Q. Shen, High-performance nanofiltration membrane intercalated by FeOOH nanorods for water nanofiltration, *Desalination* 498 (2021) 114802.
- [97] H. Abadikhah, E.N. Kalali, S. Behzadi, S.A. Khan, X. Xu, M.E. Shabestari, S. Agathopoulos, High flux thin film nanocomposite membrane incorporated with functionalized TiO₂/reduced graphene oxide nanohybrids for organic solvent nanofiltration, *Chem. Eng. Sci.* 204 (2019) 99–109.
- [98] S. Pourjafar, A. Rahimpour, M. Jahanshahi, Synthesis and characterization of PVA/PES thin film composite nanofiltration membrane modified with TiO₂ nanoparticles for better performance and surface properties, *J. Ind. Eng. Chem.* 18 (2012) 1398–1405.
- [99] C. Wei, R. Qiang, L. Lin, Y. Gao, S. Ma, X. Zhang, X. Huang, Combing three-dimensional water channels and ultra-thin skin layer enable high flux and stability of loose polyimide/SiO₂ nanofiltration membranes at low operating pressure via one step in-situ modification, *J. Membr. Sci.* 623 (2021) 118944.
- [100] S. Kamari, A. Shahbazi, High-performance nanofiltration membrane blended by Fe₃O₄@ SiO₂-CS bionanocomposite for efficient simultaneous rejection of salts/heavy metals ions/dyes with high permeability, retention increase and fouling decline, *Chem. Eng. J.* 417 (2021) 127930.
- [101] B. Borjigin, L. Yu, L. Xu, C. Zhao, J. Wang, Influence of incorporating beta zeolite nanoparticles on water permeability and ion selectivity of polyamide nanofiltration membranes, *J. Environ. Sci.* 98 (2020) 77–84.
- [102] S. Jiang, Y. Li, B.P. Ladewig, A review of reverse osmosis membrane fouling and control strategies, *Sci. Total Environ.* 595 (2017) 567–583.
- [103] S.M. Samaei, S. Gato-Trinidad, A. Altaee, Performance evaluation of reverse osmosis process in the post-treatment of mining wastewaters: case study of Costerfield mining operations, Victoria, Australia, *J. Water Proc. Eng.* 34 (2020) 101116.
- [104] D.M. Stevens, J.Y. Shu, M. Reichert, A. Roy, Next-generation nanoporous materials: progress and prospects for reverse osmosis and nanofiltration, *Ind. Eng. Chem. Res.* 56 (2017) 10526–10551.
- [105] J. Huang, J. Luo, X. Chen, S. Feng, Y. Wan, How do chemical cleaning agents act on polyamide nanofiltration membrane and fouling layer? *Ind. Eng. Chem. Res.* 59 (2020) 17653–17670.
- [106] E.M. Vrijenhoek, S. Hong, M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, *J. Membr. Sci.* 188 (2001) 115–128.
- [107] M. Safarpour, A. Khataee, V. Vatanpour, Thin film nanocomposite reverse osmosis membrane modified by reduced graphene oxide/TiO₂ with improved desalination performance, *J. Membr. Sci.* 489 (2015) 43–54.
- [108] S. Zinadini, A.A. Zinatizadeh, M. Rahimi, V. Vatanpour, H. Zangeneh, Preparation of a novel antifouling mixed matrix PES membrane by embedding graphene oxide nanoplates, *J. Membr. Sci.* 453 (2014) 292–301.
- [109] V. Vatanpour, A. Sanadgol, Surface modification of reverse osmosis membranes by grafting of polyamidoamine dendrimer containing graphene oxide nanosheets for desalination improvement, *Desalination* 491 (2020) 114442.
- [110] V. Vatanpour, S.S. Madaeni, R. Moradian, S. Zinadini, B. Astinchap, Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite, *J. Membr. Sci.* 375 (2011) 284–294.
- [111] V. Vatanpour, S.S. Madaeni, R. Moradian, S. Zinadini, B. Astinchap, Novel antibifouling nanofiltration polyethersulfone membrane fabricated from embedding TiO₂ coated multiwalled carbon nanotubes, *Sep. Purif. Technol.* 90 (2012) 69–82.
- [112] Z. Zhang, G. Kang, H. Yu, Y. Jin, Y. Cao, From reverse osmosis to nanofiltration: precise control of the pore size and charge of polyamide membranes via interfacial polymerization, *Desalination* 466 (2019) 16–23.
- [113] G. Gong, P. Wang, Z. Zhou, Y. Hu, New insights into the role of an interlayer for the fabrication of highly selective and permeable thin-film composite nanofiltration membrane, *ACS Appl. Mater. Interfaces* 11 (2019) 7349–7356.
- [114] Q. An, W.-S. Hung, S.-C. Lo, Y.-H. Li, M. De Guzman, C.-C. Hu, K.-R. Lee, Y.-C. Jean, J.-Y. Lai, Comparison between free volume characteristics of composite membranes fabricated through static and dynamic interfacial polymerization processes, *Macromolecules* 45 (2012) 3428–3435.
- [115] M.Y. Ashfaq, M.A. Al-Ghouthi, N. Zouari, Functionalization of reverse osmosis membrane with graphene oxide to reduce both membrane scaling and biofouling, *Carbon* 166 (2020) 374–387.
- [116] S. Gholami, J. López, A. Rezvani, V. Vatanpour, J.L. Cortina, Fabrication of thin-film nanocomposite nanofiltration membranes incorporated with aromatic amine-functionalized multiwalled carbon nanotubes. Rejection performance of inorganic pollutants from groundwater with improved acid and chlorine resistance, *Chem. Eng. J.* 384 (2020) 123348.
- [117] M. Armendáriz-Ontiveros, J.A. Sánchez, G.D. Isirdia, A. García, G.F. Weihs, Effect of seawater variability on endemic bacterial biofouling of a reverse osmosis membrane coated with iron nanoparticles (FeNPs), *Chem. Eng. Sci.* 223 (2020) 115753.
- [118] P. Hu, J. He, B. Tian, Z. Xu, T. Yuan, H. Sun, P. Li, Q.-J. Niu, Application of diazonium-induced anchoring process on ultrafiltration substrate for the fabrication of nanofiltration membrane with enhanced desalination performance, *Desalination* 496 (2020) 114340.
- [119] Z. Yi, F. Shao, L. Yu, N. Song, H. Dong, B. Pang, J. Yu, J. Feng, L. Dong, Chemical grafting N-GOQD of polyamide reverse osmosis membrane with improved chlorine resistance, water flux and NaCl rejection, *Desalination* 479 (2020) 114341.
- [120] Y. Mutharasi, Y. Zhang, M. Weber, C. Maletzko, T.-S. Chung, Novel reverse osmosis membranes incorporated with co-Al layered double hydroxide (LDH) with enhanced performance for brackish water desalination, *Desalination* 498 (2021) 114740.
- [121] S.S. Shahabi, N. Azizi, V. Vatanpour, Tuning thin-film composite reverse osmosis membranes using deep eutectic solvents and ionic liquids toward enhanced water permeation, *J. Membr. Sci.* 610 (2020) 118267.
- [122] S. Jeon, C.H. Park, S.S. Shin, J.-H. Lee, Fabrication and structural tailoring of reverse osmosis membranes using β-cyclodextrin-cored star polymers, *J. Membr. Sci.* 611 (2020) 118415.
- [123] Q. Hu, F. Zhou, H. Lu, N. Li, B. Peng, H. Yu, Y. Yuan, H. Zhang, Improved antifouling performance of a polyamide composite reverse osmosis membrane by surface grafting of dialdehyde carboxymethyl cellulose (DACMC), *J. Membr. Sci.* 620 (2021) 118843.
- [124] M.Y. Ashfaq, M.A. Al-Ghouthi, N. Zouari, Functionalization of reverse osmosis membrane with graphene oxide and polyacrylic acid to control biofouling and mineral scaling, *Sci. Total Environ.* 736 (2020) 139500.
- [125] B. Chen, D. Chen, X. Zhao, Radioactive wastewater treatment with modified aromatic polyamide reverse osmosis membranes via quaternary ammonium cation grafting, *Sep. Purif. Technol.* 252 (2020) 117378.
- [126] M. Ge, X. Wang, S. Wu, Y. Long, Y. Yang, J. Zhang, Highly antifouling and chlorine resistance polyamide reverse osmosis membranes with g-C₃N₄ nanosheets as nanofiller, *Sep. Purif. Technol.* 258 (2021) 117980.
- [127] Y.-F. Guan, C. Boo, X. Lu, X. Zhou, H.-Q. Yu, M. Elimelech, Surface functionalization of reverse osmosis membranes with sulfonic groups for simultaneous mitigation of silica scaling and organic fouling, *Water Res.* 185 (2020) 116203.
- [128] H. Jaramillo, C. Boo, S.M. Hashmi, M. Elimelech, Zwitterionic coating on thin-film composite membranes to delay gypsum scaling in reverse osmosis, *J. Membr. Sci.* 618 (2021) 118568.
- [129] K. Kalash, M. Kadhom, M. Al-Furaiji, Thin film nanocomposite membranes filled with MCM-41 and SBA-15 nanoparticles for brackish water desalination via reverse osmosis, *Environ. Technol. Innov.* 20 (2020) 101101.
- [130] X. Kang, X. Liu, J. Liu, Y. Wen, J. Qi, X. Li, Spin-assisted interfacial polymerization strategy for graphene oxide-polyamide composite nanofiltration membrane with high performance, *Appl. Surf. Sci.* 508 (2020) 145198.
- [131] L. Liu, X. Xie, S. Qi, R. Li, X. Zhang, X. Song, C. Gao, Thin film nanocomposite reverse osmosis membrane incorporated with UiO-66 nanoparticles for enhanced boron removal, *J. Membr. Sci.* 580 (2019) 101–109.
- [132] Y. Liu, J. Zhu, J. Zheng, X. Gao, M. Tian, X. Wang, Y.F. Xie, Y. Zhang, A. Volodin, B. Van der Bruggen, Porous organic polymer embedded thin-film nanocomposite membranes for enhanced nanofiltration performance, *J. Membr. Sci.* 602 (2020) 117982.
- [133] R. Rajakumaran, V. Boddu, M. Kumar, M.S. Shalaby, H. Abdallah, R. Chetty, Effect of ZnO morphology on GO-ZnO modified polyamide reverse osmosis membranes for desalination, *Desalination* 467 (2019) 245–256.
- [134] F. Saffarimandoab, B.Y. Gul, S. Erkoc-Iter, S. Guclu, S. Unal, B. Tunaboylu, Y. Z. Menciloglu, I. Koyuncu, Evaluation of biofouling behavior of zwitterionic silane coated reverse osmosis membranes fouled by marine bacteria, *Prog. Org. Coat.* 134 (2019) 303–311.
- [135] S.S. Shahabi, N. Azizi, V. Vatanpour, N. Yousefimehr, Novel functionalized graphitic carbon nitride incorporated thin film nanocomposite membranes for high-performance reverse osmosis desalination, *Sep. Purif. Technol.* 235 (2020) 116134.
- [136] F. Shao, L. Dong, H. Dong, Q. Zhang, M. Zhao, L. Yu, B. Pang, Y. Chen, Graphene oxide modified polyamide reverse osmosis membranes with enhanced chlorine resistance, *J. Membr. Sci.* 525 (2017) 9–17.
- [137] T. Shintani, K. Akamatsu, S. Hamada, K. Nakagawa, H. Matsuyama, T. Yoshioka, Preparation of monoamine-incorporated polyamide nanofiltration membranes by interfacial polymerization for efficient separation of divalent anions from divalent cations, *Sep. Purif. Technol.* 239 (2020) 116530.
- [138] R. Wang, Z.-X. Low, S. Liu, Y. Wang, S. Murthy, W. Shen, H. Wang, Thin-film composite polyamide membrane modified by embedding functionalized boron nitride nanosheets for reverse osmosis, *J. Membr. Sci.* 611 (2020) 118389.

- [139] Y. Wang, H. Zhang, C. Song, C. Gao, G. Zhu, Effect of aminophend/formaldehyde resin polymeric nanospheres as nanofiller on polyamide thin film nanocomposite membranes for reverse osmosis application, *J. Membr. Sci.* 614 (2020) 118496.
- [140] X. Wang, Q. Li, J. Zhang, H. Huang, S. Wu, Y. Yang, Novel thin-film reverse osmosis membrane with MXene Ti3C2Tx embedded in polyamide to enhance the water flux, anti-fouling and chlorine resistance for water desalination, *J. Membr. Sci.* 118036 (2020).
- [141] W. Yan, M. Shi, Z. Wang, Y. Zhou, L. Liu, S. Zhao, Y. Ji, J. Wang, C. Gao, Amino-modified hollow mesoporous silica nanospheres-incorporated reverse osmosis membrane with high performance, *J. Membr. Sci.* 581 (2019) 168–177.
- [142] W. Yan, L. Liu, C. Dong, S. Xie, X. Zhao, C. Gao, Surface modification of reverse osmosis membrane with tannic acid for improving chlorine resistance, *Desalination* 498 (2020) 114639.
- [143] Z. Yang, R. Takagi, X. Zhang, T. Yasui, L. Zhang, H. Matsuyama, Engineering a dual-functional sulfonated polyelectrolyte-silver nanoparticle complex on a polyamide reverse osmosis membrane for robust biofouling mitigation, *J. Membr. Sci.* 618 (2021) 118757.
- [144] C. Yu, H. Li, X. Zhang, Z. Lü, S. Yu, M. Liu, C. Gao, Polyamide thin-film composite membrane fabricated through interfacial polymerization coupled with surface amidation for improved reverse osmosis performance, *J. Membr. Sci.* 566 (2018) 87–95.
- [145] A. Ahmad, A. Abdulkarim, B. Ooi, S. Ismail, Recent development in additives modifications of polyethersulfone membrane for flux enhancement, *Chem. Eng. J.* 223 (2013) 246–267.
- [146] A.J. Atkinson, J. Wang, Z. Zhang, A. Gold, D. Jung, D. Zeng, A. Pollard, O. Coronell, Grafting of bioactive 2-aminoimidazole into active layer makes commercial RO/NF membranes anti-biofouling, *J. Membr. Sci.* 556 (2018) 85–97.
- [147] M. Liu, Q. Chen, L. Wang, S. Yu, C. Gao, Improving fouling resistance and chlorine stability of aromatic polyamide thin-film composite RO membrane by surface grafting of polyvinyl alcohol (PVA), *Desalination* 367 (2015) 11–20.
- [148] S. Gholami, A. Rezvani, V. Vatanpour, J.L. Cortina, Improving the chlorine resistance property of polyamide TFC RO membrane by polyethylene glycol diacrylate (PEGDA) coating, *Desalination* 443 (2018) 245–255.
- [149] L. Ni, J. Meng, X. Li, Y. Zhang, Surface coating on the polyamide TFC RO membrane for chlorine resistance and antifouling performance improvement, *J. Membr. Sci.* 451 (2014) 205–215.
- [150] A. Zhou, M. Almjibilee, J. Zheng, L. Wang, A thin film composite membrane prepared from monomers of vanillin and trimesoyl chloride for organic solvent nanofiltration, *Sep. Purif. Technol.* 263 (2021) 118394.
- [151] M. Safarpour, V. Vatanpour, A. Khataee, M. Esmaili, Development of a novel high flux and fouling-resistant thin film composite nanofiltration membrane by embedding reduced graphene oxide/TiO₂, *Sep. Purif. Technol.* 154 (2015) 96–107.
- [152] H. Karimipour, A. Shahbazi, V. Vatanpour, Fouling decline and retention increase of polyethersulfone membrane by incorporating melamine-based dendrimer amine functionalized graphene oxide nanosheets (GO/MDA), *J. Environ. Chem. Eng.* 9 (2021) 104849.
- [153] V. Vatanpour, H. Karimi, S.I. Ghazanlou, Y. Mansourpanah, M.R. Ganjali, A. Badiei, E. Pourbashir, M.R. Saeb, Anti-fouling polyethersulfone nanofiltration membranes aided by amine-functionalized boron nitride nanosheets with improved separation performance, *J. Environ. Chem. Eng.* 8 (2020) 104454.
- [154] S.S. Shahabi, N. Azizi, V. Vatanpour, Synthesis and characterization of novel g-C₃N₄ modified thin film nanocomposite reverse osmosis membranes to enhance desalination performance and fouling resistance, *Sep. Purif. Technol.* 215 (2019) 430–440.
- [155] Z. Zhang, G. Kang, H. Yu, Y. Jin, Y. Cao, Fabrication of a highly permeable composite nanofiltration membrane via interfacial polymerization by adding a novel acyl chloride monomer with an anhydride group, *J. Membr. Sci.* 570 (2019) 403–409.
- [156] M. Hirose, H. Ito, Y. Kamiyama, Effect of skin layer surface structures on the flux behaviour of RO membranes, *J. Membr. Sci.* 121 (1996) 209–215.
- [157] S.-Y. Kwak, Relationship of relaxation property to reverse osmosis permeability in aromatic polyamide thin-film-composite membranes, *Polymer* 40 (1999) 6361–6368.
- [158] I.J. Roh, J.-J. Kim, S.Y. Park, Mechanical properties and reverse osmosis performance of interfacially polymerized polyamide thin films, *J. Membr. Sci.* 197 (2002) 199–210.
- [159] Z. Yong, Y. Sanchuan, L. Meihong, G. Congjie, Polyamide thin film composite membrane prepared from m-phenylenediamine and m-phenylenediamine-5-sulfonic acid, *J. Membr. Sci.* 270 (2006) 162–168.
- [160] M. Wu, J. Yuan, H. Wu, Y. Su, H. Yang, X. You, R. Zhang, X. He, N.A. Khan, R. Kasher, Ultrathin nanofiltration membrane with polydopamine-covalent organic framework interlayer for enhanced permeability and structural stability, *J. Membr. Sci.* 576 (2019) 131–141.
- [161] S.-L. Li, X. Shan, Y. Zhao, Y. Hu, Fabrication of a novel nanofiltration membrane with enhanced performance via interfacial polymerization through the incorporation of a new zwitterionic diamine monomer, *ACS Appl. Mater. Interfaces* 11 (2019) 42846–42855.
- [162] K.P. Lee, G. Bargeman, R. de Rooij, A.J. Kemperman, N.E. Benes, Interfacial polymerization of cyanuric chloride and monomeric amines: pH resistant thin film composite polyamine nanofiltration membranes, *J. Membr. Sci.* 523 (2017) 487–496.
- [163] W.-S. Hung, J.-H. Liang, R.L.G. Lecaros, Q.-F. An, C.-C. Hu, K.-R. Lee, J.-Y. Lai, Effect of free volume and formation mechanisms of polyamide layers on nanofiltration membrane, *Sep. Purif. Technol.* 187 (2017) 443–452.
- [164] S.-M. Xue, C.-H. Ji, Z.-L. Xu, Y.-J. Tang, R.-H. Li, Chlorine resistant TFN nanofiltration membrane incorporated with octadecylamine-grafted GO and fluorine-containing monomer, *J. Membr. Sci.* 545 (2018) 185–195.
- [165] Y.-F. Mi, G. Xu, Y.-S. Guo, B. Wu, Q.-F. An, Development of antifouling nanofiltration membrane with zwitterionic functionalized monomer for efficient dye/salt selective separation, *J. Membr. Sci.* 601 (2020) 117795.
- [166] J. Zheng, Y. Yao, M. Li, L. Wang, X. Zhang, A non-MPD-type reverse osmosis membrane with enhanced permselectivity for brackish water desalination, *J. Membr. Sci.* 565 (2018) 104–111.
- [167] S.-L. Li, P. Wu, J. Wang, J. Wang, Y. Hu, Fabrication of high performance polyamide reverse osmosis membrane from monomer 4-morpholino-m-phenylenediamine and tailoring with zwitterions, *Desalination* 473 (2020) 114169.
- [168] J. Qin, S. Lin, S. Song, L. Zhang, H. Chen, 4-Dimethylaminopyridine promoted interfacial polymerization between hyperbranched polyesteramide and trimesoyl chloride for preparing ultralow-pressure reverse osmosis composite membrane, *ACS Appl. Mater. Interfaces* 5 (2013) 6649–6656.
- [169] A. Simpson, C. Kerr, C. Buckley, The effect of pH on the nanofiltration of the carbonate system in solution, *Desalination* 64 (1987) 305–319.
- [170] B. Van der Bruggen, Chemical modification of polyethersulfone nanofiltration membranes: a review, *J. Appl. Polym. Sci.* 114 (2009) 630–642.
- [171] A. Szymczyk, P. Fievet, Investigating transport properties of nanofiltration membranes by means of a steric, electric and dielectric exclusion model, *J. Membr. Sci.* 252 (2005) 77–88.
- [172] A.A. Shah, A. Park, Y. Yoo, S.-E. Nam, Y.-I. Park, Y.H. Cho, H. Park, Preparation of highly permeable nanofiltration membranes with interfacially polymerized biomonomers, *J. Membr. Sci.* 627 (2021) 119209.
- [173] C. Zhou, Y. Shi, C. Sun, S. Yu, M. Liu, C. Gao, Thin-film composite membranes formed by interfacial polymerization with natural material sericin and trimesoyl chloride for nanofiltration, *J. Membr. Sci.* 471 (2014) 381–391.
- [174] K.P. Lee, J. Zheng, G. Bargeman, A.J. Kemperman, N.E. Benes, pH stable thin film composite polyamine nanofiltration membranes by interfacial polymerisation, *J. Membr. Sci.* 478 (2015) 75–84.
- [175] M.M.A. Almjibilee, X. Wu, A. Zhou, X. Zheng, X. Cao, W. Li, Polyetheramide organic solvent nanofiltration membranes prepared via an interfacial assembly and polymerization procedure, *Sep. Purif. Technol.* 234 (2020) 116033.
- [176] J. Ding, H. Wu, P. Wu, Development of nanofiltration membranes using mussel-inspired sulfonated dopamine for interfacial polymerization, *J. Membr. Sci.* 598 (2020) 117658.
- [177] Y. Li, Y. Su, Y. Dong, X. Zhao, Z. Jiang, R. Zhang, J. Zhao, Separation performance of thin-film composite nanofiltration membrane through interfacial polymerization using different amine monomers, *Desalination* 333 (2014) 59–65.
- [178] W. Li, C. Bian, C. Fu, A. Zhou, C. Shi, J. Zhang, A poly (amide-co-ester) nanofiltration membrane using monomers of glucose and trimesoyl chloride, *J. Membr. Sci.* 504 (2016) 185–195.
- [179] T. Ma, Y. Su, Y. Li, R. Zhang, Y. Liu, M. He, Y. Li, N. Dong, H. Wu, Z. Jiang, Fabrication of electro-neutral nanofiltration membranes at neutral pH with antifouling surface via interfacial polymerization from a novel zwitterionic amine monomer, *J. Membr. Sci.* 503 (2016) 101–109.
- [180] J. Xue, Z. Jiao, R. Bi, R. Zhang, X. You, F. Wang, L. Zhou, Y. Su, Z. Jiang, Chlorine-resistant polyester thin film composite nanofiltration membranes prepared with β -cyclodextrin, *J. Membr. Sci.* 584 (2019) 282–289.
- [181] C. Yang, W. Xu, Y. Nan, Y. Wang, X. Chen, Novel negatively charged nanofiltration membrane based on 4, 4'-diaminodiphenylmethane for dye removal, *Sep. Purif. Technol.* 248 (2020) 117089.
- [182] A. Zhou, C. Shi, X. He, Y. Fu, A.W. Anjum, J. Zhang, W. Li, Polyarylester nanofiltration membrane prepared from monomers of vanillic alcohol and trimesoyl chloride, *Sep. Purif. Technol.* 193 (2018) 58–68.
- [183] M.B.M.Y. Ang, C.-L. Tang, M.R. De Guzman, H.L.C. Maganto, A.R. Caparanga, S.-H. Huang, H.-A. Tsai, C.-C. Hu, K.-R. Lee, J.-Y. Lai, Improved performance of thin-film nanofiltration membranes fabricated with the intervention of surfactants having different structures for water treatment, *Desalination* 481 (2020) 114352.
- [184] Y. Yao, M. Li, X. Cao, P. Zhang, W. Zhang, J. Zheng, X. Zhang, L. Wang, A novel sulfonated reverse osmosis membrane for seawater desalination: experimental and molecular dynamics studies, *J. Membr. Sci.* 550 (2018) 470–479.
- [185] A. Awad, I.H. Aljundi, Interfacial polymerization of facilitated transport polyamide membrane prepared from PIP and IPC for gas separation applications, *Korean J. Chem. Eng.* 35 (2018) 1700–1709.
- [186] L.-F. Liu, S.-C. Yu, Y. Zhou, C.-J. Gao, Study on a novel polyamide-urea reverse osmosis composite membrane (ICIC-MPD): I. Preparation and characterization of ICIC-MPD membrane, *J. Membr. Sci.* 281 (2006) 88–94.
- [187] X. Zhang, T.-H. Chen, F.-F. Chen, H. Wu, C.-Y. Yu, L.-F. Liu, C.-J. Gao, Structure adjustment for enhancing the water permeability and separation selectivity of the thin film composite nanofiltration membrane based on a dendritic hyperbranched polymer, *J. Membr. Sci.* 618 (2021) 118455.
- [188] Y. Zhao, Z. Zhang, L. Dai, S. Zhang, Preparation of a highly permeable nanofiltration membrane using a novel acyl chloride monomer with-PO(Cl)₂ group, *Desalination* 431 (2018) 56–65.
- [189] T. Wang, L. Dai, Q. Zhang, A. Li, S. Zhang, Effects of acyl chloride monomer functionality on the properties of polyamide reverse osmosis (RO) membrane, *J. Membr. Sci.* 440 (2013) 48–57.
- [190] P. Hu, Z. Xu, C. Jiang, B. Tian, X. Guo, M. Wang, Q.J. Niu, Dual-functional acyl chloride monomer for interfacial polymerization: toward enhanced water softening and antifouling performance, *Sep. Purif. Technol.* 237 (2020) 116362.
- [191] T.S. Jamil, E.S. Mansor, H. Abdallah, A. Shaban, Innovative high flux/low pressure blend thin film composite membranes for water softening, *React. Funct. Polym.* 131 (2018) 384–399.

- [192] S.K. Jewrajka, A. Reddy, H.H. Rana, S. Mandal, S. Khullar, S. Haldar, N. Joshi, P. K. Ghosh, Use of 2, 4, 6-pyridinetricarboxylic acid chloride as a novel co-monomer for the preparation of thin film composite polyamide membrane with improved bacterial resistance, *J. Membr. Sci.* 439 (2013) 87–95.
- [193] J. Sum, A. Ahmad, B. Ooi, Synthesis of thin film composite membrane using mixed dendritic poly(amidoamine) and void filling piperazine monomers, *J. Membr. Sci.* 466 (2014) 183–191.
- [194] Y.-J. Tang, Z.-L. Xu, S.-M. Xue, Y.-M. Wei, H. Yang, A chlorine-tolerant nanofiltration membrane prepared by the mixed diamine monomers of PIP and BHTTM, *J. Membr. Sci.* 498 (2016) 374–384.
- [195] Y.-J. Tang, L.-J. Wang, Z.-L. Xu, Y.-M. Wei, H. Yang, Novel high-flux thin film composite nanofiltration membranes fabricated by the NaClO pre-oxidation of the mixed diamine monomers of PIP and BHTTM in the aqueous phase solution, *J. Membr. Sci.* 502 (2016) 106–115.
- [196] B.-Q. Huang, Z.-L. Xu, H. Ding, M.-C. Miao, Y.-J. Tang, Antifouling sulfonated polyamide nanofiltration hollow fiber membrane prepared with mixed diamine monomers of BDSA and PIP, *RSC Adv.* 7 (2017) 56629–56637.
- [197] B. Li, S. Jiang, S. Yu, Y. Chen, X. Tang, X. Wu, Y. Zhong, X. Shen, S. Cui, Copolyimide aerogel using aromatic monomers and aliphatic monomers as mixing diamines, *J. Sol-Gel Sci. Technol.* 88 (2018) 386–394.
- [198] P.H. Duong, D.H. Anjum, K.-V. Peinemann, S.P. Nunes, Thin porphyrin composite membranes with enhanced organic solvent transport, *J. Membr. Sci.* 563 (2018) 684–693.
- [199] N.N. Gumbi, J. Li, B.B. Mamba, E.N. Nxumalo, Relating the performance of sulfonated thin-film composite nanofiltration membranes to structural properties of macrovoid-free polyethersulfone/sulfonated polysulfone/O-MWCNT supports, *Desalination* 474 (2020) 114176.
- [200] Y.-J. Tang, Z.-L. Xu, S.-M. Xue, Y.-M. Wei, H. Yang, Tailoring the polyester/polyamide backbone stiffness for the fabrication of high performance nanofiltration membrane, *J. Membr. Sci.* 541 (2017) 483–491.
- [201] R. Ma, Y.-L. Ji, X.-D. Weng, Q.-F. An, C.-J. Gao, High-flux and fouling-resistant reverse osmosis membrane prepared with incorporating zwitterionic amine monomers via interfacial polymerization, *Desalination* 381 (2016) 100–110.
- [202] L. Zhao, S. Liang, Y. Jin, Z. Wang, L. Hu, Y. Kang, J. Tao, W. Peng, Effect of trifunctional planar monomer on the structure and properties of polyamide membranes, *Appl. Surf. Sci.* 505 (2020) 144415.
- [203] S. Yuan, G. Zhang, J. Zheng, P. Jin, J. Zhu, J. Yang, S. Liu, P. Van Puyvelde, B. Van der Bruggen, Tuning intermolecular pores of resorcin[4]arene-based membranes for enhanced nanofiltration performance, *J. Membr. Sci.* 610 (2020) 118282.
- [204] M. He, H. Sun, H. Sun, X. Yang, P. Li, Q.J. Niu, Non-organic solvent prepared nanofiltration composite membrane from natural product tannic acid (TA) and cyclohexane-1, 4-diamine (CHD), *Sep. Purif. Technol.* 223 (2019) 250–259.
- [205] M. Kazemi, M. Jahanshahi, M. Peyravi, 1, 2, 4-Triaminobenzene-crosslinked polyamide thin-film membranes for improved flux/antifouling performance, *Mater. Chem. Phys.* 255 (2020) 123592.
- [206] Y.-I. Liu, Y.-y. Zhao, X.-m. Wang, X.-h. Wen, X. Huang, Y.F. Xie, Effect of varying piperazine concentration and post-modification on prepared nanofiltration membranes in selectively rejecting organic micropollutants and salts, *J. Membr. Sci.* 582 (2019) 274–283.
- [207] T. Ormanci-Acar, C.E. Tas, B. Keskin, E.B.S. Ozbulut, T. Turken, D. Imer, N. Tufekci, Y.Z. Menciloglu, S. Unal, I. Koyuncu, Thin-film composite nanofiltration membranes with high flux and dye rejection fabricated from disulfonated diamine monomer, *J. Membr. Sci.* 118172 (2020).
- [208] H. Peng, Q. Tang, S. Tang, J. Gong, Q. Zhao, Surface modified polyamide nanofiltration membranes with high permeability and stability, *J. Membr. Sci.* 592 (2019) 117386.
- [209] L. Ren, J. Chen, C. Wang, Q. Lu, J. Han, H. Wu, Triptycene based polyamide thin film composite membrane for high nanofiltration performance, *J. Taiwan Inst. Chem. Eng.* 101 (2019) 119–126.
- [210] H.J. Rezaia, V. Vatanpour, A. Shokkravi, M. Ehsani, Study of synergetic effect and comparison of novel sulfonated and carboxylated bulky diamine-diol and piperazine in preparation of negative charge NF membrane, *Sep. Purif. Technol.* 222 (2019) 284–296.
- [211] H. Wang, L. Li, X. Zhang, S. Zhang, Polyamide thin-film composite membranes prepared from a novel triamine 3, 5-diamino-N-(4-aminophenyl)-benzamide monomer and m-phenylenediamine, *J. Membr. Sci.* 353 (2010) 78–84.
- [212] B. Yuan, H. Sun, S. Zhao, H. Yang, P. Wang, P. Li, H. Sun, Q.J. Niu, Semi-aromatic polyamide nanofiltration membranes with tuned surface charge and pore size distribution designed for the efficient removal of Ca^{2+} and Mg^{2+} , *Sep. Purif. Technol.* 220 (2019) 162–175.
- [213] Y. Zhao, Z. Zhang, L. Dai, S. Zhang, Preparation of high water flux and antifouling RO membranes using a novel diacyl chloride monomer with a phosphonate group, *J. Membr. Sci.* 536 (2017) 98–107.