Chapter 4

Thin Film Nanocomposite of Nanofiltration Membrane for Water Softening and Desalination

Muhammad Hanis Tajuddin^{1,2}, Muhammad Faris Hamid^{1,2}, Norhaniza Yusof^{1,2*},
Ahmad Fauzi Ismail^{1,2*}

¹Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia,
81310 UTM Skudai, Johor Darul Ta'zim, Malaysia.

²School of Chemical and Energy Engineering (FCEE), Faculty of Engineering Universiti
Teknologi Malaysia, 81310 UTM Skudai, Johor Darul Ta'zim, Malaysia.

norhaniza@petroleum.utm.my & afauzi@utm.my

Abstract

This chapter discusses about nanofiltration (NF) membrane for water softening and desalination. The NF membrane system and thin film composite (TFC) membranes are discussed in general followed by their drawbacks. Next, recent trend of nanofillers in thin film nanocomposite (TFN) membrane is critically discussed and highlighted. The advantages and challenges of TFN membrane for water softening and desalination application are thoroughly analyzed. Lastly, the future directions of the TFN membrane for practical application are addressed.

Keywords

Thin Film Nanocomposite, Nanofiltration, Desalination, Water Softening, Membrane Fouling

Contents

Thin Film Nanocomposite of Nanofiltration Membrane for Water Softening and Desalination.....	69
1. Introduction.....	70
2. Desalination and water softening	71
3. Nanofiltration membranes and its drawbacks	75

3.1	A glance at nanofiltration process	75
3.2	Major drawbacks of NF membrane.....	76
4.	Thin film composite (TFC) membrane.....	77
4.1	Interfacial polymerization (IP)	78
4.2	Parameters of NF membrane fabrication.....	79
4.3	Other TFC membrane preparation techniques	81
4.4	Advantages and challenges of TFC membrane.....	81
5.	Recent trends of nanofillers TFN membrane	82
5.1	Metal and metal oxide nanoparticles	83
5.2	Carbon-based materials	86
5.3	Nanofibers materials.....	88
5.4	Metal organic framework	88
5.5	Layered double hydroxides nanofillers	91
6.	Challenges of incorporating nanomaterials	93
7.	Membrane fouling: A unique problem for water filtration	94
7.1	Common foulant types in membrane filtration	94
7.2	How to mitigate fouling of membrane	96
Conclusion.....		98
References		99

1. Introduction

Significant population growth has increased the demand of clean water which led to water shortage, specifically in water-stressed region. Different water sources such as brackish water [1], seawater [2] and ground water [3] have been explored to meet the demand of clean water. However, these types of water need to be treated in order to remove dissolved solute and hardness in the water before it is safely used for human consumption using desalination and water softening technologies, respectively. Briefly, desalination is a process of converting seawater into drinkable water by the removal of suspended and dissolved particles including water hardness from seawater using desalination technologies [4]. Desalination technologies include thermal processes such as multistage flash distillation (MSF), multi effect distillation (MED), vapor compression

(VC) and membrane processes such as sea water reverse osmosis (SWRO) and electrodialysis (ED) [5,6]. The two most popular desalination technologies are RO and MSF in which they account for 80% of world's desalination capacity [7].

Meanwhile, water softening is a process to remove water hardness. Water hardness in tap water is attributed by the presence of certain inorganic minerals such as calcium and magnesium and they are mainly accumulated within the water pipes [8]. The presence of these compounds renders the water flow that causes from clogging in piping system due to the mineral crystallization [9]. Besides that, the presence of hardness also reduces the compatibility of water with soap and detergent efficiency [3]. Therefore, it is necessary to remove hardness from water using either classical or new methods of water purification.

Conventional methods of water softening, such as lime softening and ion-exchange process have been widely employed for water softening process [10,11]. However, incomplete separation and high operational cost limit their application in water softening process. To overcome the limitations of conventional methods, attention is given to more promising methods, such as membrane technologies. Therefore, membrane technology has attracted great attention in the past recent years and grown steadily with vast applications, such as gas separation, desalination and wastewater treatment.

2. Desalination and water softening

Desalination is a process of removal salinity from saltwater or seawater. Salinity refers to concentration of dissolved salt that normally present in their ionic state, in a given volume of water. Salinity of seawater usually is around 35 g/L [12]. Since seawater consists mostly of NaCl salt, and because of NaCl dissociates into monovalent sodium (Na^+) and chloride (Cl^-) ions, studies of desalination have been focusing on the removal of NaCl [13]. As monovalent ion, Na^+ and Cl^- have relatively smaller hydrated diameters, compared to the pore diameter of the membrane, therefore NaCl possesses intrinsically higher diffusivity. This will cause separation of NaCl by membrane processes with larger pore size (refer Fig. 1) to be ineffective. Therefore, the use of NF alone for desalination would be impractical. Normally, NF is used as pre-treatment step to be coupled with reverse osmosis (RO) membrane in SWRO desalination plant [14]. Unlike other pressurized membrane processes, RO alone can be used to desalinate salt water due to its tight pore size that is able to retain small ionic species such Na^+ and Cl^- .

However, the use of other membrane processes such as microfiltration (MF), ultrafiltration (UF) or NF in hybrid with reverse osmosis (RO) membrane in SWRO desalination plant could reduce the plant's operational cost in term of energy and chemical consumption [14]. Under normal circumstances, either one of those

aforementioned membrane processes is installed at the pre-treatment stage to enhance the quality of water entering the RO membrane system. Usually, MF and UF is used to remove coarse particles (Fig. 1), while NF is used to divalent salts and water hardness.

Water hardness then is referring to the presence of calcium (Ca^{2+}), magnesium (Mg^{2+}) and its companion anion, such as sulphate ions (SO_4^{2-}) in water stream [15,16]. Water softening is a recognized technology in separation of multivalent ion from various water streams. Water softening had been used in many industrial applications, such as production of drinking water, cooling water and purification of wastewater. Moreover, it has been extensively employed in softening of seawater, surface water (rivers, lakes and stream), groundwater and brackish water. Yet, in typical water hardness contain counter valent ion, such as SO_4^{2-} ions with concentration from 100 ppm in groundwater to 2500 ppm in seawater [16]. In brackish water conditions, the presence of hardness is 500 mg/L of CaCO_3 . Thus, according to Malaysia Standard Quality, maximum acceptable limits for hard water is 500 mg/L [9]. Water softening make up of approximately 20-30% of industrial and residential waste water treatment with a specific market share of 2.5 billion dollars in 2010 for residential area and 7.3 billion in 2010 for industrial application [17,18].

Conventionally, water hardness can be eliminated by lime softening and ion exchange process. Lime softening utilizes chemical precipitation method in which lime is added to precipitate magnesium ions and calcium ions. The advantage of lime softening process is available lime source, no pollution to the natural water and able to decrease organic matter silicate as well as iron [19]. However, the major drawbacks of this process are the production of sludge and excessive use of chemicals which led to higher operating cost [10]. Furthermore, this conventional method has limited capacity as the demand of hardness removal is increased.

The ion exchange process is widely employed for water softening. The softening process utilizes salt saturated, for example, sodium chloride resin beads regenerate the resin beads [17]. In this process, capturing of calcium and magnesium occurred and sodium ions are released until saturation is reached. The saturated materials are regenerated using a very high sodium chloride solution. Ion exchange process detriments in terms of huge consumption of the salt brine used for regeneration, meanwhile calcium ions exchanged by sodium ions increase the water salinity [20].

Capacitive deionization (CDI) is another promising technology for water softening due to low energy consumption and environmental friendliness [21,22]. Basically, in CDI configuration cell, the feed solution will flow through both pair of electrode (carbon porous) and during polarization process the negative ions will be attracted to negatively

surface of electrode. However, utilization of CDI technology always hindered by presence of dissolved salts in pore volume of carbon electrode resulting in energy inefficient. The available method for water softening is summarized as in Table 1.

Table 1. Summary of available method for water softening

Method	Advantage	Disadvantage	Ref.
Lime Softening	Extensive source of lime. No pollution to natural water	Huge in volume of sludge. Excessive use of chemicals	[17]
Ion exchange	Ease of operation. Can be used in small scale	High consumption of salt brine. Increase salinity	[20]
Capacitive deionization	Environmentally friendly. Low energy consumption	Dissolved salt present in pore volume of carbon electrode	[23]
Membrane technology	Simple in operation. No chemical addition	Membrane fouling and scaling	[24]

One of the notable breakthroughs of membrane process is solving the limitation possessed by current technologies for water softening. Membrane technology can serve as potential solution of water softening process. Pressure-driven membrane can be classified into MF, UF, NF and RO as illustrated in Fig. 1.

Among these membrane processes, water softening and desalination process often utilizes either NF or RO membrane. The key feature that distinguishes RO and NF TFC membranes is that NF allows monovalent salts to pass through, while retaining multivalent ions, such as magnesium and calcium. Thus, NF is often used as pre-treatment method in SWRO desalination plant to remove water hardness. On the other hand, RO is widely employed to separate monovalent salts, such as sodium chloride (NaCl). Compared to RO, NF is favorable in water softening process mainly due to its lower operating pressure, resulting in the reduction of operation costs of separation plant. It is expected that the global growth of NF membrane to reach about \$445 million with a significant increase of 157% in 2019 as compared to the year 2012, which is only \$172 million as reported by BCC research [26]

Figure 1. Classification of classical membrane filtration system [25].

Most of NF and RO membranes are generally TFC. TFC membranes consist of an ultrathin layer, which is formed by interfacial polymerization (IP) over microporous substrate. In general, IP is a reaction process between two monomers; polyfunctional amine dissolved in water solution and polyfunctional acid chloride dissolved in hydrocarbon solvent. The active layer or ultra-thin layer is generally made by polyamide (PA) from the cross-linked of semi-aromatic PA. The PA layer plays a vital role in the selective barrier in water and solute transport across the membranes thus its structure considerably influences the membrane separation performances [27]. Owing to its unique structure, the properties of ultra-thin layer and porous substrate can be independently tailored to enhance the membrane performance [28]. In spite of the excellent separation performance and stable structures, the PA TFC membranes are still associated with trade-off effect between water flux and salt rejection. Many attempts have been carried out to improve the performance of TFC membrane. For example, incorporating nanofillers, such as silver nanoparticles (Ag NPs) [29], graphene oxide (GO) [30], carbon nanotube (CNT) [31], silica [32], titanate nanotube (TNT) [33] and halloysite nanotube (HNT) [34], either within PA layer or porous substrate. Upon the addition of nanofillers, the thin film membrane is normally referred to as TFN membrane

3. Nanofiltration membranes and its drawbacks

3.1 A glance at nanofiltration process

Over the last 20 years, the NF study has shown sparks interest among the researchers in many different areas. Based on data obtained from the Scopus database, a total of 10192 papers have been published in NF membrane. As shown in Fig. 2, the main area covers by NF membrane were in chemical engineering (20%), chemistry (20%), environmental science (15%) and materials science (15%). During data collection, we noticed that the research area in NF membrane still gains interest and keeps growing steadily over the past few years. Therefore, some commercial NF membranes, such as NF270 (Dow Filtec), NF200 (Dow Filtec), N90 (Dow Filtec) and UTC20 (Toray) are available that could be used in the removal of divalent salts.

Figure 2. Different subject areas of NF applications according to Scopus database analysis (access on 22 June 2020).

Besides, there are many review articles published, focussing on NF membranes. Hilal *et al.* (2004) published an article that was extensively focused on NF membrane and their application in water treatment [35]. Mohammad and co-workers also widely discussed the recent progress of the NF membrane, [36]. Moreover, Van der Bruggen and co-workers addressed some drawbacks of NF application and methods to overcome them [37]. Review by Lau *et al.* (2014) also discussed the characterization method for NF membrane [38]. Furthermore, the recent trend of nanomaterials in NF, RO and forward osmosis (FO) were extensively review by [24,39–41]. Despite that, another recent review

has been published, focusing on chemistry and fabrication of polymeric NF membrane [42].

Most of the pressure-driven membrane separation processes (MF, UF and RO) are highly influenced by their size exclusions. However, the solute retention by most of the NF membrane is mainly controlled by membrane surface charges (Donnan effect) and size-exclusion. Based on the Donnan exclusion theory, negatively charged membranes have stronger repulsive attractions towards divalent anions (SO_4^{2-}), compared with monovalent ions (Cl^-). Moreover, SO_4^{2-} ions have larger hydrated radius, ion radius and lower diffusion coefficient encountered greater steric hindrance resistance. Due to this fact, the rejection of sulphate salts (Na_2SO_4 , MgSO_4) was higher compared with chlorides salts (MgCl_2 , NaCl). Furthermore, Mg^{2+} ions as a counter ion have greater effect on the negative electric field than Na^+ . Therefore, Donnan exclusion effect between MgSO_4 and the membrane surface is getting weaker thus subsequently loss the retention of MgSO_4 compared with Na_2SO_4 . According to Donnan exclusion mechanism, the rejection of the salts having the same anion primarily determined by diffusion coefficient of cations. For example, Na^+ has higher diffusivity compared with Mg^{2+} that caused the less rejection of NaCl than MgCl_2 .

3.2 Major drawbacks of NF membrane

As the growth of NF technology is rapidly increasing, it becomes more selective to remove divalent ions. It is more feasible than RO membrane in water softening and pre-treatment of water desalination process, ascribed by its intrinsic properties, such as lower operating pressure and higher water permeation. A common method to form NF membranes is through the IP of an acyl chloride monomer and an amine monomer [43]. This reaction forms the thin PA rejection layer that is often supported by a porous substrate. The loose PA layer network with small pores in TFC membrane allows higher water permeation and sustaining the higher divalent salts rejection [42,44]. However, one of the major drawbacks of TFC membrane is their performances are largely controlled by their water permeability, solutes selectivity and fouling resistances. Due to these circumstances, TFC membrane suffers from selectivity/permeability or trade-off effects in achieving the excellent performances of NF separation process. Many attempts have been made to create a TFC membrane with high water permeation without sacrificing the salts retention [45]. In past few years, various approaches have been employed to improve water flux and separation performance of TFC through the use of novel monomer [46] or incorporating inorganic nanofiller [24] either in PA layer or substrate layer. Thus, with the addition of nanofillers into the membrane, membrane properties can

be improved which could increase membrane hydrophilicity or additional pathways for water transportation across the membrane structures.

Furthermore, the PA layer in TFC membrane primarily controls (mainly focus) the membrane performance in terms of permeability, selectivity and fouling resistance instead of modifying the substrate layer, which mainly plays as supporting role to the overall membrane structure [47]. With the emerging nanomaterials, layered double hydroxide, (LDH) could serve as potential fillers to be incorporated into PA layer. However, incorporation of LDH into TFC membrane is still in infancy, and fundamental understanding of this material compatibility within polymeric TFC has remained opaque.

Another major issue faced by most of the membrane-based water separation processes is extensive membrane fouling. It is a phenomenon where membrane performance declines in a long run operation. Fouling is also a major contributor that limits membrane performance, causing a decline of flux, could degrade membrane and increasing the in energy consumption [36]. Besides that, as the source of water is not only containing the minerals salts in their feeds, but also has other companion contaminant, such as protein, macromolecules and oils. Therefore, it is necessary to systematically evaluate the membrane performances with different types of foulants such as centrimonium bromide (CTAB) and bovine serum albumin (BSA).

4. Thin film composite (TFC) membrane

Generally, commercial TFC membrane consists of three layers mainly ultra-thin top layer, a porous substrate layer and non-woven layer as demonstrated in Fig. 3. It has been a major type of NF membrane since its first introduction in 1970s. The porous substrate layer usually serves as mechanical support for thin film, whereas the properties of ultra-thin layer is important for membrane performance [48]. There were several method reported in fabrication of TFC membranes, such as photo-initiated, plasma-initiated grafting, dip-coating and IP [48–50]. Among them, IP technique is widely employed in the fabrication of TFC membrane due to better improvement in selectivity and membrane fouling [36].

Figure 3. Cross-section of a typical TFC membrane [51]

4.1 Interfacial polymerization (IP)

The concept of IP was first introduced by Morgan in 1965 [52]. On top of that, TFC membrane was first fabricated by Cadotte and co-workers in the 1970s and widely used in various application, such as disinfection by-products, desalinate seawater or remove heavy metals [24,40]. IP has become a practical and favourable technique for fabrication of ultra-thin layer of composite membrane like NF and RO. To date, fabrications of TFC through IP process have drawn attention in past decade significantly due to better improvement in membrane characteristics, such as membrane fouling and selectivity.

Generally, the crosslinked PA layer is formed by reacting two monomers in IP, functional amine in aqueous phase and acyl chloride in organic phase on porous substrate as depicted in Fig. 4 [28,53]. The membrane substrate such as polysulfone (PSf) and polyether sulfone (PES) is fabricated by phase inversion. The membrane is first immersed in amine aqueous solution which later transferred into acid chloride in organic solution. Alternatively, nanoparticles (NPs) may be introduced either into the aqueous amine or into the organic phase. Finally, the polymerization reaction takes place between both monomers resulting in a formation of thin film.

Figure 4. Schematic diagram of IP process for TFN synthesis [24].

4.2 Parameters of NF membrane fabrication

In IP process, there were several factors that affect the formation of thin film layer on the substrate layer. Choices of monomers, type of solvents and post-treatment procedure are several parameters that influenced the formation of thin film layer. Various monomers are being used in the formation of TFC through IP, such as m-phenyldiamine (MPD), trimesoyl chloride (TMC), isophthaloyl chloride (IPC) and piperazine (PIP) as shown in Table 2. Conventionally, piperazine (PIP) and TMC established as the most favourable monomer pair in NF membrane fabrication [11,54].

Most of the fabricated NF and RO membranes are derived from cross-linked aromatic PA through IP between acyl chloride and aliphatic/aromatic diamine [28,55]. The selective thin layer or surface layer play an essential role in TFC membrane as it will determine the overall permeability, solute retention and efficiency of the membrane [36,56]. Therefore, the IP method is progressively studied to further improve their characteristics and separation performances.

The choice of solvent is another important factor in IP in which most of the organic solvents like n-hexane, cyclohexane or heptane being used. Besides that, IP reaction time is one of the main parameters in fabrication of TFC membrane. Misdan *et al.* (2015) proposed that the polymerization took place within 10-15 seconds in order to produce optimum membrane performances [57]. TFC membrane fabricated by IP is also subjected

to post-treatment process, especially by using temperature. The common curing temperature is ranging from 40-120°C [58]. This post-treatment process purposely performed to stabilize thin layer by removing the residual organic solvent and crosslinking through dehydration of amine and carboxylic acids. However, too high of curing temperatures would damage the porosity of PA layer which leads to a decrease in water flux [59].

Table 2. Commonly used monomers for PA formation [46].

Monomer	Chemical structure	Molecular weight (g/mol)
Amine		
i) m-phenylenediamine (MPD)	<p><i>m</i>-phenylenediamine (MPD)</p>	108.10
ii) piperazine (PIP)	<p>piperazine (PIP)</p>	86.14
Acid chloride		
i) trimesoyl chloride (TMC)	<p>trimesoyl chloride (TMC)</p>	265.48
ii) isophthaloyl chloride (IPC)	<p>isophthaloyl chloride (IPC)</p>	203.02

4.3 Other TFC membrane preparation techniques

Thin film layers could be fabricated with different techniques, such as plasma polymerization, UV grafting and spin coating. In plasma polymerization method, nitrogen-containing plasma is applied to the membrane surface to generate nitrogen functional groups that may improve hydrophilicity. In 2012, Wang and co-workers employed modification by grafting plasma 2-acrylamido-2-methylpropanesulfonic acid (AMPS) on PSf hollow fibre UF membrane with plasma method [60]. Besides that, UV grafting technique also performed by chemical bonding between active layer and substrate. Deng *et al.* (2011) used UV-grafting with methacryloethyl trimethyl ammonium chloride (DMC) on top of PSf substrate [61]. In spin coating method by Li and Barbari, the coating material is applied at the centre of substrate which rotates at high speed [62]. The centrifugal forces spread throughout the coating material on a substrate which led to the formation of thin film.

4.4 Advantages and challenges of TFC membrane

Fabrication of TFC membrane by IP has provided a significant advantage owing to its unique structures, such as ultra-thin selective layer and porous substrate of TFC membrane. By employing this method, both layers (PA thin layer and substrate layer) can be independently optimized and controlled to achieve desired selectively while retaining excellent mechanical strength and compression resistance. This intrinsic property allows the fabricated TFC membrane to achieve high water flux and salt rejection. The PA thin layer plays an essential role in TFC membrane as it will determine the overall permeability, solute retention and efficiency of the membrane [36,56]. Several researchers have addressed that the ultra-thin skin layer of TFC membrane is determinant in separation performance to achieve high salt rejection and improved water permeability [28,53,63].

Despite having a superior property, TFC membrane suffered from structural deterioration due to exposure of chlorine and membrane fouling. Membrane fouling is one of major hindrance in TFC membrane. It increases the operational cost and decreases membrane lifespan [64]. Therefore, chemical cleaning is necessary to remove organic fouling or biofouling on membrane surface. Chlorination is another step where it is used for disinfecting the water. When TFC exposed to chloride ion derived from water disinfectant, it will attack the amide nitrogen and ring bonded to amide nitrogen cause structural changes in PA network [65]. This process also causes the membrane degradation and lower the salt rejection [66].

Many researchers attempt to modify TFC membrane by surface modification, impregnated inorganic nanofillers in ultrathin layer or porous substrate. Addition of inorganic nanofillers is believed to improve not only membrane hydrophilicity, but also reduce the fouling tendency as well as increase the salt rejection. According to Mohammad *et al.* (2015) [36], incorporated NPs have gained noteworthy attention due to their ability to increase membrane permeability, mechanical properties, hydrophilicity and selectivity.

5. Recent trends of nanofillers TFN membrane

Improvement of TFC membrane has been extensively studied in order to enhance their separation performances. In recent years, many efforts were made by researchers to improve TFC membrane, such as focusing on substrate properties, introduction of novel monomers [46] and impregnating NPs [67]. The most common NPs utilized in the fabrication of TFN membranes, are zeolites [68–70], TiO₂ [71], Ag, CNTs and silica [24]. Recently, many researchers have been focused on incorporating inorganic materials into membrane matrix. It is believed that incorporation of additives would play an important role in increasing the degree of polymerization and controlling the amine diffusion rate towards PA surface. Moreover, the inorganic nanofillers can be dispersed either in aqueous or in organic phase. NPs materials have the potential to improve membrane structure and possess the ability to control membrane fouling [72] and increase hydrophilicity [36].

Polymer nanocomposite membranes are new class membranes that contain both organic polymers and inorganic nanoscale materials which is believed to exhibit higher performance compared with standard membrane [41]. NPs have the potentiality to improve membrane structure and possess the ability to control membrane fouling [72] and increase hydrophilicity [36]. The TFN structure described in Fig. 5 is fabricated on a commercial membrane substrate. Commercial membranes are usually constructed on non-woven or fibrous which is below the porous support layer. The main purpose of this non-woven structure is to provide mechanical strength for composite membrane from deforming in operation. In the end, the efforts of embedding NPs are to enhance the performances of the membrane composite towards water softening and desalination.

Figure 5. Schematic representation of TFN structure [73].

5.1 Metal and metal oxide nanoparticles

Among the NPs that being studied, silver nanoparticles (Ag NPs) have drawn great attention owing to its antibacterial properties. A filler that has antibacterial properties can deactivate microorganisms during water filtration and reduce the bio-fouling problem as well as improve its hydrophilicity. Kim *et al.* (2012) developed TFC membrane by incorporating of Ag NPs into thin film layer and PSf substrate membrane containing CNTs [74]. The results proved that the addition of Ag NPs slightly increases the Na_2SO_4 from 94.7 to 95.6% and TFN membrane has shown an antibacterial effect. Another research reported by Ben-Sasson *et al.* (2014) where impregnated Ag NPs were used as biocides into TFC RO membrane for water purification process. Incorporating Ag NPs has demonstrated improvement of bio fouling resistance and virus removal [75].

In fabrication of TFC PA NF membrane, Ag NPs were dispersed in the organic phase [29]. TFC membrane shows improve in anti-biofouling properties with addition of Ag NPs. Moreover, immobilized Ag NPs on membrane surface also employed in order to improve TFC membrane performances. The study has shown that Ag NPs impregnated in TFN membrane exhibit increase in membrane hydrophilicity ($32.2 \pm 0.4^\circ$) and improved pure water flux ($88.7 \text{ L/m}^2\cdot\text{h}$) compared with TFC membrane ($56.7 \pm 2.2^\circ$) and $67.1 \text{ L/m}^2\cdot\text{h}$ [76].

However, the presence of Ag NPs only enhances membrane bio-fouling while ineffective for improving membrane permeability and does not have significant influence in salt rejection [74]. Moreover, the challenge possess by Ag NPs in bulk matrices is weak resistance during washing. Therefore, Ag NPs can be released as suspended NPs or silver ions in dissolved form [24]. With that, the effectiveness of Ag NPs as antimicrobial agent is diminished. Despite having great antibacterial activities, addition of Ag NPs is limited

relatively to high cost thus making it not feasible to be employed [75]. Furthermore, the study investigated by Yin *et al.* (2013) [76] shown that NaCl rejection slightly decreased from 95.1% (TFC membrane) to 93.6 % with the addition of immobilized Ag NPs.

Titanium dioxide (TiO_2) has received tremendous attention due to its excellent hydrophilicity and photocatalytic ability to decompose organic compounds and antibacterial effects. Lee *et al.* (2008) incorporated TiO_2 NPs into PA layer of TFC NF membrane. Results revealed that increasing the TiO_2 loading from 0–5 wt%, the membrane flux declined slightly, whereas MgSO_4 rejection increased. However, further increase of TiO_2 up to 10 wt% showed significant flux increase, but extremely poor salt rejection (<5%) [77]. Pourjafar *et al.* (2012) impregnated TiO_2 into polyvinyl amide on top of PES substrate. With addition of 0.5 wt% TiO_2 NPs, the NaCl rejection was increased from 28 to 41% compared with pristine TFC membrane [78]. Another attempt was made by Rajaeian *et al.* (2013), introducing the modified TiO_2 using an amino silane coupling agent aiming to minimize particle agglomeration of TiO_2 . The modified TiO_2 exhibited higher water flux compared with TFC control membrane where the pure water flux increases steadily from 11.2 to 27 $\text{L/m}^2\cdot\text{h}$ corresponding to be increasing in loading from 0.005 to 0.1 wt%. Moreover, NaCl rejection was slightly improved to 54% with small loading of modified TiO_2 [79]. Besides that, the presence of TiO_2 in membrane has improved hydrophilicity and mechanical strength of membrane [80]. However, despite excellent properties own by TiO_2 their application always hindered by particle agglomeration resulting in poor membrane performance [81].

Silica-based inorganic materials have attracted considerable interest of many membrane researchers especially in utilizing it as filler in membrane fabrication. Incorporating of small amount of silica content into PA layer can improve thermo stability of TFN membrane [82]. Moreover, silica based nanofillers possess superior properties, such as high mechanical strength, high hydrophilicity and special water transfer molecule compared with pristine TFC membrane [32]. Jadav and Singh (2009) synthesized two types of silica NPs, aiming to obtain a chemically stable PA membrane with improved performances. Introduction of silica NPs during IP process significantly improved the water flux of PA membrane from 10.2 to 40.8 $\text{L/m}^2\cdot\text{h}$ of 2000 ppm salt (NaCl) rejection under 250 psig [82].

Another reported research from Ghaemi (2017) utilized acrylate-alumoxane NPs, aiming to improve antifouling properties and selectivity of TFC membrane. Based on their reported experimental data, a significant improvement was observed in MgSO_4 and MgCl_2 rejection of 83% and 70% for TFNC₂ (TFN membrane prepared by 0.025 g of the NPs) compared TFC and 53% and 47% upon the addition of acrylate–alumoxane, respectively. However, TFNC₃ (TFN membrane prepared by 0.05 g of the NPs) exhibited

unsatisfactory rejection. The low rejection of TFNC₃ was attributed by unsuccessful coating of nanomaterials on PES substrate. Meanwhile, enhancement in Mg²⁺ ion rejection was contributed by reduction of pore size after formation of polypyrrole (PPy) thin layer on substrate layer. Moreover, the TFC membrane possesses positively surface charge resulting in Donnan repulsion as primary separation mechanism of particular ions. Furthermore, insignificant rejection between MgSO₄ and MgCl₂ implying Mg²⁺ ions mainly rejected ions instead of SO₄²⁻ ions due to positively charged surfaced membrane. Despite that, TFNC₂ exhibited superior results compared with other membrane due to formation of tighter and cross-linked structure with C=C bonds in acrylate-alumoxane NPs [83]. Although incorporation of acrylate alumoxane showed promising results for fabrication of TFC membrane with improved selectivity in water softening, more research still required for improvement in softening application.

Recently, mesoporous silica NPs (MSN) have significant interest because of its uniform, controllable porosity, high specific surface area, good surface hydrophilicity and low cost [40]. Another reported research by Wu *et al.* (2013) prepared modified mesoporous silica NPs (mMSN) as nanofiller into PA layer of TFN membrane. With increasing amount of mMSN NPs in PA, layer membrane has increased the water flux until it reaches to a maximum of 32.4 L/m².h. Moreover, the fabricated TFN membrane were able to keep a relatively high rejection of Na₂SO₄ (>80%) [84]. An attempt was made by Bao *et al.* (2013) by synthesizing monodispersed spherical mesoporous nanosilica incorporated in PA TFC RO membranes. Consequently, with addition of nanosilica, the water flux of resultant TFN RO membrane was increased from 19 to 53 L/h.m² compare with TFC RO while salt rejection was 96% [85]. Recently, Li *et al.* (2015) investigated the effects of silica nanospheres incorporated into poly(piperazine) amide layer aiming to improve TFC membrane separation performance. With addition silica nanospheres, the separation performances of fabricated TFN membrane was significantly increased to 95.94 ± 0.31% accompanied with permeate flux of 67.43 ± 0.85 L/m².h compared with TFC membrane 91.53 ± 0.21% accompanied with permeate flux of 62.53 ± 1.10 L/m².h [32].

Incorporating silica NPs into PA layer of TFC membrane has shown improvement in salt rejection ability and water flux as well as antifouling properties. However, despite having excellent performance, silica loading needs to be controlled because excessive amount might lead to decrease the degree of cross-linking of PA layer. This problem could arise defect in TFN membrane and affect membrane separation performance [40,86].

5.2 Carbon-based materials

Carbon-based nanomaterials, such as CNT and graphene derivative emerge as another option for modification of TFC membrane. According to Zhang *et al.* (2016), CNT has unique thermal, mechanical and electrical properties [87]. Moreover, CNT has been applying in vast application, such as gas separation membranes, membrane distillation (MD), FO and RO membrane [88]. Zarrabi *et al.* (2016) introduced amine functionalized multi-walled carbon nanotube (NH₂-MWCNT) into PA layer of TFC membrane during IP. The maximum rejection of Na₂SO₄ and NaCl salt was about 95.7% and 36.7%, respectively with the loading of 0.005wt% NH₂-MWCNT. Furthermore, improvement of the flux might come from functionalization of MWCNT with NH₂ as it increased the hydrophilicity of the membrane [89].

On the other hand, a novel thin layer of MWCNT was incorporated between skin layer of thin film and MF substrate to enhance permeation flux and salt rejection [90]. The results obtained show that modified thin film exhibited high permeation flux of 105 L/m²h with 95% of Na₂SO₄ rejection. This improved result was due to incorporation of interlayer of MWCNT which makes the substrate more porous and defect free skin layer. Recently, Zheng *et al.* (2017) introduced sulfonated MWCNT into thin film to improve its solubility in aqueous solution. The experimented results demonstrated an increase in water flux by 79.4 ± 5.7 L/m².h which is 1.6 times higher than pristine TFC. Moreover, the TFN membrane able to retain higher Na₂SO₄ rejection of 96.8% upon addition of sulfonated MWCNT up to 0.02 wt% [91].

Incorporation of CNT has demonstrated improve performance upon addition in PA layer or substrate layer. Despite having excellent performances, pristine CNT has limited reaction in solvents, surfaces or polymers [92]. This can inevitably hinder the IP process and reduce the performances of membrane.

Graphene oxide (GO) is carbon-based nanomaterials with intrinsic properties, such as high surface area, great mechanical properties and superior hydrophilicity. GO has progressed rapidly into water treatment process due to its abundant oxygen functional groups, such as epoxy, hydroxyl and carboxyl as depicted in Fig. 6 [87]. Reported works by Ali *et al.*, (2016) introduced GO nanosheets into PA layer membrane in an effort to improve TFC membrane. By adding GO nanosheets, the water flux increased 39% compared with pristine TFC, which had water flux of 21.4 L/m².h [93]. An attempt was made by incorporating reduced graphene oxide (rGO)/TiO₂ into thin film layer in order to enhance desalination performance, antifouling and chlorine resistance properties [81]. Lai *et al.*, (2016) incorporated GO nanosheet into PSf substrate to study the separation performance of the newly developed TFN made of PSf-GO substrate. From their

experimental results, we noticed that all fabricated TFN membranes exhibited high rejection of Na_2SO_4 (94%). Furthermore, TFN (0.3 wt% GO) showed that higher rejection of NaCl , MgCl_2 and MgSO_4 compared with TFC and other TFN membrane. This membrane achieved 59.5% of NaCl , 62.1% of MgCl_2 and 91.1% of MgSO_4 rejection in comparison to 31%, 67.1% and 80.4% obtained by using TFC membrane, respectively. Moreover, TFN (0.3 wt%) also exhibited highest permeability with PWP of 2.43 $\text{L/m}^2\text{h.bar}$ [94]. From the experimented results with variety of inorganic salts tested, it shows a great potential for TFN membrane in water softening application.

With the addition of hydrophilic additives, such as rGO/TiO_2 , the water flux of the membrane was increased from 48.3 (TFC) to 61.4 (rGO/TiO_2) $\text{L/m}^2\text{.h}$ [95]. Besides that, Mansourpanah *et al.* (2015) also introduced novel modifier GO with polyethylene glycol (PEG) into PA layer of TFC membrane. The resulting NF membrane exhibited high Na_2SO_4 salt rejection (93%) compared with unmodified TFC membrane (63%). Besides, the enhancement of salt rejection might be attributed to the presence of the modified PEG/GO nanosheet which has $-\text{COOH}$ and $-\text{OH}$ functional groups that reduced the membrane pore size [50].

Figure 6. Schematic image of GO structure [63].

In summary, GO has demonstrated better performance upon addition in PA layer or substrate layer. Improvement of water flux, higher salt rejection and improved surface hydrophilicity are among the significant contribution of GO. Despite having a superior property, higher dispersion of GO is difficult to reach which significantly affects its modulus, strength and surface wet ability. Furthermore, increase in cost of large

production of GO limits its usage in industry and the lower dispersion of GO remains as the main barrier to be overcome before its employment in another application [96].

5.3 Nanofibers materials

Nanofibers have gained a lot of attention and are widely applied in various applications, such as energy, gas separation membrane and water treatments [97]. In water treatment application, nanofibrous membranes have been either applied in NF process for removal of bivalent ions or desalination through RO and FO processes [98]. Electrospun nanofibers are produced by electrospinning method, which is a simple and versatile technique for membrane fabrication.

Another research reported by Yoon *et al.* (2009) studied polyacrylonitrile (PAN) nanofibers as support layer in comparison with PAN UF membrane in fabrication of TFC membrane. The experimental results revealed that the significant increase in permeate flux, which is 2.4 times higher than TFC membrane. The higher flux achieved might attribute to large open pore structure generated by electrospun nanofibers. Furthermore, the rejection ability of TFC was 99.4 % at 0.25% of PIP solution [99]. Besides that, Kaur *et al.* (2012) fabricated thin film nanofibrous composite (TFNC) membrane with PAN nanofibers support layer. Based on their research works, it reveals the optimum TFNC membrane with 8wt% of PAN which is able to separate MgSO_4 of 89% with the flux of $220 \text{ L/m}^2\cdot\text{h}$ [100].

5.4 Metal organic framework

Metal organic framework (MOF) is a porous crystalline material that has gained a significant interest in membrane separations research [101]. Fig. 7 shows the scanning electron microscopy (SEM) image of zeolitic imidazolate framework (ZIF-8) and particle distribution of ZIF-8 within the range of 120-200 nm. In 2015, for the first time, the porous metal organic framework (MOF) was impregnated into PA layer of TFN based RO membrane [40]. Previously, MOF was widely used in polymer to form mixed matrix membrane (MMM) for gas separation [102,103]. Zeolitic imidazolate framework-8 (ZIF-8) is thermally and chemically stable MOF while possessing similar structure as zeolite and same pore configuration. The experimental results demonstrated that ZIF-8 (0.4 w/v% in TMC hexane) has increased the water flux up to $50 \text{ L/m}^2\cdot\text{h}$, which is 162% higher than pristine TFC membrane. Meanwhile, the NaCl rejection was found to be 99% at 15.5 bar and 2000 ppm NaCl feed [104]. Despite all the excellent properties and performances of ZIF-8, extended research is required to study incorporation of MOFs into TFC membrane for desalination.

Figure 7. (a) SEM image of ZIF-8 and (b) particle distribution of ZIF-8 [104].

An overview of recent progress in inorganic fillers is demonstrated in Table 3. It can be seen that research effort has been extensively conducted by employing a wide variety of nanomaterials (e.g., silver, TiO₂, CNT, GO and MOF) for NF, RO and FO application in TFC membrane. As revealed in Table 3, it has been shown that the effects of nanofillers in TFC membrane separation, such as selectivity, antifouling properties, surface hydrophilicity and antibacterial properties are summarized. However, some materials, such as silver metal do not play role in separation performance, but it does improve antibacterial properties of fabricated membrane.

Table 3. Summary of TFN membrane with their nanofillers for improved membrane performances.

TFN		Membrane type	Performance	References
Thin layer	Nanofiller			
PA	Ag NPs	NF	No change in water flux and salt rejection Good antimicrobial activity at 10% of polymer in organic phase	[29]
PA	TiO ₂	NF	Optimum water flux was 9.1 L/m ² .h MgSO ₄ rejection was 95%	[77]

PA	Ag NPs	NF	Surface hydrophilicity increased Salt rejection slightly increased from 94.7 to 95.6% Increased in biofouling resistance	[74]
PA	Al ₂ O ₃ NPs	NF	Surface hydrophilicity increased Pure water flux increased No change in salt rejection	[105]
PA	Aminosilanized TiO ₂	NF	Pure water flux and selectivity increased NaCl rejection: 54% Optimal water flux was 12.3 L/m ² .h	[79]
PA	Modified mesoporous silica	NF	Optimal water flux was 32.4 L/m ² .h Na ₂ SO ₄ rejection was greater than 80%	[84]
PA	Ag NPs	RO	Improved bio-fouling resistance and virus removal	[75]
PA	rGO/TiO ₂	NF	Improved water flux from 48.3 to 61.4 L/m ² .h Increased in Na ₂ SO ₄ rejection (93.57%)	[95]
PA	Silica nanosphere	NF	Improved in membrane hydrophilicity Enhanced in water flux by 22.65 L/m ² .h Increased in MgSO ₄ rejection (94.81%) at 0.5 Mpa	[32]
PA	PEG/GO	NF	Enhanced in Na ₂ SO ₄ rejection (93%) Decreased in water flux from 35 to 15 L/m ² .h	[50]
PA	ZIF-8	RO	Increased in water flux about 50 L/m ² .h 98.5% of 2000 ppm NaCl rejection at 15.5 bar	[104]

PA	Mg-Al LDH	RO	Improved water flux from 36.6 to 41.7 L/m ² .h Increased in NaCl rejection:99.3% Enhanced in membrane hydrophilicity	[106]
PA	NH ₂ -MWCNT	NF	Increased in Na ₂ SO ₄ rejection (95.72%) Improved in antifouling ability	[89]
PA	Al(OH) ₃	NF	Increased in water flux: 55 L/m ² .h Improved MgSO ₄ rejection: 95.6%	[107]
PPy	Acrylate-alumoxane	NF	Improved in pure water flux from 9 to 32 L/m ² .h Improved salt rejection:80% Satisfying resistance against fouling	[83]
PA	Sulfonated-MWCNT	NF	Increased in water flux from 57 to 79.4 L/m ² .h Improved in Na ₂ SO ₄ rejection:96.8%	[91]

5.5 Layered double hydroxides nanofillers

Layered materials have been extensively gaining interest among researchers because of their ability to intercalate and exchange ions in layered structure. Examples of layered materials are LDH, layered perovskites, layered transition metal oxide and hydroxyl double salts [108]. From these examples, they are known to have a layered structure that consists of metal ions (either di-or trivalent) surrounded by hydroxyl ions. LDH particularly is a group of two dimensional anionic clays. The general formula of LDH structures is $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[(A^{n-})_{x/n}.yH_2O]$, where M(II) is divalent cation: Mg²⁺, Zn²⁺, Ca²⁺, Cu²⁺ etc., M(III) is trivalent cation: Al³⁺, Fe³⁺ and Cr³⁺, whereas Aⁿ⁻ is an interlayer anion. Anions, such as Cl⁻ and NO₃³⁻ are intercalated between the layers (see Fig. 8) and classified as one member of the clay minerals family [109]. Furthermore, LDH is hydrophilic in nature due to the presence of OH⁻ group at its surface and its positive charge is primarily attributed from the isomorphous substitution of clay layer [110].

Figure 8. Schematic diagram represented LDH structures [111].

LDH has been utilized in many applications, such as heavy metals removal, photostability and flame retardancy. With that, Mg-Al LDH is utilized for Pb removal from aqueous solution [112]. Mahjoubi and co-workers employed Zn-Al LDH as adsorbent for dye removal [113]. Furthermore, Co-Ni LDH has been utilized for energy storage devices [114]. The most common method used to synthesize LDH is co-precipitation method [115,116].

Even though LDH materials are not highly porous as zeolite or other MOF, their special structures lie in interlayer gallery which could provide pathway for water and solute transportation. These features were also supported by the hydroxyl functionality that can facilitate water molecules across the membrane. With these special features being mentioned the applicability of LDH in membrane technology could provide another new membrane design for highly permeation and water retention in their own separation process. Many LDH materials are not yet widely explored by researchers in water softening application, its implementation in different area for water treatments (adsorption of heavy metal and natural organic removals) has shown promising results

and can be used in this current research to investigate its effects into TFC based membranes towards water softening by NF process.

6. Challenges of incorporating nanomaterials

The progress of TFC membrane in water purification has been extensively studied in recent years. Despite the significant interest and potential demonstrated by nanomaterials in membrane technologies, there are some obstacles in employing them. Addressing these challenges may be the key for improvement in TFN membrane for various applications in future. One of the primary drawbacks encountered by TFN membrane fabrication is the agglomeration of nanomaterials in PA layer. Limited dispersion mainly occurs due to nanoparticles agglomeration and uneven distribution in polymer matrix. The field emission scanning electron microscopy (FE-SEM) images as shown in Fig. 9(b) reveals that particle agglomeration indicated by an arrow in PA ultra-thin layer, which probably reduces the active surface area of nanoparticles and contribute to formation of defects in PA structure. The agglomeration of nanoparticles might change nanocomposite membranes properties, such as pore size, hydrophilicity and antifouling properties. This phenomenon mainly attributed to low dispersion rate of nanofillers in either organic or aqueous solutions used during IP process. Aggregation of nanoparticles may lead to non-uniform dispersion particularly in non-polar organic solvent and contribute to inhomogeneous spread out on top of substrate layer surface [24].

Figure 9. Zeolite NPs incorporated TFN with different NPs concentration, (a) 500 mg/L and (b) 1000 mg/L [70].

The compatibility of nanomaterials with PA matrix is crucial to determine the optimal membrane performance and stability of nanofillers in polymer matrix. Moreover, lack of interaction between nanomaterials and PA matrix would probably cause nanomaterials to be leached out during IP. Furthermore, evaluation of the potential effect in nanomaterials leaching to the environment and its environmental toxicity needs to be assessed periodically.

7. Membrane fouling: A unique problem for water filtration

In membrane technology process, fouling is one of the main limitations that causes the declined in membrane performances. The performance of membrane separation is highly influenced by water permeability and rejection of salts. Membrane fouling can be defined as the deposition or accumulation of suspended or precipitation that occurred on the exterior of the membrane surface. Fouling can negatively impact the productivity and permeate quality in industrial application such as desalination process that can cause an increasing operating pressure. It leads to increase in energy consumption, frequent membrane cleaning and shortened membrane lifespan.

Similarly, in the context of desalination and water softening, membrane fouling is inevitable. Since seawater contains organic, inorganic and biological compound, desalination membrane would be at risk of all types of fouling as described in the next section. Meanwhile, membrane for water softening process is mainly susceptible to inorganic scaling as it only deals with inorganic divalent salt.

7.1 Common foulant types in membrane filtration

Membrane fouling can be categorised into four types which are organic fouling, inorganic scaling, biofouling and colloidal fouling as illustrated in Fig. 10. The common foulants in the water purification process including emulsified oil, natural organic matters, mineral scales, macromolecules and biofoulants [117].

Figure 10. Formation of organic fouling on membrane [118].

As shown in Fig. 11, membrane scaling is mostly occurred due to precipitation of inorganic salts on the membrane surface and/or caused by the concentration of these salts when they reach their solubility limits. The terms scaling is referred to deposition of certain inorganic salt like CaCO_3 , CaSO_4 , BaSO_4 , MgSO_4 etc. on the membrane surface. Moreover, high pressure membrane, which is from the concentration polarization, known as the main factor contributing to the increase in salt concentration thus leading to particle deposition [119]. Another type of fouling, organic fouling is a deposition substance in feed solution that adheres on top of the membrane surface. Natural organic matters (NOM), protein, oils, macromolecules and anti-foaming agents are some common foulants that cause the formation of organic layer on top of the membrane surface which mainly contributed from adsorption of substance. Besides that, an organic fouling is believed to be the key factor that causes the declination of water flux in membrane system specifically when involves the filtration of water containing highly natural organic matters [120].

Figure 11. Mechanism of inorganic scaling on membrane surface [121].

Membrane performances are affected by the colloidal fouling, which is caused by ubiquitous colloidal particles ranging from nanometres to few micrometres in wastewater effluent. One of the major contributors to the colloidal fouling is due to the deposition of particles, and the degree of fouling is highly influenced on the solution chemistry i.e. ionic strength, the presence of specific ions like bivalent ions or multivalent ions and pH [122]. Biofouling is another class of fouling that attributed to the growth of microbial cells with secreted biopolymers that adhere onto the membrane surface. Generally, the attached microorganisms can grow rapidly at the expenses of nutrients in feed solution thus forming biological film on top of membrane surface [123]. Consequently, the biofouling not only affected the membrane transport process, but also biodegrades the PA layer by hydrolysis. The occurrence of biofouling is closely related with the encapsulation of high molecular weight natural polymers, such as extracellular polymeric substances (EPS) [124].

7.2 How to mitigate fouling of membrane

The most obvious solution to this aforementioned problem is membrane cleaning using sodium hypochlorite solution. However, this cleaning process leads to degradation of polymer materials due to long terms exposure of harsh chemicals. One of the effective methods to mitigate fouling is by rendering the antifouling properties through the design

of membranes as illustrated in Fig. 12. As of now, several novel modifications have been established to improve and customize the membrane structure in order to enhance its antifouling properties. Generally, the modifications can be developed by reducing the surface roughness, altered the surface hydrophilicity, polymer grafting and introducing the surface functionalities as can be seen in Fig. 13.

Figure 12. Fouling resistant surface of a membrane [120].

Recently, the nanocomposite membrane has emerged as one of the advanced materials in improving the membrane fouling. Nanocomposite materials offered various advantages, such as low surface fouling, durability in harsh condition without affecting the salt rejection properties [125]. Incorporating nanofillers into thin film membrane can be designated as one of the effective methods in improving the fouling resistances in membrane process. Many nanomaterials have been widely applied in combating the fouling problems, such as carbon-based materials (CNT, graphene, GO, rGO etc.), silver NPs, copper NPs etc. Moreover, the surface modifications by polymer grafting, zwitterionic, polydopamine coating and layer by layer assembly techniques are also convenient due to their multifunctionality and simplicity.

Figure 13. Summary of surface modification for antifouling enhancement strategies in membrane process [126].

Conclusion

TFN membrane has gained a lot of attention in variety of areas or discipline and served as potential alternative in NF technology. The development and improvement of TFN membrane are an important research in not only for water softening, but also for desalination. Fabrication of TFN membrane can overcome the limitation of TFC membrane in terms of trade-off between permeability and selectivity. Practically, TFC is a good membrane to be used for desalination and treatment of water hardness due to its nanopores which results in excellent divalent salt rejection and good retention of monovalent ions. However, due to the trade-off effect, water flux is usually compromised and impacts in low water permeability.

Therefore, incorporation of nanofillers, such as silica or zeolite into PA layer is proven by exhibited enhanced water permeability. Besides that, impregnating nanofillers in PA layer has shown remarkable performance in antifouling and antibacterial properties compare with conventional TFC membrane. Moreover, with addition of nanomaterials in PA layer also improve membrane stability against chlorine resistance. It is worth to

highlight that improvement of membrane by using nanomaterials can greatly affected the membrane performance.

Finally, the practical application of TFN is still in early stage for water treatment. Most of fabrication method is still in laboratory scale and very few reports in large scale production. Thus, with continuous research it is possible to evaluate the effectiveness of TFN in large scale including materials supplies and long-term stability of membranes under practical application.

References

- [1] Y. Song, T. Li, J. Zhou, Z. Li, C. Gao, Analysis of nanofiltration membrane performance during softening process of simulated brackish groundwater, *Desalination*. 399 (2016) 159–164. <https://doi.org/0.1016/j.desal.2016.09.004>
- [2] N.A. Ahmad, P.S. Goh, K.C. Wong, A.K. Zulhairun, A.F. Ismail, Enhancing desalination performance of thin film composite membrane through layer by layer assembly of oppositely charged titania nanosheet, *Desalination*. 476 (2020) 114167. <https://doi.org/0.1016/j.desal.2019.114167>
- [3] A.R. Anim-Mensah, W.B. Krantz, R. Govind, Studies on polymeric nanofiltration-based water softening and the effect of anion properties on the softening process, *Eur. Polym. J.* 44 (2008) 2244–2252. <https://doi.org/0.1016/j.eurpolymj.2008.04.036>
- [4] Z.S. Tai, M.H.A. Aziz, M.H.D. Othman, A.F. Ismail, M.A. Rahman, J. Jaafar, Chapter 8 - An Overview of Membrane Distillation, in: A.F. Ismail, M.A. Rahman, M.H.D. Othman, T. Matsuura (Eds.), *Membr. Sep. Princ. Appl.*, Elsevier, 2019: pp. 251–281. <https://doi.org/10.1016/B978-0-12-812815-2.00008-9>
- [5] S. Al-Amshawee, M.Y.B.M. Yunus, A.A.M. Azoddein, D.G. Hassell, I.H. Dakhil, H.A. Hasan, Electrodialysis desalination for water and wastewater: A review, *Chem. Eng. J.* 380 (2020) 122231. <https://doi.org/10.1016/j.cej.2019.122231>
- [6] F.A. AlMarzooqi, A.A. [Al Ghaferi], I. Saadat, N. Hilal, Application of Capacitive Deionisation in water desalination: A review, *Desalination*. 342 (2014) 3–15. <https://doi.org/10.1016/j.desal.2014.02.031>
- [7] M.A. Eltawil, Z. Zhengming, L. Yuan, A review of renewable energy technologies integrated with desalination systems, *Renew. Sustain. Energy Rev.* 13 (2009) 2245–2262. <https://doi.org/0.1016/j.rser.2009.06.011>

- [8] T.N. Tuan, S. Chung, J.K. Lee, J. Lee, Improvement of water softening efficiency in capacitive deionization by ultra purification process of reduced graphene oxide, *Curr. Appl. Phys.* 15 (2015) 1397–1401. <https://doi.org/0.1016/j.cap.2015.08.001>
- [9] N.N.A. Kadir, M. Shahadat, S. Ismail, Formulation study for softening of hard water using surfactant modified bentonite adsorbent coating, *Appl. Clay Sci.* 137 (2017) 168–175. <https://doi.org/0.1016/j.clay.2016.12.025>
- [10] L. Setiawan, L. Shi, R. Wang, Dual layer composite nanofiltration hollow fiber membranes for low-pressure water softening, *Polym. (United Kingdom)*. 55 (2014) 1367–1374. <https://doi.org/0.1016/j.polymer.2013.12.032>
- [11] W. Fang, L. Shi, R. Wang, Mixed polyamide-based composite nanofiltration hollow fiber membranes with improved low-pressure water softening capability, *J. Memb. Sci.* 468 (2014) 52–61. <https://doi.org/0.1016/j.memsci.2014.05.047>
- [12] N. Ghaffour, J. Bundschuh, H. Mahmoudi, M.F.A. Goosen, Renewable energy-driven desalination technologies: A comprehensive review on challenges and potential applications of integrated systems, *Desalination*. 356 (2015) 94–114. <https://doi.org/10.1016/j.desal.2014.10.024>
- [13] Y.-N. Wang, R. Wang, Chapter 1 - Reverse Osmosis Membrane Separation Technology, in: A.F. Ismail, M.A. Rahman, M.H.D. Othman, T. Matsuura (Eds.), *Membr. Sep. Princ. Appl.*, Elsevier, 2019: pp. 1–45. <https://doi.org/10.1016/B978-0-12-812815-2.00001-6>
- [14] N. Ghaffour, T.M. Missimer, G.L. Amy, Technical review and evaluation of the economics of water desalination: Current and future challenges for better water supply sustainability, *Desalination*. 309 (2013) 197–207. <https://doi.org/0.1016/j.desal.2012.10.015>
- [15] A. Sharjeel, S. Anwar, A. Nasir, H. Rashid, Design, Development and Performance of Optimum Water Softener, *Earth Sci. Pakistan*. 3 (2019) 23–28. <https://doi.org/0.26480/esp.01.2019.23.28>
- [16] C. Liu, L. Shi, R. Wang, Crosslinked layer-by-layer polyelectrolyte nanofiltration hollow fiber membrane for low-pressure water softening with the presence of SO₄²⁻ in feed water, *J. Memb. Sci.* 486 (2015) 169–176. <https://doi.org/0.1016/j.memsci.2015.03.050>
- [17] M.A. Arugula, K.S. Brastad, S.D. Minter, Z. He, Enzyme catalyzed electricity-driven water softening system, *Enzyme Microb. Technol.* 51 (2012) 396–401. <https://doi.org/0.1016/j.enzmictec.2012.08.009>

- [18] K.S. Brastad, Z. He, Water softening using microbial desalination cell technology, *Desalination*. 309 (2013) 32–37. <https://doi.org/0.1016/j.desal.2012.09.015>
- [19] Y. Chen, R. Fan, D. An, Y. Cheng, H. Tan, Water softening by induced crystallization in fluidized bed, *J. Environ. Sci.* (2016) 2–9. <https://doi.org/0.1016/j.jes.2016.08.014>
- [20] B. Van der Bruggen, H. Goossens, P.A. Everard, K. Stengée, W. Rogge, Cost-benefit analysis of central softening for production of drinking water, *J. Environ. Manage.* 91 (2009) 541–549. <https://doi.org/0.1016/j.jenvman.2009.09.024>
- [21] S.J. Seo, H. Jeon, J.K. Lee, G.Y. Kim, D. Park, H. Nojima, J. Lee, S.H. Moon, Investigation on removal of hardness ions by capacitive deionization (CDI) for water softening applications, *Water Res.* 44 (2010) 2267–2275. <https://doi.org/0.1016/j.watres.2009.10.020>
- [22] T.-H. Yu, H.-Y. Shiu, M. Lee, P.-T. Chiueh, C.-H. Hou, Life cycle assessment of environmental impacts and energy demand for capacitive deionization technology, *Desalination*. 399 (2016) 53–60. <https://doi.org/0.1016/j.desal.2016.08.007>
- [23] Y.J. Kim, J.H. Choi, Improvement of desalination efficiency in capacitive deionization using a carbon electrode coated with an ion-exchange polymer, *Water Res.* 44 (2010) 990–996. <https://doi.org/0.1016/j.watres.2009.10.017>
- [24] J. Yin, B. Deng, Polymer-matrix nanocomposite membranes for water treatment, *J. Memb. Sci.* 479 (2015) 256–275. <https://doi.org/0.1016/j.memsci.2014.11.019>
- [25] P. Wu, M. Imai, Novel Biopolymer Composite Membrane Involved with Selective Mass Transfer and Excellent Water Permeability, in: *Adv. Desalin., InTech*, 2012. <https://doi.org/0.5772/50697>
- [26] S. Cumming, Global Nanofiltration Membranes Market to Reach \$445.1 Million in 2019; Water and Wastewater Claim 74.6% Market Share, *BCC Res.* (2014)
- [27] L. Lin, T.M. Weigand, M.W. Farthing, P. Jutaporn, C.T. Miller, O. Coronell, Relative importance of geometrical and intrinsic water transport properties of active layers in the water permeability of polyamide thin-film composite membranes, *J. Memb. Sci.* (2018) 1–36. <https://doi.org/0.1016/j.memsci.2018.08.002>
- [28] J. Xiang, Z. Xie, M. Hoang, K. Zhang, Effect of amine salt surfactants on the performance of thin film composite poly(piperazine-amide) nanofiltration membranes, *Desalination*. 315 (2013) 156–163. <https://doi.org/0.1016/j.desal.2012.10.038>
- [29] S.Y. Lee, H.J. Kim, R. Patel, S.J. Im, J.H. Kim, B.R. Min, Silver nanoparticles immobilized on thin film composite polyamide membrane : characterization ,

- nanofiltration , antifouling properties, *Polym. Adv. Technol.* 18 (2007) 562–568.
<https://doi.org/0.1002/pat>
- [30] M.J. Park, S. Phuntsho, T. He, G.M. Nisola, L.D. Tijing, X.M. Li, G. Chen, W.J. Chung, H.K. Shon, Graphene oxide incorporated polysulfone substrate for the fabrication of flat-sheet thin-film composite forward osmosis membranes, *J. Memb. Sci.* 493 (2015). <https://doi.org/0.1016/j.memsci.2015.06.053>
- [31] S. Morales-Torres, C.M.P. Esteves, J.L. Figueiredo, A.M.T. Silva, Thin-film composite forward osmosis membranes based on polysulfone supports blended with nanostructured carbon materials, *J. Memb. Sci.* 520 (2016) 326–336.
<https://doi.org/0.1016/j.memsci.2016.07.009>
- [32] Q. Li, Y. Wang, J. Song, Y. Guan, H. Yu, X. Pan, F. Wu, M. Zhang, Influence of silica nanospheres on the separation performance of thin film composite poly(piperazine-amide) nanofiltration membranes, *Appl. Surf. Sci.* 324 (2015) 757–764. <https://doi.org/0.1016/j.apsusc.2014.11.031>
- [33] D. Emadzadeh, M. Ghanbari, W.J. Lau, M. Rahbari-Sisakht, D. Rana, T. Matsuura, B. Kruczek, A.F. Ismail, Surface modification of thin film composite membrane by nanoporous titanate nanoparticles for improving combined organic and inorganic antifouling properties, *Mater. Sci. Eng. C.* 75 (2017) 463–470.
<https://doi.org/0.1016/j.msec.2017.02.079>
- [34] T. Ormanci-Acar, F. Celebi, B. Keskin, O. Mutlu-Salmanlı, M. Agtas, T. Turken, A. Tufani, D.Y. Imer, G.O. Ince, T.U. Demir, Y.Z. Menciloglu, S. Unal, I. Koyuncu, Fabrication and characterization of temperature and pH resistant thin film nanocomposite membranes embedded with halloysite nanotubes for dye rejection, *Desalination.* 429 (2018) 20–32. <https://doi.org/0.1016/j.desal.2017.12.005>
- [35] N. Hilal, H. Al-Zoubi, N.A. Darwish, A.W. Mohammad, M. Abu Arabi, A comprehensive review of nanofiltration membranes: Treatment, pretreatment, modelling, and atomic force microscopy, *Desalination.* 170 (2004) 281–308.
<https://doi.org/0.1016/j.desal.2004.01.007>
- [36] A.W. Mohammad, Y.H. Teow, W.L. Ang, Y.T. Chung, D.L. Oatley-Radcliffe, N. Hilal, Nanofiltration membranes review: Recent advances and future prospects, *Desalination.* 356 (2015) 226–254. <https://doi.org/0.1016/j.desal.2014.10.043>
- [37] B. Van der Bruggen, M. Mänttari, M. Nyström, Drawbacks of applying nanofiltration and how to avoid them: A review, *Sep. Purif. Technol.* 63 (2008) 251–263. <https://doi.org/0.1016/j.seppur.2008.05.010>

- [38] W.J. Lau, A.F. Ismail, P.S. Goh, N. Hilal, B.S. Ooi, Characterization Methods of Thin Film Composite Nanofiltration Membranes, *Sep. Purif. Rev.* 44 (2014) 135–156. <https://doi.org/0.1080/15422119.2014.882355>
- [39] W.J. Lau, S. Gray, T. Matsuura, D. Emadzadeh, J. Paul Chen, A.F. Ismail, A review on polyamide thin film nanocomposite (TFN) membranes: History, applications, challenges and approaches, *Water Res.* 80 (2015) 306–324. <https://doi.org/0.1016/j.watres.2015.04.037>
- [40] D. Li, Y. Yan, H. Wang, Recent advances in polymer and polymer composite membranes for reverse and forward osmosis processes, *Prog. Polym. Sci.* 61 (2015) 104–155. <https://doi.org/0.1016/j.progpolymsci.2016.03.003>
- [41] S. Al Aani, C.J. Wright, M.A. Atieh, N. Hilal, Engineering nanocomposite membranes: Addressing current challenges and future opportunities, *Desalination*. (2016). <https://doi.org/0.1016/j.desal.2016.08.001>
- [42] M. Paul, S.D. Jons, Chemistry and fabrication of polymeric nanofiltration membranes: A review, *Polymer (Guildf)*. 103 (2016) 417–456. <https://doi.org/0.1016/j.polymer.2016.07.085>
- [43] M.B.M.Y. Ang, Y.L. Ji, S.H. Huang, H.A. Tsai, W.S. Hung, C.C. Hu, K.R. Lee, J.Y. Lai, Incorporation of carboxylic monoamines into thin-film composite polyamide membranes to enhance nanofiltration performance, *J. Memb. Sci.* 539 (2017) 52–64. <https://doi.org/0.1016/j.memsci.2017.05.062>
- [44] W. Ye, J. Lin, R. Borrego, D. Chen, A. Sotto, P. Luis, M. Liu, S. Zhao, C.Y. Tang, B. Van der Bruggen, Advanced desalination of dye/NaCl mixures by a loose nanofiltration membrane for digital ink-jet printing, *Sep. Purif. Technol.* 197 (2018) 27–35. <https://doi.org/0.1016/j.seppur.2017.12.045>
- [45] J. Zhu, S. Yuan, A. Uliana, J. Hou, J. Li, X. Li, M. Tian, Y. Chen, A. Volodin, B. Van der Bruggen, High-flux thin film composite membranes for nanofiltration mediated by a rapid co-deposition of polydopamine/piperazine, *J. Memb. Sci.* 554 (2018) 97–108. <https://doi.org/0.1016/j.memsci.2018.03.004>
- [46] A.F. Ismail, M. Padaki, N. Hilal, T. Matsuura, W.J. Lau, Thin film composite membrane - Recent development and future potential, *Desalination*. 356 (2015) 140–148. <https://doi.org/0.1016/j.desal.2014.10.042>
- [47] Y. Ji, W. Qian, Y. Yu, Q. An, L. Liu, Y. Zhou, C. Gao, Recent developments in nanofiltration membranes based on nanomaterials, *Chinese J. Chem. Eng.* 25 (2017) 1639–1652. <https://doi.org/0.1016/j.cjche.2017.04.014>

- [48] N.K. Saha, S. V. Joshi, Performance evaluation of thin film composite polyamide nanofiltration membrane with variation in monomer type, *J. Memb. Sci.* 342 (2009) 60–69. <https://doi.org/0.1016/j.memsci.2009.06.025>
- [49] S. Yu, Q. Zhou, S. Shuai, G. Yao, M. Ma, C. Gao, Thin-film composite nanofiltration membranes with improved acid stability prepared from naphthalene-1,3,6-trisulfonylchloride (NTSC) and trimesoyl chloride (TMC), *Desalination*. 315 (2013) 164–172. <https://doi.org/0.1016/j.desal.2012.09.011>
- [50] Y. Mansourpanah, H. Shahebrahimi, E. Kolvari, PEG-modified GO nanosheets, a desired additive to increase the rejection and antifouling characteristics of polyamide thin layer membranes, *Chem. Eng. Res. Des.* 104 (2015) 530–540. <https://doi.org/0.1016/j.cherd.2015.09.002>
- [51] S.Y. Kwak, S.H. Kim, S.S. Kim, Hybrid organic/inorganic reverse osmosis (RO) membrane for bactericidal anti-fouling. 1. Preparation and characterization of TiO₂ nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane, *Environ. Sci. Technol.* 35 (2001) 2388–2394. <https://doi.org/0.1021/es0017099>
- [52] W.J. Lau, A.F. Ismail, N. Misdan, M.A. Kassim, A recent progress in thin film composite membrane: A review, *Desalination*. 287 (2012) 190–199. <https://doi.org/0.1016/j.desal.2011.04.004>
- [53] M. Liu, Y. Zheng, S. Shuai, Q. Zhou, S. Yu, C. Gao, Thin-film composite membrane formed by interfacial polymerization of polyvinylamine (PVAm) and trimesoyl chloride (TMC) for nanofiltration, *Desalination*. 288 (2012) 98–107. <https://doi.org/0.1016/j.desal.2011.12.018>
- [54] M. Dalwani, N.E. Benes, G. Bargeman, D. Stamatialis, M. Wessling, Effect of pH on the performance of polyamide/polyacrylonitrile based thin film composite membranes, *J. Memb. Sci.* 372 (2011) 228–238. <https://doi.org/0.1016/j.memsci.2011.02.012>
- [55] Y.-F. Mi, Q. Zhao, Y.-L. Ji, Q.-F. An, C.-J. Gao, A novel route for surface zwitterionic functionalization of polyamide nanofiltration membranes with improved performance, *J. Memb. Sci.* 490 (2015) 311–320. <https://doi.org/0.1016/j.memsci.2015.04.072>
- [56] L. Lin, R. Lopez, G.Z. Ramon, O. Coronell, Investigating the void structure of the polyamide active layers of thin-film composite membranes, *J. Memb. Sci.* 497 (2016) 365–376. <https://doi.org/0.1016/j.memsci.2015.09.020>

- [57] N. Misdan, W.J. Lau, C.S. Ong, A.F. Ismail, T. Matsuura, Study on the thin film composite poly(piperazine-amide) nanofiltration membranes made of different polymeric substrates: Effect of operating conditions, *Korean J. Chem. Eng.* 32 (2015) 753–760. <https://doi.org/0.1007/s11814-014-0261-6>
- [58] A.K. Ghosh, B.H. Jeong, X. Huang, E.M. V Hoek, Impacts of reaction and curing conditions on polyamide composite reverse osmosis membrane properties, *J. Memb. Sci.* 311 (2008) 34–45. <https://doi.org/0.1016/j.memsci.2007.11.038>
- [59] S. Hermans, R. Bernstein, A. Volodin, I.F.J. Vankelecom, Study of synthesis parameters and active layer morphology of interfacially polymerized polyamide-polysulfone membranes, *React. Funct. Polym.* 86 (2015) 199–208. <https://doi.org/0.1016/j.reactfunctpolym.2014.09.013>
- [60] X. lei Wang, J. fu Wei, Z. Dai, K. yin Zhao, H. Zhang, Preparation and characterization of negatively charged hollow fiber nanofiltration membrane by plasma-induced graft polymerization, *Desalination*. 286 (2012) 138–144. <https://doi.org/0.1016/j.desal.2011.11.014>
- [61] H. Deng, Y. Xu, Q. Chen, X. Wei, B. Zhu, High flux positively charged nanofiltration membranes prepared by UV-initiated graft polymerization of methacryloethyl trimethyl ammonium chloride (DMC) onto polysulfone membranes, *J. Memb. Sci.* 366 (2011) 363–372. doi:<https://doi.org/10.1016/j.memsci.2010.10.029>
- [62] R.H. Li, T.A. Barbari, Performance of poly(vinyl alcohol) thin-gel composite ultrafiltration membranes, *J. Memb. Sci.* 105 (1995) 71–78. [https://doi.org/0.1016/0376-7388\(95\)00048-H](https://doi.org/0.1016/0376-7388(95)00048-H)
- [63] 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. Memb. Sci.* 483 (2015) 128–135. <https://doi.org/0.1016/j.memsci.2015.02.045>
- [64] F. Yan, H. Chen, Y. Lü, Z. Lü, S. Yu, M. Liu, C. Gao, Improving the water permeability and antifouling property of thin-film composite polyamide nanofiltration membrane by modifying the active layer with triethanolamine, *J. Memb. Sci.* 513 (2016) 108–116. <https://doi.org/0.1016/j.memsci.2016.04.049>
- [65] J.H. Lee, J.Y. Chung, E.P. Chan, C.M. Stafford, Correlating chlorine-induced changes in mechanical properties to performance in polyamide-based thin film composite membranes, *J. Memb. Sci.* 433 (2013) 72–79. <https://doi.org/0.1016/j.memsci.2013.01.026>

- [66] D. Zhao, S. Yu, A review of recent advance in fouling mitigation of NF/RO membranes in water treatment: pretreatment, membrane modification, and chemical cleaning, *Desalin. Water Treat.* 55 (2014) 1–22.
<https://doi.org/0.1080/19443994.2014.928804>
- [67] S. Zhu, S. Zhao, Z. Wang, X. Tian, M. Shi, J. Wang, S. Wang, Improved performance of polyamide thin-film composite nanofiltration membrane by using polyetersulfone/polyaniline membrane as the substrate, *J. Memb. Sci.* 493 (2015) 263–274. <https://doi.org/0.1016/j.memsci.2015.07.013>
- [68] M. Fathizadeh, A. Aroujalian, A. Raisi, Effect of added NaX nano-zeolite into polyamide as a top thin layer of membrane on water flux and salt rejection in a reverse osmosis process, *J. Memb. Sci.* 375 (2011) 88–95.
<https://doi.org/0.1016/j.memsci.2011.03.017>
- [69] N. Ma, J. Wei, R. Liao, C.Y. Tang, Zeolite-polyamide thin film nanocomposite membranes: Towards enhanced performance for forward osmosis, *J. Memb. Sci.* 405–406 (2012) 149–157. <https://doi.org/0.1016/j.memsci.2012.03.002>
- [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.
<https://doi.org/0.1016/j.seppur.2016.04.043>
- [71] E. Bet-moushoul, Y. Mansourpanah, K. Farhadi, M. Tabatabaei, TiO₂ nanocomposite based polymeric membranes: a review on performance improvement for various applications in chemical engineering processes, *Chem. Eng. J.* 283 (2015) 29–46. <https://doi.org/0.1016/j.cej.2015.06.124>
- [72] A.L. Ahmad, A.A. Abdulkarim, B.S. Ooi, S. Ismail, Recent development in additives modifications of polyethersulfone membrane for flux enhancement, *Chem. Eng. J.* 223 (2013) 246–267. <https://doi.org/0.1016/j.cej.2013.02.130>
- [73] S. Hermans, H. Mariën, C. Van Goethem, I.F. Vankelecom, Recent developments in thin film (nano)composite membranes for solvent resistant nanofiltration, *Curr. Opin. Chem. Eng.* 8 (2015) 45–54. <https://doi.org/0.1016/j.coche.2015.01.009>
- [74] E.S. Kim, G. Hwang, M. Gamal El-Din, Y. Liu, Development of nanosilver and multi-walled carbon nanotubes thin-film nanocomposite membrane for enhanced water treatment, *J. Memb. Sci.* 394–395 (2012) 37–48.
<https://doi.org/0.1016/j.memsci.2011.11.041>

- [75] M. Ben-Sasson, X. Lu, E. Bar-Zeev, K.R. Zodrow, S. Nejati, G. Qi, E.P. Giannelis, M. Elimelech, In situ formation of silver nanoparticles on thin-film composite reverse osmosis membranes for biofouling mitigation, *Water Res.* 62 (2014) 260–270. <https://doi.org/0.1016/j.watres.2014.05.049>
- [76] J. Yin, Y. Yang, Z. Hu, B. Deng, Attachment of silver nanoparticles (AgNPs) onto thin-film composite (TFC) membranes through covalent bonding to reduce membrane biofouling, *J. Memb. Sci.* 441 (2013) 73–82. <https://doi.org/0.1016/j.memsci.2013.03.060>
- [77] H.S. Lee, S.J. Im, J.H. Kim, H.J. Kim, J.P. Kim, B.R. Min, Polyamide thin-film nanofiltration membranes containing TiO₂ nanoparticles, *Desalination.* 219 (2008) 48–56. <https://doi.org/0.1016/j.desal.2007.06.003>
- [78] 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. <https://doi.org/0.1016/j.jiec.2012.01.041>
- [79] B. Rajaeian, A. Rahimpour, M.O. Tade, S. Liu, Fabrication and characterization of polyamide thin film nanocomposite (TFN) nanofiltration membrane impregnated with TiO₂ nanoparticles, *Desalination.* 313 (2013) 176–188. <https://doi.org/0.1016/j.desal.2012.12.012>
- [80] L.Y. Ng, A.W. Mohammad, C.P. Leo, N. Hilal, Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review, *Desalination.* 308 (2013) 15–33. <https://doi.org/0.1016/j.desal.2010.11.033>
- [81] M. Safarpour, A. Khataee, V. Vatanpour, Thin film nanocomposite reverse osmosis membrane modified by reduced graphene oxide/TiO₂ with improved desalination performance, *J. Memb. Sci.* 489 (2015) 43–54. [doi:https://doi.org/10.1016/j.memsci.2015.04.010](https://doi.org/10.1016/j.memsci.2015.04.010)
- [82] G.L. Jadav, P.S. Singh, Synthesis of novel silica-polyamide nanocomposite membrane with enhanced properties, 328 (2009) 257–267. <https://doi.org/0.1016/j.memsci.2008.12.014>
- [83] N. Ghaemi, Novel antifouling nano-enhanced thin-film composite membrane containing cross-linkable acrylate-alumoxane nanoparticles for water softening, *J. Colloid Interface Sci.* 485 (2017) 81–90. <https://doi.org/0.1016/j.jcis.2016.09.035>

- [84] H. Wu, B. Tang, P. Wu, Optimizing polyamide thin film composite membrane covalently bonded with modified mesoporous silica nanoparticles, *J. Memb. Sci.* 428 (2013) 341–348. <https://doi.org/0.1016/j.memsci.2012.10.053>
- [85] M. Bao, G. Zhu, L. Wang, M. Wang, C. Gao, Preparation of monodispersed spherical mesoporous nanosilica-polyamide thin film composite reverse osmosis membranes via interfacial polymerization, *Desalination*. 309 (2013) 261–266. <https://doi.org/0.1016/j.desal.2012.10.028>
- [86] D. Hu, Z.-L. Xu, C. Chen, Polypiperazine-amide nanofiltration membrane containing silica nanoparticles prepared by interfacial polymerization, *Des.* 301 (2012) 75–81. <https://doi.org/0.1016/j.desal.2012.06.015>
- [87] Y. Zhang, B. Wu, H. Xu, H. Liu, M. Wang, Y. He, B. Pan, Nanomaterials-enabled water and wastewater treatment, *NanoImpact*. 3–4 (2016) 22–39. <https://doi.org/0.1016/j.impact.2016.09.004>
- [88] J.N. Shen, C.C. Yu, H.M. Ruan, C.J. Gao, B. Van der Bruggen, Preparation and characterization of thin-film nanocomposite membranes embedded with poly(methyl methacrylate) hydrophobic modified multiwalled carbon nanotubes by interfacial polymerization, *J. Memb. Sci.* 442 (2013) 18–26. <https://doi.org/0.1016/j.memsci.2013.04.018>
- [89] H. Zarrabi, M.E. Yekavalangi, V. Vatanpour, A. Shockravi, M. Safarpour, Improvement in desalination performance of thin film nanocomposite nanofiltration membrane using amine-functionalized multiwalled carbon nanotube, *Desalination*. 394 (2016) 83–90. <https://doi.org/0.1016/j.desal.2016.05.002>
- [90] M.B. Wu, Y. Lv, H.C. Yang, L.F. Liu, X. Zhang, Z.K. Xu, Thin film composite membranes combining carbon nanotube intermediate layer and microfiltration support for high nanofiltration performances, *J. Memb. Sci.* 515 (2016) 238–244. <https://doi.org/0.1016/j.memsci.2016.05.056>
- [91] J. Zheng, M. Li, K. Yu, J. Hu, X. Zhang, L. Wang, Sulfonated multiwall carbon nanotubes assisted thin-film nanocomposite membrane with enhanced water flux and anti-fouling property, *J. Memb. Sci.* 524 (2017) 344–353. <https://doi.org/0.1016/j.memsci.2016.11.032>
- [92] S. Roy, S.A. Ntim, S. Mitra, K.K. Sirkar, Facile fabrication of superior nanofiltration membranes from interfacially polymerized CNT-polymer composites, *J. Memb. Sci.* 375 (2011) 81–87. <https://doi.org/0.1016/j.memsci.2011.03.012>

- [93] M.E.A. Ali, L. Wang, X. Wang, X. Feng, Thin film composite membranes embedded with graphene oxide for water desalination, *Desalination*. 386 (2016) 67–76. <https://doi.org/0.1016/j.desal.2016.02.034>
- [94] G.S. Lai, W.J. Lau, P.S. Goh, A.F. Ismail, N. Yusof, Y.H. Tan, Graphene oxide incorporated thin film nanocomposite nanofiltration membrane for enhanced salt removal performance, *Desalination*. 387 (2016) 14–24. <https://doi.org/0.1016/j.desal.2016.03.007>
- [95] M. Safarpour, V. Vatanpour, A. Khataee, M. Esmaeili, 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. <https://doi.org/10.1016/j.seppur.2015.09.039>
- [96] A. Ammar, A.M. Al-Enizi, M.A. AlMaadeed, A. Karim, Influence of graphene oxide on mechanical, morphological, barrier, and electrical properties of polymer membranes, *Arab. J. Chem.* 9 (2016) 274–286. <https://doi.org/0.1016/j.arabjc.2015.07.006>
- [97] X. Wang, B.S. Hsiao, Electrospun nanofiber membranes, *Curr. Opin. Chem. Eng.* 12 (2016) 62–81. <https://doi.org/0.1016/j.coche.2016.03.001>
- [98] S. Subramanian, R. Seeram, New directions in nano filtration applications — Are nano fi bers the right materials as membranes in desalination ?, 308 (2013) 198–208. <https://doi.org/0.1016/j.desal.2012.08.014>
- [99] K. Yoon, B.S. Hsiao, B. Chu, High flux nanofiltration membranes based on interfacially polymerized polyamide barrier layer on polyacrylonitrile nanofibrous scaffolds, *J. Memb. Sci.* 326 (2009) 484–492. <https://doi.org/0.1016/j.memsci.2008.10.023>
- [100] S. Kaur, S. Sundarrajan, D. Rana, T. Matsuura, S. Ramakrishna, Influence of electrospun fiber size on the separation efficiency of thin film nanofiltration composite membrane, *J. Memb. Sci.* 392–393 (2012) 101–111. <https://doi.org/0.1016/j.memsci.2011.12.005>
- [101] Y. Li, L.H. Wee, J.A. Martens, I.F.J. Vankelecom, Interfacial synthesis of ZIF-8 membranes with improved nanofiltration performance, *J. Memb. Sci.* (2016). <https://doi.org/10.1016/j.memsci.2016.09.065>
- [102] S. Sorribas, P. Gorgojo, C. Téllez, J. Coronas, A.G. Livingston, High flux thin film nanocomposite membranes based on metal-organic frameworks for organic solvent

- nanofiltration, *J. Am. Chem. Soc.* 135 (2013) 15201–15208.
<https://doi.org/0.1021/ja407665w>
- [103] Y. Lin, Metal organic framework membranes for separation applications, *Curr. Opin. Chem. Eng.* 8 (2015) 21–28. <https://doi.org/0.1016/j.coche.2015.01.006>
- [104] J. Duan, Y. Pan, F. Pacheco, E. Litwiller, Z. Lai, I. Pinnau, High-performance polyamide thin-film-nanocomposite reverse osmosis membranes containing hydrophobic zeolitic imidazolate framework-8, *J. Memb. Sci.* 476 (2015) 303–310. <https://doi.org/0.1016/j.memsci.2014.11.038>
- [105] T.A. Saleh, V.K. Gupta, Synthesis and characterization of alumina nano-particles polyamide membrane with enhanced flux rejection performance, *Sep. Purif. Technol.* 89 (2012) 245–251. <https://doi.org/0.1016/j.seppur.2012.01.039>
- [106] H. Dong, L. Wu, L. Zhang, H. Chen, C. Gao, Clay nanosheets as charged filler materials for high-performance and fouling-resistant thin film nanocomposite membranes, *J. Memb. Sci.* 494 (2015) 92–103. <https://doi.org/0.1016/j.memsci.2015.07.049>
- [107] H. Li, W. Shi, Y. Zhang, Q. Du, X. Qin, Y. Su, Improved performance of poly(piperazine amide) composite nanofiltration membranes by adding aluminum hydroxide nanospheres, *Sep. Purif. Technol.* 166 (2016) 240–251. <https://doi.org/0.1016/j.seppur.2016.04.024>
- [108] S.B. Tyagi, A. Kharkwal, Nitu, M. Kharkwal, R. Sharma, Synthesis and Characterization of Layered Double Hydroxides Containing Optically Active Transition Metal Ion, *Solid State Sci.* 63 (2017) 93–102. <https://doi.org/0.1016/j.solidstatesciences.2016.11.012>
- [109] M.H. Tajuddin, N. Yusof, W. Norharyati, W. Salleh, Incorporation of layered double nanomaterials in thin film nanocomposite nanofiltration membrane for magnesium sulphate removal, *E3S Web Conf.* 02003 (2018) 0–7. <https://doi.org/10.1051/e3sconf/20183402003>
- [110] Z. Meng, Y. Zhang, Q. Zhang, X. Chen, L. Liu, Novel synthesis of layered double hydroxides (LDHs) from zinc hydroxide, *Appl. Surf. Sci.* 396 (2017) 799–803. <https://doi.org/0.1016/j.apsusc.2016.11.032>
- [111] M.A. Djebbi, M. Braiek, P. Namour, A. Ben Haj Amara, N. Jaffrezic-Renault, Layered double hydroxide materials coated carbon electrode: New challenge to future electrochemical power devices, *Appl. Surf. Sci.* 386 (2016) 352–363. <https://doi.org/0.1016/j.apsusc.2016.06.032>

- [112] D. Zhao, G. Sheng, J. Hu, C. Chen, X. Wang, The adsorption of Pb(II) on Mg₂Al layered double hydroxide, *Chem. Eng. J.* 171 (2011) 167–174.
<https://doi.org/0.1016/j.cej.2011.03.082>
- [113] F.Z. Mahjoubi, A. Khalidi, M. Abdenouni, N. Barka, Zn–Al layered double hydroxides intercalated with carbonate, nitrate, chloride and sulfate ions: Synthesis, characterization and dyes removal properties, *J. Taibah Univ. Sci.* 11 (2015) 90–100.
<https://doi.org/0.1016/j.jtusci.2015.10.007>
- [114] X. Meng, M. Feng, H. Zhang, Z. Ma, C. Zhang, Solvothermal synthesis of cobalt/nickel layered double hydroxides for energy storage devices, *J. Alloys Compd.* 695 (2016) 3522–3529. <https://doi.org/0.1016/j.jallcom.2016.11.419>
- [115] S.S.L. Sobhana, D.R. Bogati, M. Reza, J. Gustafsson, P. Fardim, Cellulose biotemplates for layered double hydroxides networks, *Microporous Mesoporous Mater.* 225 (2016) 66–73. <https://doi.org/0.1016/j.micromeso.2015.12.009>
- [116] F.L. Theiss, G.A. Ayoko, R.L. Frost, Synthesis of layered double hydroxides containing Mg²⁺, Zn²⁺, Ca²⁺ and Al³⁺ layer cations by co-precipitation methods - A review, *Appl. Surf. Sci.* 383 (2016) 200–213.
<https://doi.org/0.1016/j.apsusc.2016.04.150>
- [117] Y.R. Chang, Y.J. Lee, D.J. Lee, Membrane fouling during water or wastewater treatments: Current research updated, *J. Taiwan Inst. Chem. Eng.* 94 (2019) 88–96.
<https://doi.org/0.1016/j.jtice.2017.12.019>
- [118] A. Tiraferri, Membrane-based water treatment to increase water supply, (2014) 1–13. <http://www.colloid.ch/index.php?name=membranes>
- [119] P.S. Goh, W.J. Lau, M.H.D. Othman, A.F. Ismail, Membrane fouling in desalination and its mitigation strategies, *Desalination.* 425 (2018) 130–155.
<https://doi.org/0.1016/j.desal.2017.10.018>
- [120] J. Ayyavoo, T.P.N. Nguyen, B.M. Jun, I.C. Kim, Y.N. Kwon, Protection of polymeric membranes with antifouling surfacing via surface modifications, *Colloids Surfaces A Physicochem. Eng. Asp.* 506 (2016) 190–201.
<https://doi.org/0.1016/j.colsurfa.2016.06.026>
- [121] C. Piyadasa, H.F. Ridgway, T.R. Yeager, M.B. Stewart, C. Pelekani, S.R. Gray, J.D. Orbell, The application of electromagnetic fields to the control of the scaling and biofouling of reverse osmosis membranes - A review, *Desalination.* 418 (2017) 19–34.
[doi:https://doi.org/10.1016/j.desal.2017.05.017](https://doi.org/10.1016/j.desal.2017.05.017)

- [122] J. Kim, M. Jun, M. Park, H. Kyong, S. Kim, J. Ha, Influence of colloidal fouling on pressure retarded osmosis, *Desalination*. 389 (2016) 207–214
- [123] A. Mollahosseini, A. Rahimpour, A new concept in polymeric thin-film composite nanofiltration membranes with antibacterial properties, *Biofouling*. 29 (2013) 537–548. <https://doi.org/0.1080/08927014.2013.777953>
- [124] C.S. Ong, P.S. Goh, W.J. Lau, N. Misdan, A.F. Ismail, Nanomaterials for biofouling and scaling mitigation of thin film composite membrane: A review, *Desalination*. 393 (2016) 2–15. <https://doi.org/0.1016/j.desal.2016.01.007>
- [125] J.H. Jhaveri, Z.V.P. Murthy, A comprehensive review on anti-fouling nanocomposite membranes for pressure driven membrane separation processes, *Desalination*. 379 (2016) 137–154. <https://doi.org/0.1016/j.desal.2015.11.009>
- [126] G. Kang, Y. Cao, Development of antifouling reverse osmosis membranes for water treatment: A review, *Water Res.* 46 (2012) 584–600. doi:<https://doi.org/10.1016/j.watres.2011.11.041>