Journal of Membrane Science & Research

journal homepage: www.msrjournal.com

Review Paper

The Potential of Nanoparticles for Upgrading Thin Film Nanocomposite Membranes – A Review

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ARTICLE INFO

Received 2015-07-19
Revised 2015-08-14
Accepted 2015-09-05
Available online 2015-09-05

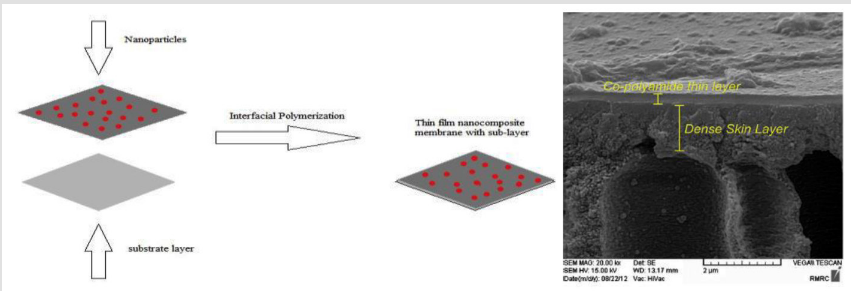
KEYWORDS

Thin film
Nanocomposite
Nanoparticles
Interfacial polymerization
Support layer

HIGHLIGHTS

- Developments of TFC membranes
- Applications of nanoparticles in the TFN
- Performance of TFN new generations
- Fabrication and evaluations of TFN

GRAPHICAL ABSTRACT



ABSTRACT

Over the past decade, many applications were intended for filtration by membrane technology especially the thin film composite (TFC) membranes. In advanced developments of thin film membranes, an attempt was made to spread a new generation of membranes called thin film nano composite (TFN) membranes. However, in the last generation of TFNs, an ultrathin selective film of nanoparticles is coated on the porous sub-layer with different procedures (i.e. interfacial polymerization (IP), dip coating and Plasma polymerization) which contained nanoparticles in a scale of 20-200 nm. Thin film nanocomposite membranes are the last generation of RO membranes which are known as the best appliance in the nanofiltration researches. In this realm, with the help of nanotechnology, membrane science has introduced a novel gamut in science and technology. By using new nanoparticles and nanocomposites among the structure of membranes, the TFNs were born to help the separation and purification processes. To fabricate high efficiency thin film nanocomposites, many manners, theories and additive particles are modified and chosen with regards to time and applications which can increase selectivity, permeability and porosity in addition to the reduction of fouling or improvement of salt rejection. The current review is written to seek the maze of thin film nanocomposite membranes in the past few years with the goal of clarifications of this novel method of filtration, its outlook, nanoparticles and applications which were used before and can be used in the future.

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1. Introduction

Recently, from the academic world as well as industrial sectors, many applications were intended for filtration methods [1-3]. The most important of these applications are waste water treatment, medical uses, liquid food and juice industry, energies and other significant separation fields [1, 4-10]. With regards to worldwide climate changes, the desalination process and pure water will be an important concern. Thus, purification of water or desalting water with the filtration method should be considered [11, 12]. In this field, a

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variety of membranes due to their function and their performance can be selected; as an example, particle filtration, microfiltration, ultrafiltration (UF as the pre-filtration of NF or RO), nanofiltration (NF) and reverse osmosis (RO) filtration. Their differences are in the pore sizes, operation conditions (temperature, pressure, pH and etc.), basic materials and functions. Table 1 has been gathered and prepared to show comparative data regarding the performance and the characteristics of each membrane.

One of the most common membrane methods for desalination is the employment of reverse osmosis membranes (RO). Utilization of these membranes due their many advantages, for instance their low preparation cost, higher water flux, higher stability, and low membrane fouling, is widely increased [13, 14]. Although many methods exist for this purpose, using RO membranes has obtained the most agreement in numerous situations.

Table. 1. Comparison data about membranes employment for the water purification.

Membrane	Principal generation materials	Separating material size (μm)	Operating pH	Operating Pressure (psi)	Operating Temperature	Mean Rejection	Types of material in size	Ref.
Particle filtration (various types)		>1	Depends	Depends	Depends	>90%	Sand, flour, yeast cell	
Microfiltration	Cellulose acetate, polysulfone, polyether sulfone	0.1 - 10	Depends	14-58	Depends	90-98%	Bacteria, paint pigment	Perry's Chemical Engineers' Handbook
Ultrafiltration	Cellulose acetate, polysulfone, polyether sulfone, polyamide	0.01 - 0.1	2-13	9-100	Depends	90-100% pathogen removal	Silica, carbon, albumin	[93-96]
Nanofiltration		0.01-0.001	Large intervals	High range	High range	90-99%	Salts and metal ions	[97]
Reverse osmosis	cellulose triacetate, Cellulose acetate, polysulfone, polyether sulfone, polyamide, trimesoyl chloride, MPD	0.001-0.0001	6.8-8.1	10-1200	High range	90-99.98%	Aqueous salts, metal ions, sugars, virus	[98]

Based on the structural characteristics, RO membranes are separated in two principal branches which are named dense asymmetric membranes and thin film composite membranes. The second group is more admitted. Both have a porous substrate layer known as sub-layer usually in the polymer gender. Dense asymmetric membranes have a dense layer upon that polymeric layer but the thin film composite groups have a selective thin layer as interfacial polymeric surface on their sub-layer [13, 15]. In recent developments of thin film membranes, an attempt is made to spread a new generation of membranes called thin film nanocomposite (TFN) membranes instead of the traditional thin film composites (TFC) [16, 17]. In the fabrication and preparation of TFC membranes, no nanoparticle is used and with regard to the wide range of nanoparticles and their advantages, a lot of benefits have been lost. For instance, some nanoparticles could increase the surface porosity or also hydrophilicity such as TiO_2 nanoparticles [18].

In the last generation of TFNs, an ultrathin selective film of nanoparticles is coated on the porous sub-layer with different procedures (i.e. interfacial polymerization (IP), dip coating and Plasma polymerization) which has a thickness between 20-200 nm [15, 19, 20]. As shown in Figure 1, the structure is composed of two distinct layers where the thin film polymeric layer is coated on the porous base layer [15].

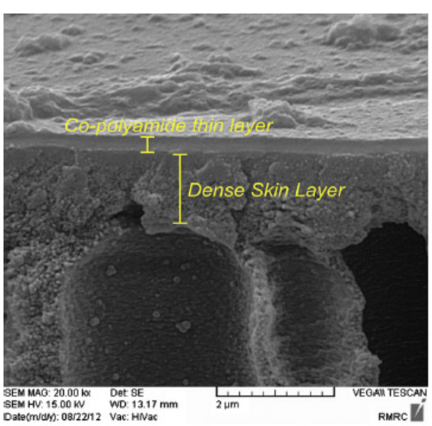

Fig. 1. The cross-section SEM images of TFN-SRNF membrane [15].

Thin film nanocomposite membranes are the last generation of RO membranes which are known as the best appliance in nanofiltration researches. Due to the change of nanocomposite in lieu of traditional composites in their structure, they have obtained many new advantages. TFN membranes have prepared excellent situations for purification of any waste water with any kind of salt, improved membrane surface, capability of separating organic compounds or salts with low molecular weight (up to 200 $g.mol^{-1}$) and even very small molecules in the liquid phase [21]. In addition, containing a wide range of selectivity makes them preferable and many scientific articles and essays were published in this realm [12, 13, 22-24].

The current review is written to seek the maze of thin film nanocomposite membranes in recent years with the goal of clarifications of this novel method of filtration, its outlook, nanoparticles and materials which were used before and can be used in the future. In addition, the comparison of nanocomposite membranes and the traditional thin film composite membranes, their advantages and disadvantages are surveyed.

2. TFN membrane structure

As mentioned before, TFN membranes are formed of at least two separated parts. One selective polymeric layer with a thickness of up to 500 nm is coated on a porous layer named substrate or sub-layer with different methods. Figure 2 shows the SEM image of the two discussed layers [25].

Two principal strategies are considered in the fabrication of layers of thin film nanocomposite membranes: use of nanoparticles 1) in a substrate layer to develop characterizations or/and 2) in a selective layer to improve thickness, roughness, selectivity and permeability. In this category, nanoparticles are also used with regard to their valency and operations in different conditions.

Some procedures are interfacial polymerization (IP), dip coating and Plasma polymerization [26]. Among these methods, interfacial polymerization is more common. However, in this method, large amounts of the costly solvent are needed, but all of the above methods have advantages and disadvantages. For instance, the IP methods are mostly used for the synthesis of polyamide monomers and the desired product is obtained at a low temperature, with a fast kinetics [27]. For fabrication of protective polymers against corrosion, cold, and UV (i.e. plastics), the dip coating method is reasonable. The plasma polymerization is also often used in the gas systems, and it is very useful for a fabrication of polymers in micrometer diameters also when the polymer is solvent insoluble [28]. Thus, due to the polymer properties of the thin layer and also their applications, membranes can be employed in various operating situations. Figure 3 shows a schematic of the interfacial polymerization method in which nanoparticles are used in the top layer and Figure 4 shows a schematic with an example TiO_2 as a nanoparticle from an experiment by Peyravi et al. [15].

Generally, the nanoparticles influence on three important traits of a membrane can be concluded: 1) hydrophilicity, 2) roughness and 3) performance.

Experiments and studies have shown that most of the nanoparticles are used to provide a better hydrophilicity and porosity on the membrane surface.

Thus, the flux and roughness will be subsequently changed.

On the other hand, with utilization of nanoparticles in the thin film active layer, the pores size could be decreased and due to this pore size reduction, the rejection of the membrane can be influenced. Further, due to the inorganic nature of nanoparticles and their utilization on the surface of membranes, inflation and swelling are decreased and a high chemical and mechanical stability will be achieved in the TFN membranes. According to schematic diagram of Figure 5, a relation between three main components of the membrane triangle on the structure and performance of TFN will be perused and discussed in this article.

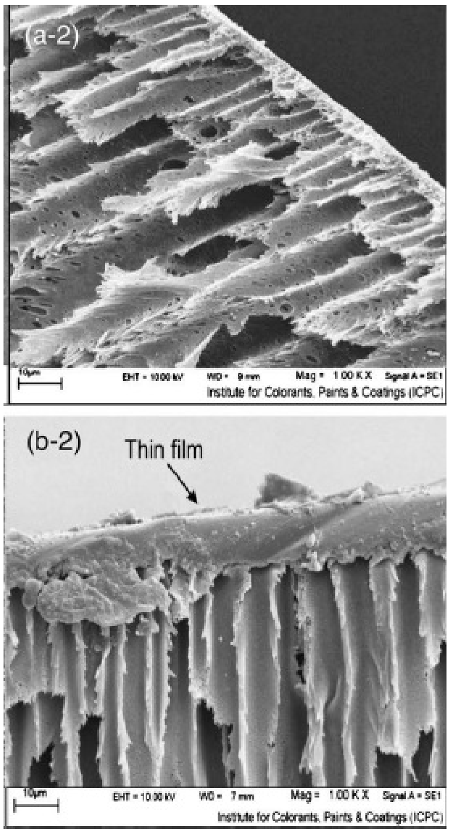

Fig. 2. SEM images of a-2) PSF base layer and b-2) thin film coated layer [25].

2.1. Porous sub-layer

This is an important part of the membrane as the base component. Many articles and researches in this field have been published and manufacturing of the porous substrate has been continued with different methods and materials. In the last decade, lots of improvements and developments have been observed in this field, for instance, decreasing thickness or increasing the stability of the substrate layer [24, 29].

Selectivity in this layer is not important but it should prepare a strong base for the top selective and thin film layer. As a result, stability, permeability, hydrophilicity, high flux, and well pore distribution are crucial characteristics that should be attended to. Thus, materials and particularly nanoparticles should be selected with high accuracy to get the most benefits. Some papers and essays are discussed and their results are given.

A polyacrylonitrile (PAN; MW=150,000) is one of the polymeric materials which was used for production of substrate with a thickness of about 60 macro meters via the phase inversion method by Kang et al. The sub-layer with a pore size of 10 nm on the front and 20-50 nm on the back side was fabricated and it was coated with a different charge layer process. This caused a very good porosity and also compatibility between the sub-layer and thin layer [30].

Another group of scientists that used TFN membranes in their investigation were Eun-Sik Kim and Baolin Deng. In their experiments, the porous sub-layer was made of polysulfone (PSf) that was used many times as the material of substrates in the fabrication of TFN due to its high hydrophilic surface. In this project, the PSf support layer of the membrane (30 k MWCO) was made with ultrafiltration (UF) to increase the performance and the good hydrophilic membrane was achieved in addition a narrow pore distribution [31].

In the same year with Kim and Deng, Fathizadeh et al. prepared another porous layer for their membrane (PES) via the phase inversion method. In that process, the DMAC solvent was employed to dissolve a mixture of 15 wt% PES and 5 wt% PUP. The TFN membrane was synthesized with the interfacial polymerization. In this mixture and the membrane that were fabricated, a high flux and rejection yield are resulted [32].

In year 2013, Ma et al. also introduced a polysulfone nano-composite substrate as the porous layer. The zeolite nanoparticle was incorporated in polysulfone to improve the water flux. Due to the addition of nanoparticle into the sub-layer, surface improvement porosity was shown and a greater hydrophilic membrane with higher water permeability is achieved [33].

A novel substrate was fabricated by Zhong et al. which has new characters [34]. For the manufacturing of this membrane, a thin film was coated inside the hallow fiber substrate. The sub-layer was made of sulfonated polyphenylene sulfonates. As mentioned before, poly sulfone is a common substrate [35, 36]. In this category of development, nanofibers have been considered in recent years because of their fantastic available surface and high porosity [37, 38].

You et al. were one of those scientists who manufactured a novel nanofibrous substrate which was used in low pressures and also with high flux of water in TFN membranes. This high performance membrane was generated with the base of polyacrylonitrile (PAN) for utilizing the separation of oil and water emulsion due to its excellent mechanical properties as a nanofibrous sub-layer [39].

Fabrication of the base sub-layer and also PSF layers have an industry scale method and device that is prepared in our research center. Figure 6 shows the automatic system for generation of PSF or the base ultrafiltration layer [40]. In their study, a high permeable thin film membrane was fabricated with three different nanoparticles in their structure. Figures 7 and 8 show the original images of AFM from the base form of the flat sheet membrane which was generated with the automatic system and the surface of the membrane with the nanoparticles on, respectively [40].

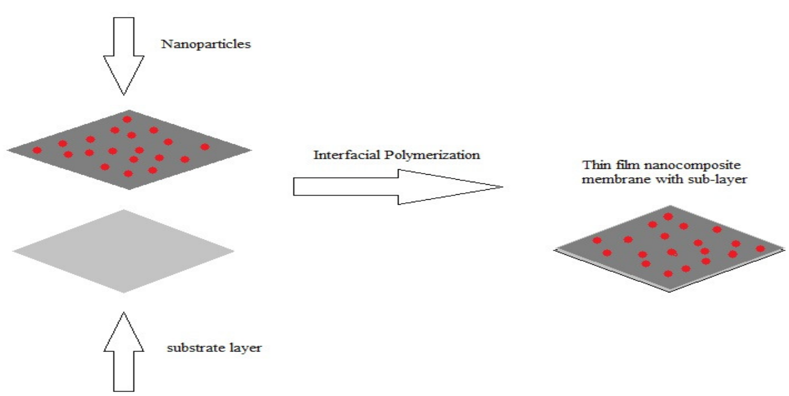

Fig. 3. Schematic of interfacial polymerization.

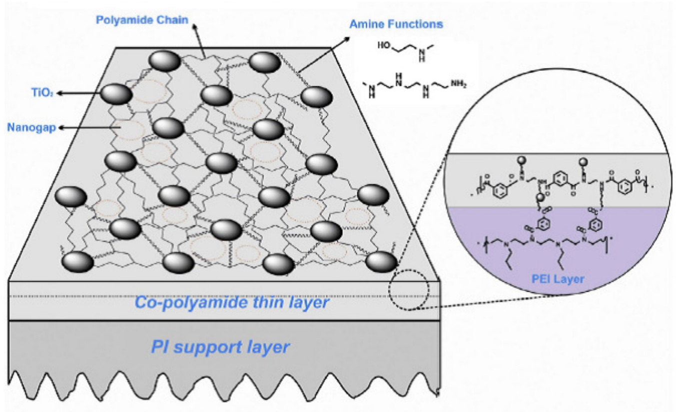

Fig. 4. Schematic of TFN structure with TiO_2 as the nanoparticles.

In Figure 9 dispensation of polymer utilizations in the substrate structure is shown. The polysulfone group such as PSF, CPSF, APSF and SPSF are the most favorite monomers which were used in recent years and are very stable with high flux and the porosity membrane is fabricated with this group. However, the new methods and procedures are expected to be found for fabrication of new sub-layers also in the form of nanofibers and hallow fibers in the near future. Properties of some useful polymers are shown in Table 2.

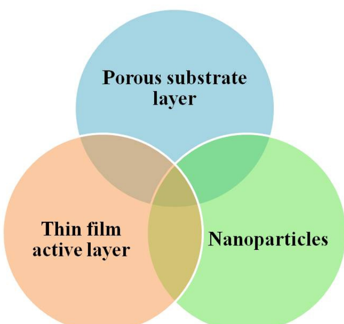

Fig. 5. A relation between three main layers of TFN.

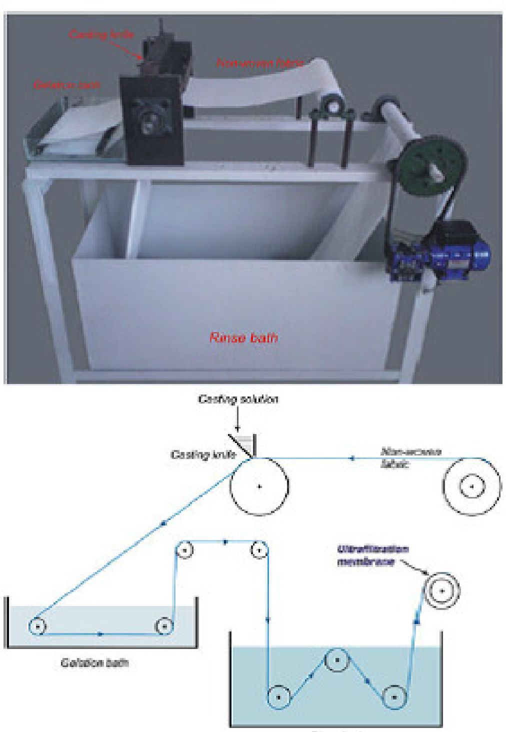

Fig. 6. Automatic system for the sub-layer fabrication in the industry scale [40].

2.2. Thin film nanocomposite layer

Rapid developments in TFC membranes have led to the fabrication of a new class of these membranes which are named TFN membranes including the synthetized nanoparticle in their structure to make their performance better [41-43]. With regards to their applications, many different monomers were used for the generation of this layer to prepare the best thickness, roughness and selectivity due to their function.

Nowadays many efforts have been made and studies have been carried out to find an optimum of monomers and process conditions to manufacture the thin film nanocomposite polymeric layer. In this fraction, some researches and papers in recent years have been surveyed and well discussed. Some literatures have been classified into three groups of nanofiltration (NF), Forward osmosis (FO) and Reverse osmosis (RO).

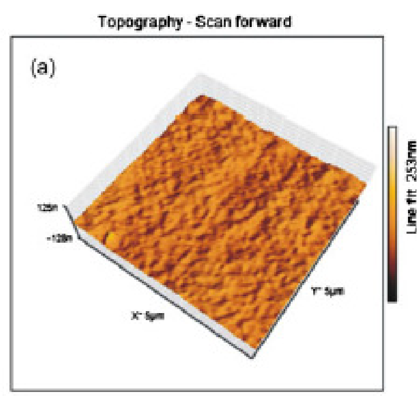

Fig. 7. Origin AFM image of PES sub-layer generated with automatic device [40].

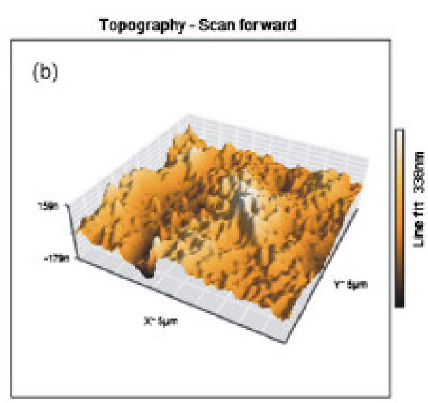

Fig. 8. AFM image of TFC, with the PES substrate layer [40].

2.2.1. Nanofiltration (NF)

An experiment was performed by Li et al. and the influence of silica was studied in the separation process betterment. They have studied the effect of silica nanospheres in the thin layer which coated three different support layers via interfacial polymerization and the results were compared. The main studied layers were made of trimesoyl chloride (TMC), piperazine (PIP) and polysulfone (PS) [44].

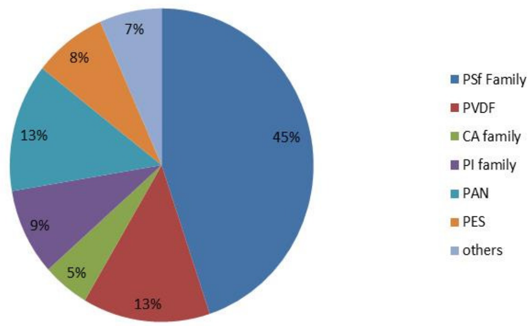

Fig. 9. Comparison of substrate monomers worldwide.

Table 2. Characteristics of common polymers which are used in sub-layer fabrication.

Polymer	Solubility	Hydrophilicity	Chemical stability	Mechanical stability	Ref.
Polysulfone (PSF)	Good in organic solvents like DMF	Hydrophobic	High	High-strength and compaction resistant	[24, 35, 99, 100]
Polyacrylonitrile (PAN)	In less-polar organic solvents	Hydrophobic	Good	High temperature resistance and strength	[101-104]
Cellulose acetate propionate (CAP)	In ink solvents	Hydrophobic	Stable structure	High melting point	[105-109]
PES/SPSF Polyethersulfone/sulfonated polysulfone	Needs additives	Hydrophilic	Chemical resistance	Good thermal stability and mechanical strength	[110, 111]
Polyethersulfone (PES)	In classic solvents	Hydrophilic	High chemical resistance	High resistance to heat	[112-115]
PVP/PSF	High- and in water	Hydrophilic	Good miscibility	Good	[116]

Silica is a hydrophilic material and the use of silica nanospheres can improve the hydrophilicity of the membrane surface. It can be concluded that silica nanospheres clearly increased salt rejection and flux. In the study mentioned above, the water flux was elevated from 19.3 to 22.65 L/m^2h compared with the non-existence of silica nanoparticles [44]. The layer presented a promotion in divalent or ionic selectivity in the separation process. This TFN membrane was gained in the softening of $MgSO_4$ in an aqueous situation in another study [45].

Formation of appropriate sites on the nanofiltration membrane surface for binding TiO_2 photo-catalyst and their performance and fouling-resistant capability has been studied before [41]. However, a new poly (vinyl alcohol) (PVA) with titanium dioxide (TiO_2) composite has been prepared in the study by Pourjafar et al. They have used a novel cross-flow system for analyzing the performance of the membrane. Figure 10 shows the schematic of their system and the setup procedure that has been described in the references [46]. In this study, a very good dispersion of nanoparticles on the surface of the membrane has been achieved. The XRD, SEM and AFM analyses can confirm their good results. Figure 11 shows the SEM image of their membrane surface [47]. In another study, the antibacterial effect of TFN with the same nanoparticles of TiO2 has been studied by them. Figure 12 shows the demonstration that this membrane had the antibacterial properties [48].

An investigation on water treatment was done in 2013 by Zhang et al. that perused silver-PEGylated dendrimer nanocomposite as an anti-fouling agent for nanocomposite membranes. The nanocomposite of silver-polyethylene glycol was availed on the surface of the TFN membrane to decrease the fouling of bacteria and also proteins in water purification. After utilization of this membrane in the project, important improvement in hydrophilicity was found and attachment of the bovine serum albumin (BSA) and E.coli obviously reduced alongside the fouling reduction up to 99.8% [49].

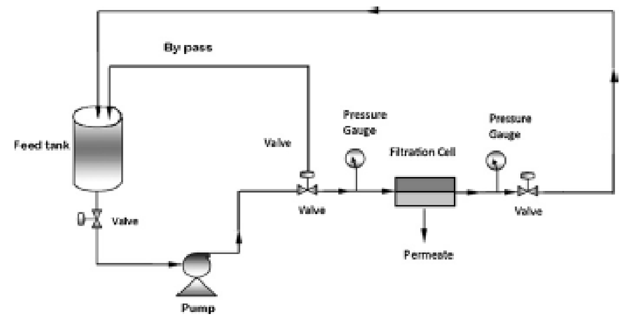

Fig. 10. Schematic of new cross-flow system for analyzing performance of TFN [47].

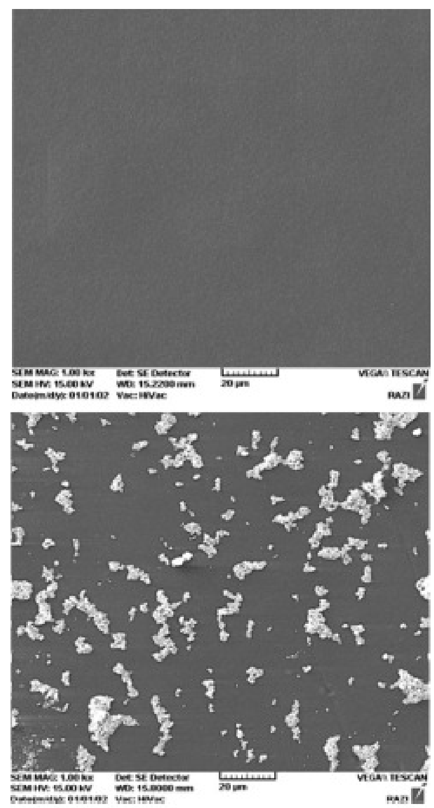

Fig. 11. Good dispersion of TiO_2 nanoparticles on the surface of membrane [47].

Buonomenna studied the effect of nanoparticles on the surface of membranes in the recent decade and made a comparison between the application of nano composites in reverse osmosis (RO) and forward osmosis (FO) [50]. In 2013, Wu et al. improved the interfacial polymerization to optimize the multi-walled carbon nanotubes-polyester thin film coated with triethanol amine (TEOA) and trimesoyl chloride (TMC) on the base of the PSF support membrane. The results showed that an increase of MWNTs concentration in the aqueous phase up to 0.05 mg/ml caused an increase in water permeability and long term stability. To compare the two categories, classical TFC was manufactured and pure water flux and Na_2SO_4 rejection were studied on both TFN and TFC cases in the same situations. Despite the changes in the salt rejection, the flux of pure water has been increased [51].
For improvement of selectivity and also permeability, Shen et al. used the interfacial polymerization method to coat PMMA-MWNTs. With this process, water flux increased perspicuity and salt rejection reached 99%. Grafting the MWNTs with poly (methyl methacrylate) PMMA obviously increases the hydrophobicity of the membrane [52].

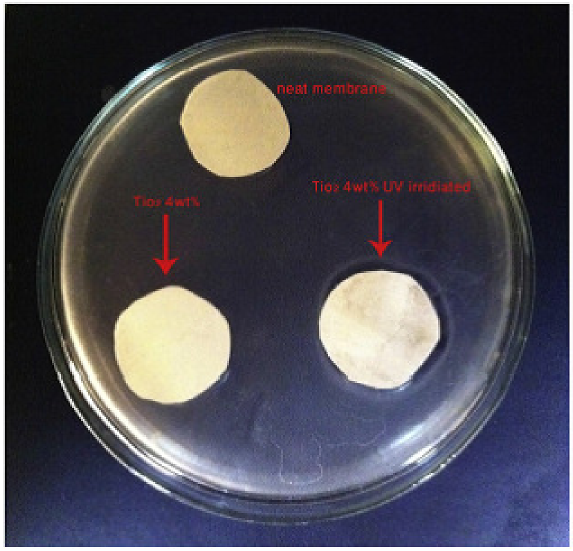

Fig. 12. Comparison of TiO_2 antibacterial effects in TFN structure [48].

2.2.2. Forward osmosis (FO)

A new membrane for dehydration of alcohol solutions in aqueous phase was prepared by Fathizadeh et al. [53]. The phase inversion method was used to synthesize a mPAN substrate layer and the polyamide active layer containing nano NaX zeolite was deposited on the porous sub-layer by the hydrothermal technique [54]. Nano NaX zeolite is a hydrophilic particle in a crystal size in a nanometer scale and thus, the hydrophilicity of the membrane increased with regards to the utilization of this material. The use of NaX zeolite caused the growth in roughness and for this reason, permeation was increased [32].

The water selectivity was influenced by increment of zeolite nanoparticles with the penetration of water inside the pores of the zeolite. However, isobutanol is unable to act like water so this kind of TFN membrane is perfect for dehydration of isobutanol-water mixture because of its high selectivity. It also has good performance in the separation of the ethanol-isobutanol blend (ethanol is similar to water) [53].

Kang et al. explained the influence of zeolite in TFN membranes again, but in this case the layer-by-layer assembly technique was considered. For this, negatively charged Lind type A (LTA) zeolite was sandwiched between two distinct polyelectrolyte layers. Negatively charged poly (acrylic acid) or PAA, positively charged polyethylenimine or PEI with LTA were provided by a trilayer via interaction of electrostatics. SEM showed that zeolite was better kept in the trilayer in comparison with the PAA and PEI bilayer, and this composite also generated a good roughness in addition to its perfect stability and thickness [30].

Daraei et al. also fabricated nanoclay/chitosan on the polyvinylidene fluoride (PVDF) substrate layer. Nanoclay has a very good adsorption capability and so it has a good performance in separations, and it can also cause interaction between the layers. The manufactured membrane was employed to study the removal of methylene blue from water [55].

2.2.3. Reverse osmosis (RO)

In the last year (2015), a research was accomplished by Ghanbari et al. which studied the effect of using cyclohexane instead of n-hexane as the organic solvent to provide a high dispersion in halloysite nanotubes (HNTs) for water desalination on the PSF substrate. The results showed that some functions were increased such as hydrophilicity, solubility, diffusion and roughness. However, salt rejection is decreased from 93% to 78% in TFN membranes with HNTs [16, 56].

Another experiment was done to optimize TFC and make the novel TFN membranes by modified nanoparticles of mesoporous silica with the covalent bonding once more by Ghanbari et al. [57]. For that research, a mesoporous silica nanoparticle (mMSN) polyamide (PA) thin film was synthesized by interfacial polymerization of PIP and TMC on that substrate layer. At first mMSN and TMC were reacted, and then silica nanoparticles were linked with an active layer via covalent binding. After fabrication of the membrane, some experiments were done and the results explained that in the rejection of Na_2SO_4 mMSN membranes have two base characteristics: 1) mesostructured for better water flux and 2) the functional group caused better interaction with the polymer and thus prepared a very good anti-fouling ability [57].

Wu et al. scrutinized a new approach of TFN membranes generation. They studied some new nanomaterials in the thin layer to prevent the membrane from fouling with microbes and stop their growth on the surface of the membranes. For this reason, with a slow release of nano silvers with antimicrobial nano particles, the generation of bacteria was controlled. Nano zeolite was coated on the surface to provide a carrier for Ag to link via covalent binding after the amine group and nano zeolite linked and Ag^+ loaded on the surface. At about 7.2 mg/m^2 loading of silver, a strong antimicrobial activity occurred. For water purification, this technique is simple and easy to barricade the activity of bacteria [58].

To make brackish water purify with nanoparticles, Dong et al. suggested utilization of NaY zeolite nanoparticles with a size smaller than 200nm in reverse osmosis membranes. Namvar-Mahboub et al. modified SiO_2 on PEI as the organic solvent for nanofiltration (OSN) [59].

In other projects of our group, another nanoparticle was manufactured as solvent in nanofiltration. TiO_2 was functionalized to coat on the active site of the membrane. SEM showed the multi-layer structure and different agents can bond on the surface covalently or physically. Some copolymers with excellent solubility in high polar solvents have been used in this work and a very good matrix on PSF has been achieved that is shown in Figure 13 [15].

Based on Lau's review paper in 2012 and some other lectures which were overviewed [29], all the developments in recent years in thin film nanocomposite membranes were studied. There are two groups of amine monomers and acyl chloride monomers which are used in the fabrication of TFNs that are aggregated in Table 3.

Generally, the best performance in purification and desalination is the property of TFNs. Nanoparticles can improve many thin film composition specifications such as productivity, selectivity, stability and fouling resistance, and this leads to the great development for the membrane industry from TFC to TFN [26, 36, 60-65].

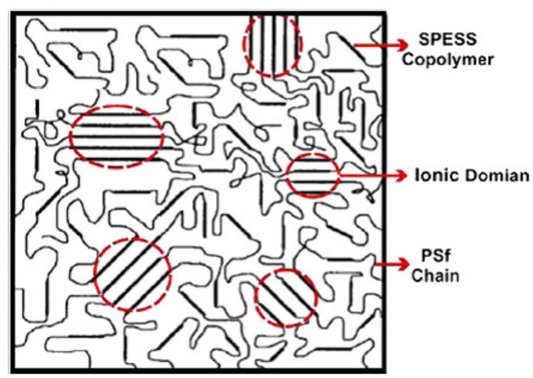

Fig. 13. Ionic domain formation of SPESS copolymers in the PSF matrix.

3. Additives

In addition to two principal layers in TFN membranes, one more layer of additives regarding the condition and application of the membrane could be operational which is made of additives. On the other hand, additives can be used as the particle in the main structure of those two identified layers. Additives can improve the characterizations of the membrane like performances or porosity and also for stabilizing nanoparticles in the structure of the membrane additives could be used. In traditional filtrations without any nanoparticle or additive, the principal of operation was only the difference in size. However, in a new generation of membranes, some adsorbent or strengthener particles can be employed and this leads to the better membrane structure and performance. For instance, Voo et al. have studied the effect of additives to make epoxy TFN membranes flexible due to the poor resistance of epoxy systems to cracks and the need of flexibility in the operation. For that reason, flexibilizing resins (FR-1), polyol resins (FR-2), toughening resins (FR-3) synthetic diamond (SD) were investigated in varied traits of mechanical, thermos-mechanical and also thermal stability [66].

It was understood that degradation on the mechanical properties is decreased for FR-1 and FR-3 but no increase occurs for SD nanofillers. However, flexibility, stiffness and tensile strength are increased when SD nanofillers are utilized.

In other research related to additives, four hydrophilic materials were observed and their influences on TFN membrane efficiency were compared by Zhao et al. The materials were added in *m*-Phenylenediamine (MPD) solution to react with TMC in the structure of the sub-layer [67].

o-aminobenzoic acid-trimethylamine salt (o-ABA-TEA) which has a similar structure to MPD, influenced the water flux from 21.6 gfd to 36.7 gfd by an increase of 0 %wt to 2.45 %wt. The second one is *m*-aminobenzoic acid-trimethylamine salt (m-ABA-TEA), and has more similarity to MPD and could increase the flux from 21.6 gfd to 36.3 gfd. The third one 2-(2-hydroxyethyl)pyridine which contains a reactive –oh group could modify the salt rejection by 98% and water flux of 40 gfd in optimum conditions. But the last one was 4-(2-hydroxyethyl) morpholine which modified the lower salt rejection and higher water flux. (97.6% rejection and 40.8 gfd flux) [67].

Faizur Rahman has experimented reverse osmosis membranes with and without additives, and for this reason four composites (antiscalants) were utilized, SHMP, STD100, STD101 and FM 101. STD composites are commercial additives and their benefits are demonstrated, FM 101 is also a better conventional additive which has defendable performance. In this experiment, temperature and pH were optimized at 50 °C and about 6.5 sequences [68]. Another work prepared a bilayer of Ag as an additive to a thin film and responses were observed by Chapelle et al. [69]. The Ag ultra-thin bilayer led the project to a better gas selectivity and also sensitivity.

Table 3. Popular monomers based on the Lau review paper [29].

Amine monomer	Acyl chloride monomer
m-Phenylenediamine (MPD) [24, 117-120]	Trimesoyl chloride (TMC) [120-123]
Piperazine (PIP) [41, 124, 125]	5-Isocyanatoisophthaloyl chloride (ICIC) [126]
Triethanolamine (TEOA) [127, 128]	om-Biphenyl tetraacyl chloride (om-BTEC) [23]
Sulfonated cardopoly (arylene ether sulfone) (SPES-NH2) [129]	mm-Biphenyl tetraacyl chloride (mm-BTEC) [23, 24]
p-Phenylenediamine (PPD) [29, 38]	Isophthaloyl chloride (IPC) [130, 131]
3,5-Diamino-N-(4-aminophenyl) benzamide (DABA) [122, 132]	Cyclohexane-1,3,5-tricarbonyl chloride (HTC) [133]
Disulfonatedbis[4(3aminophenoxy)phenyl] sulfone (S-BAPS) [134]	op-Biphenyl tetraacyl chloride (op-BTEC) [23]
Hexafluoroalcohol-mphenylenediamine (HFA-MPD) [27]	Pyridine-2,4,6-tricarbonyl trichloride (PTC) [23]
m-Phenylenediamine-4-methyl (MMPD) [135]	5-Chloroformyloxyisophthaloyl chloride (CFIC) [122]
1,3-Cyclohexanebis(methylamine) (CHMA) [29]	
Sulfonated poly(arylene ether sulfone) containing sulfonic acid and amino groups (SDADPS) [136]	

4. Nanoparticles

The numbers of nanoparticles were observed in many researches as discussed formerly in this article. Two principal methods have been used in the literatures to add nanoparticles into the membrane structure as additive. First is solving the nanoparticles in the aqueous or organic solvents. In this procedure, the nanoparticles have been loaded on the membrane while the layer has been fabricated. However, the second one is the *in situ* method. In this method, nanoparticles will be formed in the membrane structure. For this purpose, they are mostly used for the formation of the metal nanoparticles, metal salts solved in the solvents and then the exclusive reducing agent filter to the membrane. After the reduction step occurred, the nanoparticles formed in the membrane [70].

Here some other useful nanoparticles are studied, for instance the one step method of synthesis of Pt nanoparticles for fabrication of the SnO_2 nanocomposite thin film membranes were classified by Kim et al. [71]. In this research, with the formation of Pt nanoparticles, resistance was decreased due to the long time heating of the membrane to synthesize nanoparticles. However, optical and electrical properties were not changed.

In one of the newest works of Liu et al. in 2015, a novel TFN membrane was prepared and the effects of SAPO-34 nanoparticles were studied. The substrate of this hallow fiber membrane was a dual-layer of PES/PVDF. The membrane showed a large nanoporosity and due to this porosity, high rejection and flux were achieved [72].

A new synthetic nanoparticle has been extracted from the *Hibiscus subdariffa* leaf in Bala et al. experiments for anti-bacterial usages. In the future it can be a good nanoparticle for the anti-fouling agent on the surface of membranes [73].

For the water purification, another work has been studied by Al-Hobaib et al. In this experiment, the nanoparticles of magnesium titanium oxide ($MgTiO_3$) were used as a filler with different concentrations to achieve a better performance. Water flux and the salt rejection were observed and the TFN membrane showed a high performance in these two parameters. The permeability was increased from 26 to 44.6 L/m^2 and rejection of about 98% was prepared with a low concentration of nanoparticles [74]. However, one of the useful nanoparticles as an anti-fouling agent is silver. The photo reduction and soft reduction methods were used to synthesize Ag nanoparticles by Wolosiuk et al. [75]. 4-mercaptopyridine was used as the probe molecule. Ag nanoparticles showed a stable performance on prohibition of bacterial growth. Another work also used Ag nanoparticles for bio-fouling mitigation [70]. Although the roughness, hydrophilicity and salt selectivity were not impacted, about 75 percent of live bacteria was attached to the surface. However, slight reduction in flux was observed.

To increase the water flux in an experiment by Duan et al., a hydrophobic zeolite imidazolate framework-8 (ZIF-8) was employed as nanoparticle in the PA selective layer. The membrane including lab made nanoparticles showed a water permeate increase to 3.35 L/m^2·h·bar [76].

Generally, among methods of TFN membrane fabrication (i.e. interfacial polymerization, layer-by-layer modifications, UV grafting or UV photografting, electron beam irradiation and plasma treatment), interfacial polymerization is the best choice besides using additive or nanoparticle additives. In summary, some of the most important nanoparticles which have been used in the structure of TFN are prepared in Table 4 with limited details. Briefly, nanoparticles could improve many properties of membranes, for instance roughness, biofouling, water flux, permeability, salt rejection, porosity, stability and etc. One of the main characterizations in the membrane is the hydrophilicity that can be improved by the usage of nanoparticles.

5. Applications

According to the review article which was published recently by Mohammad et al., more than a quarter of published articles on the subject of TFC and TFN from 2008 are about applications of those membranes and also approximately twenty percent are about fabrication methods. Therefore, about half the published articles in this category is related to the methods and applications. Thus, the importance of the topic is represented. The most important matter in the issues is the concern of water purification and/or wastewater treatment with nanofiltration and its advances in desalinations [77].

Applications of TFN membranes are divided to several classes such as desalination as the most useful application, environmental applications, and utilizations in biotechnological fields as well as the food industry.

5.1. Desalination

Due to some problems such as fouling in the desalination process, industrial utilization of TFN membranes is in the early stage. However, researches about applications of TFN membranes especially for the desalination process is the main concentrate of scientists' society studies and also many achievements have be gained [17, 56, 78-81]. The future of these researches can be seen in the development of membranes for brackish water and seawater desalination usages [82].

5.2. Environment

Worldwide primary concern nowadays is the treatment of wastewaters to generate high quality water via the usage of nanoparticles in the TFN membranes fabrication. The significant utilization of membranes for environmental applications is the separation of toxicant particles (i.e. arsenic) [83-85], salts (i.e. Na_2SO_4 and $MgSO_4$) [86-88], proteins, nuclear or pharmaceutical wastes [89, 90], removal of organic pollutants (i.e. industrial by-products) and hormones from water and its purification, some at a bench scale and some others in commercial or plant scales.

In comparison to other methods of wastewater treatment, for instance using activated sludge or microorganisms in biotechnology, the TFN membrane way of purification due to its high quality of products and lower operating cost can be more useful and reasonable.

5.3. Biotechnology and biochemical engineering

According to the development of biotechnology and its entrance to other sciences, and the connection between biotechnology and engineering, utilization of membranes has increasingly grown in many fields of industry and many researches in laboratories. One example is the usage of TFN membranes to purify medicines and make biological products in high quality and purity. Plenty of perusals like the recovery of organic solvents are yet in laboratory scale but a bright future is considered for membranes modifications and also in the medical sciences [15, 26, 91].

Table 4. A brief explanation related to the some of most important nanoparticles.

Nanoparticles	Solubility	Usage position	Size	Performance	Ref.
Silver (Ag)	Soluble in water, acetone, ammonia, ether and insoluble in ethanol	Thin film active layer	20-131 nm	Anti-biofouling	[137]
Platinum (Pt)	Insoluble in ether, dissolved in ammonia, HCL		60-120 nm	Temperature resistance, antioxidants inhibitor	[71, 138]
Titanium Dioxide (TiO_2)	Insoluble in water	Coated on active site	20 nm (in a study)	Increase water flux, surface bonding	[36, 139]
Magnesium Titanium Oxide ($MgTiO_3$)	Soluble in acid, ammonia and insoluble in alcohol	Used as filler	About 80 nm	Better water flux, salt rejection and permeability	[74]
Silica Nanoparticles	Solubility in water depends on crystalline form (poorly soluble)	Thin film active layer	About 100 nm	Improved hydrophilicity, increased rejection and water flux	[14]
Zeolite Nanoparticles	Little known of zeolite solubility and it depends on many situations	Substrate layer	Smaller than 200 nm	Improved porosity, permeability and increased flux	

5.4. Food industry

Due to the importance of quality in the food processes, utilization of TFN membranes for separation in this field has increased in recent years. Some operations have used membranes from past years such as beverage and dairy production. However, with the development of membranes and generation of novel and efficient TFNs, other food industries (i.e. juice and non-alcoholic drinks) are recruiting membranes nowadays. Separation of hazardous parts like cholesterol and keeping useful compositions like antioxidants is another fundamental concern of the food industry and it can be possible with membrane science. Other functional operations of TFNs in the food industry are preservation of natural colors, separation of NaCl, keeping nutrients and an optimized amount of compositions in the food separation processes [92].

6. Conclusions

Owing to the requirement of many industries and sciences for separation and production of high quality materials, a low cost, reliable and high yield method is needed and TFN membranes can prepare the perfect setting for these purposes. Membranes are very suitable due to their high selectivity and other exclusive characterizations, albeit many laboratory scale projects were not commercialized yet.

With the help of nanotechnology, membrane science has introduced a novel gamut in science and technology. By using new nanoparticles and nanocomposites among the structure of membranes, the TFNs were born to help the separation and purification processes. In order to fabricate high efficiency thin film nanocomposites, many parameters namely increasing selectivity, permeability and porosity besides the reduction of fouling or improvement of salt rejection, need to be taken into account. In addition, many manners, theories and additive particles are also modified and chosen with regards to time and application. In conclusion and to the best of our knowledge, using TMC in fabrication of the base layer and the nanosilica in other parts are the most favorite particles so far.

From the provided figures it can be obtained that many analyzing methods and devices have been employed to reach many characterizations of each membrane, for instance the very rough and dense films that were formed on the PSF or PES support layer could be seen by the usage of SEM or AFM analyses (some SEM and AFM analyses was shown before in this study). The high roughness and density increase the capacity of TFN for the water softening process.

The interfacial polymerization method is commonly used to prepare a stable top layer on the PSF ultrafiltration support layer. In some cases, for improving the performance of membranes, surfactants (i.e. SDS) have been used to affect the morphology of TFN and get the high rejection or flux.

In this process, high hydrophilicity can lead to the high performance in permeability of the membrane, so that many nanoparticles have been used to increase the hydrophilicity of the TFN surface. They can also make the membrane smoother and or decrease tendency and fouling.

In addition to all the above, some disadvantages of this group of membranes might also be considered. For instance, at high pressure, the polyamide layer loses the fitting structure and the lower porosity may be achieved. Moreover, oxidation always treats these membranes. Therefore, it has a long way ahead of TFNs to finding a way to the industrial field from pilot or lab scale due to their high cost solvents and nanoparticles, and also the fabrication of this category of membrane needs high accuracy in timing and material purity. In this process, biofouling can greatly occur and leads to resistance to the water flow rate. Therefore, further studies in this field are undeniable.

7. Acknowledgements

The authors would like to appreciate distinguished colleagues from inside and/or abroad for their productive discussion during preparation of this review paper.

8. References

[1] M.E. Ersahin, H. Ozgun, R.K. Dereli, I. Ozturk, K. Roest, J.B. van Lier, A review on dynamic membrane filtration: materials, applications and future perspectives, Bioresour. Technol. 122 (2012) 196-206.
[2] R.W. Field, G.K. Pearce, Critical, sustainable and threshold fluxes for membrane filtration with water industry applications, Adv. Colloid Interface Sci. 164 (2011) 38-44.
[3] K.-M. Yao, M.T. Habibian, C.R. O'Melia, Water and waste water filtration: Concepts and applications, Environ. Sci. Technol. 5 (1971) 1105-1112.
[4] K. Chon, S.J. Kim, J. Moon, J. Cho, Combined coagulation-disk filtration process as a pretreatment of ultrafiltration and reverse osmosis membrane for wastewater reclamation: an autopsy study of a pilot plant, Wat. Res. 46 (2012) 1803-1816.
[5] C. Dutton, S.C. Anisfeld, H. Ernstberger, A novel sediment fingerprinting method using filtration: application to the Mara River, East Africa, J. Soil. Sediment. 13 (2013) 1708-1723.
[6] C. Fisher, T.L. Grahovac, M.E. Schafer, R.D. Shippert, K.G. Marra, J.P. Rubin, Comparison of harvest and processing techniques for fat grafting and adipose stem cell isolation, Plastic Reconstr. Surg. 132 (2013) 351-361.
[7] A. Fothergill, V. Kasinathan, J. Hyman, J. Walsh, T. Drake, Y.F.W. Wang, Rapid identification of bacteria and yeasts from positive-blood-culture bottles by using a lysis-filtration method and matrix-assisted laser desorption ionization–time of flight mass spectrum analysis with the SARAMIS database, J. Clinical Microb. 51 (2013) 805-809.
[8] A.W. Mohammad, C.Y. Ng, Y.P. Lim, G.H. Ng, Ultrafiltration in food processing industry: review on applications, membrane fouling, and fouling control, Food Bioprocess Technol. 5 (2012) 1143-1156.
[9] C. Ramos, F. Zecchino, D. Ezquerra, V. Diez, Chemical cleaning of membrane from an anaerobic membrane bioreactor treating food industry wastewater, J. Membr. Sci. 458 (2014) 179-188.
[10] D.P. Zagklis, E.C. Arvaniti, V.G. Papadakis, C.A. Paraskeva, Sustainability analysis and benchmarking of olive mill wastewater treatment methods, J. Chem. Technol. Biotechnol. 88 (2013) 742-750.

[11] J. Duan, E. Litwiller, I. Pinnau, Preparation and water desalination properties of POSS-polyamide nanocomposite reverse osmosis membrane, J. Membr. Sci. 473 (2015) 157-164.
[12] E.-S. Kim, G. Hwang, M.G. El-Din, Y. Liu, Development of nanosilver and multi-walled carbon nanotubes thin-film nanocomposite membrane for enhanced water treatment, J. Membr Sci. 394 (2012) 37-48.
[13] B. Rajaeian, A. Rahimpour, M.O. Tade, S. Liu, Fabrication and characterization of polyamide thin film nanocomposite (TFN) nanofiltration membrane impregnated with TiO_2 nanoparticles, Desalination 313 (2013) 176-188.
[14] J. Yin, E.-S. Kim, J. Yang, B. Deng, Fabrication of a novel thin-film nanocomposite (TFN) membrane containing MCM-41 silica nanoparticles (NPs) for water purification, J. Membr. Sci. 423 (2012) 238-246.
[15] M. Peyravi, M. Jahanshahi, A. Rahimpour, A. Javadi, S. Hajavi, Novel thin film nanocomposite membrane incorporated with functionalized TiO_2 nanoparticles for organic solvent nanofiltration, Chem. Eng. J. 241 (2014) 155-166.
[16] M. Ghanbari, D. Emadzadeh, W. Lau, S. Lai, T. Matsuura, A. Ismail, Synthesis and characterization of novel thin film nanocomposite (TFN) membrane embedded with halloysite nanotubes (HNTs) for water desalination, Desalination 358 (2015) 33-41.
[17] N. Misdan, W.J. Lau, A.F. Ismail, Seawater Reverse Osmosis (SWRO) desalination by thin-film composite membrane—Current development, challenges and future prospects, Desalination 287 (2012) 228-237.
[18] M.-L. Luo, J.-Q. Zhao, W. Tang, C.-S. Pu, Hydrophilic modification of poly (ether sulfone) ultrafiltration membrane surface by self-assembly of TiO_2 nanoparticles, Appl. Surf. Sci. 249 (2005) 76-84.
[19] V. Kochkodan, N. Hilal, A comprehensive review on surface modified polymer membrane for biofouling mitigation, Desalination 356 (2015) 187-207.
[20] L.A. Perry, O. Coronell, Reliable, bench-top measurements of charge density in the active layers of thin-film composite and nanocomposite membrane using quartz crystal microbalance technol., J. Membr. Sci. 429 (2013) 23-33.
[21] D. Li, H. Wang, Recent developments in reverse osmosis desalination membranes, J. Mater. Chem. 20 (2010) 4551-4566.
[22] M. Amini, M. Jahanshahi, A. Rahimpour, Synthesis of novel thin film nanocomposite (TFN) forward osmosis membranes using functionalized multi-walled carbon nanotubes, J. Membr. Sci. 435 (2013) 233-241.
[23] A. Ismail, M. Padaki, N. Hilal, T. Matsuura, W. Lau, Thin film composite membrane—Recent development and future potential, Desalination 356 (2015) 140-148.
[24] A. Mollahosseini, A. Rahimpour, Interfacially polymerized thin film nanofiltration membranes on TiO_2 coated polysulfone substrate, J. Indust. Eng. Chem. 20 (2014) 1261-1268.
[25] M. Jahanshahi, A. Rahimpour, M. Peyravi, Developing thin film composite poly (piperazine-amide) and poly (vinyl-alcohol) nanofiltration membranes, Desalination 257 (2010) 129-136.
[26] S. Hermans, H. Mariën, C. Van Goethem, I.F. Vankelecom, Recent developments in thin film (nano) composite membranes for solvent resistant nanofiltration, Current Opinion Chem. Eng. 8 (2015) 45-54.
[27] P.W. Morgan, S.L. Kwolek, Interfacial polycondensation. II. Fundamentals of polymer formation at liquid interfaces, J. Polym. Sci. 40 (1959) 299-327.
[28] H. Yasuda, Glow discharge polymerization, Thin Film Processes, (1978) 361-396.
[29] 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.
[30] Y. Kang, L. Emdadi, M.J. Lee, D. Liu, B. Mi, Layer-by-Layer Assembly of Zeolite/Polyelectrolyte Nanocomposite Membranes with High Zeolite Loading, Environ. Sci. Technol. Letters 1 (2014) 504-509.
[31] 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.
[32] 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. Membr. Sci. 375 (2011) 88-95.
[33] N. Ma, J. Wei, S. Qi, Y. Zhao, Y. Gao, C.Y. Tang, Nanocomposite substrates for controlling internal concentration polarization in forward osmosis membranes, J. Membr. Sci. 441 (2013) 54-62.
[34] P. Zhong, X. Fu, T.-S. Chung, M. Weber, C. Maletzko, Development of thin-film composite forward osmosis hollow fiber membranes using direct sulfonated polyphenylenesulfone (sPPSU) as membrane substrates, Environ Sci. Technol. 47 (2013) 7430-7436.
[35] B. Deng, Effects of Polysulfone (PSf) Support Layer on the Performance of Thin-Film Composite (TFC) Membranes, J. Chem. Proc. Eng. 1 (2014) 1-8.
[36] D. Emadzadeh, W.J. Lau, M. Rahbari-Sisakht, A. Daneshfar, M. Ghanbari, A. Mayahi, T. Matsuura, A.F. Ismail, A novel thin film nanocomposite reverse osmosis membrane with superior anti-organic fouling affinity for water desalination, Desalination 368 (2014) 106-113.
[37] 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.
[38] S. Subramanian, R. Seeram, New directions in nanofiltration appl.—Are nanofibers the right material as membranes in desalination?, Desalination 308 (2013) 198-208.
[39] H. You, X. Li, Y. Yang, B. Wang, Z. Li, X. Wang, M. Zhu, B.S. Hsiao, High flux low pressure thin film nanocomposite ultrafiltration membranes based on nanofibrous substrates, Sep. Purif. Technol. 108 (2013) 143-151.
[40] A. Rahimpour, M. Jahanshahi, M. Peyravi, S. Khalili, Interlaboratory studies of highly permeable thin-film composite polyamide nanofiltration membrane, Polymers Adv. Technol. 23 (2012) 884-893.
[41] C.J. Kurth, B. Burk, Thin Film Nanocomposite Reverse Osmosis Membranes, Aquananotechnol.: Global Prospects, (2014) 305.
[42] A. Tiraferri, Improving the Performance and Antifouling Properties of Thin-Film Composite Membranes for Water Separation Technologies, Yale University, 2012.
[43] X. Pan, Y. Zhao, S. Liu, C.L. Korzeniewski, S. Wang, Z. Fan, Comparing graphene-TiO_2 nanowire and graphene-TiO_2 nanoparticle composite photocatalysts, ACS Appl. Mater. Interf. 4 (2012) 3944-3950.
[44] 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.
[45] B.W. Su, S.S. Han, Investigation on Preparation and Performance of Self-Assembly Nanofiltration Based on the Coordination, in: Adv. Mater. Res., Trans Tech Publication 2012, pp. 604-608.
[46] Y. Mansourpanah, S. Madaeni, A. Rahimpour, A. Farhadian, A. Taheri, Formation of appropriate sites on nanofiltration membrane surface for binding TiO_2 photo-catalyst: performance, characterization and fouling-resistant capability, J. Membr. Sci. 330 (2009) 297-306.
[47] S. Pourjafar, A. Rahimpour, M. Jahanshahi, Synthesis and characterization of PVA/PES thin film composite nanofiltration membrane modified with TiO_2 nanoparticles for better performance and surface properties, J. Indust. Eng. Chem. 18 (2012) 1398-1405.
[48] A. Rahimpour, M. Jahanshahi, B. Rajaeian, M. Rahimnejad, TiO_2 entrapped nano-composite PVDF/SPES membranes: Preparation, characterization, antifouling and antibacterial properties, Desalination 278 (2011) 343-353.
[49] S. Zhang, G. Qiu, Y.P. Ting, T.-S. Chung, Silver–PEGylated dendrimer nanocomposite coating for anti-fouling thin film composite membranes for water treatment, Colloids Surfaces A: Physicochem. Eng. Aspects 436 (2013) 207-214.
[50] M. Buonomenna, Nano-enhanced reverse osmosis membranes, Desalination 314 (2013) 73-88.
[51] H. Wu, B. Tang, P. Wu, Optimization, characterization and nanofiltration properties test of MWNTs/polyester thin film nanocomposite membrane, J. Membr. Sci. 428 (2013) 425-433.
[52] J. Nan Shen, C. Chao Yu, H. Min Ruan, C. Jie 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. Membr. Sci. 442 (2013) 18-26.
[53] M. Fathizadeh, A. Aroujalian, A. Raisi, M. Fotouhi, Preparation and characterization of thin film nanocomposite membrane for pervaporative dehydration of aqueous alcohol solutions, Desalination 314 (2013) 20-27.
[54] M. Asghari, A. Mahmudi, V. Zargar, G. Khanbabaei, Effect of polyethyleneglycol on CH_4 permeation through poly (amide-b-ethylene oxide)-based nanocomposite membranes, Appl. Surf. Sci. 318 (2014) 218-222.
[55] P. Daraei, S.S. Madaeni, E. Salehi, N. Ghaemi, H.S. Ghari, M.A. Khadivi, E. Rostami, Novel thin film composite membrane fabricated by mixed matrix nanoclay/chitosan on PVDF microfiltration support: Preparation, characterization and performance in dye removal, J. Membr. Sci. 436 (2013) 97-108.
[56] M. Ghanbari, D. Emadzadeh, W. Lau, T. Matsuura, A. Ismail, Synthesis and characterization of novel thin film nanocomposite reverse osmosis membranes with improved organic fouling properties for water desalination, RSC Adv. 5 (2015) 21268-21276.
[57] H. Wu, B. Tang, P. Wu, Optimizing polyamide thin film composite membrane covalently bonded with modified mesoporous silica nanoparticles, J. Membr. Sci. 428 (2013) 341-348.
[58] J. Wu, C. Yu, Q. Li, Regenerable antimicrobial activity in polyamide thin film nanocomposite membranes, J. Membr. Sci. 476 (2015) 119-127.
[59] H. Dong, L. Zhao, L. Zhang, H. Chen, C. Gao, W.W. Ho, High-flux reverse osmosis membranes incorporated with NaY zeolite nanoparticles for brackish water desalination, J. Membr. Sci. 476 (2015) 373-383.
[60] M.B. Dixon, D. Kim-Hak, Improving second-pass permeate quality using thin film nanocomposite (TFN) membranes, Desal. Water Treat. 55 (2014) 2962-2966.
[61] H. Huang, X. Qu, H. Dong, L. Zhang, H. Chen, Role of NaA zeolites in the interfacial polymerization process towards a polyamide nanocomposite reverse osmosis membrane, RSC Adv. 3 (2013) 8203-8207.
[62] D. Emadzadeh, W. Lau, T. Matsuura, N. Hilal, A. Ismail, The potential of thin film nanocomposite membrane in reducing organic fouling in forward osmosis process, Desalination 348 (2014) 82-88.
[63] V. Vatanpour, M. Esmaeili, M.H.D.A. Farahani, Fouling reduction and retention increment of polyethersulfone nanofiltration membranes embedded by amine-functionalized multi-walled carbon nanotubes, J. Membr. Sci. 466 (2014) 70-81.
[64] J. Kim, A. Sotto, J. Chang, D. Nam, A. Boromand, B. Van der Bruggen, Embedding TiO_2 nanoparticles versus surface coating by layer-by-layer deposition on nanoporous polymeric films, Microporous Mesoporous Mater. 173 (2013) 121-128.
[65] G.-d. Kang, Y.-m. Cao, Development of antifouling reverse osmosis membranes for water treatment: a review, Wat. Res. 46 (2012) 584-600.
[66] R. Voo, M. Mariatti, L. Sim, Flexibility improvement of epoxy nanocomposites thin films using various flexibilizing additives, Composites B: Eng. 43 (2012) 3037-3043.
[67] L. Zhao, P.C.-Y. Chang, W.W. Ho, High-flux reverse osmosis membranes incorporated with hydrophilic additives for brackish water desalination, Desalination 308 (2013) 225-232.
[68] F. Rahman, Calcium sulfate precipitation studies with scale inhibitors for reverse osmosis desalination, Desalination 319 (2013) 79-84.
[69] A. Chapelle, I. El Younsi, S. Vitale, Y. Thimont, T. Nelis, L. Presmanes, A. Barnabé, P. Tailhades, Improved semiconducting $CuO/CuFe_2O_4$ nanostructured thin films for CO_2 gas sensing, Sensors and Actuators B: Chem. 204 (2014) 407-413.
[70] 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, Wat. Res. 62 (2014) 260-270.
[71] H. Kim, K.-M. Kang, W. Han, Y.C. Chang, H.-H. Park, In-situ incorporation of Pt nanoparticles in fluorine-doped SnO_2 nanocomposite thin films by a one-step synthesis, Chem. Lett. (2015).

[72] T.-Y. Liu, Z.-H. Liu, R.-X. Zhang, Y. Wang, B. Van der Bruggen, X.-L. Wang, Fabrication of a thin film nanocomposite hollow fiber nanofiltration membrane for wastewater treatment, J. Membr. Sci. 488 (2015) 92-102.

[73] N. Bala, S. Saha, M. Chakraborty, M. Maiti, S. Das, R. Basu, P. Nandy, Green synthesis of zinc oxide nanoparticles using Hibiscus subdariffa leaf extract: effect of temperature on synthesis, anti-bacterial activity and anti-diabetic activity, RSC Adv. 5 (2015) 4993-5003.

[74] A. AL-Hobaib, J. El Ghoul, L. El Mir, Fabrication of polyamide membrane reached by $MgTiO_3$ nanoparticles for ground water purification, Desal. Water Treat. 57 (2015) 8639-8648.

[75] A. Wolosiuk, N.s.G. Tognalli, E.D. Martínez, M. Granada, M.C. Fuertes, H. Troiani, S.A. Bilmes, A. Fainstein, G.J. Soler-Illia, Silver nanoparticle-mesoporous oxide nanocomposite thin films: A platform for spatially homogeneous SERS-active substrates with enhanced stability, ACS Appl. Mater. Interf. 6 (2014) 5263-5272.

[76] 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. Membr. Sci. 476 (2015) 303-310.

[77] A. Mohammad, Y. Teow, W. Ang, Y. Chung, D. Oatley-Radcliffe, N. Hilal, Nanofiltration membranes review: Recent advances and future prospects, Desalination 356 (2015) 226-254.

[78] D. Kim-Hak, M.B. Dixon, M.A. Galan, F. Boisseau, J. Gallastegui, R. Martina, Santa Barbara, Curacao desalination plant expansion using NanoH_2O thin film nanocomposite (TFN) SWRO membrane, Desal. Water Treat. 55 (2015) 2446-2452.

[79] D. Li, H. Wang, Thin film nanocomposite membranes for water desalination, Funct. Nanostruct. Mater. Membr. Water Treat. 6 (2013) 163-194.

[80] H. Dong, X.-Y. Qu, L. Zhang, L.-H. Cheng, H.-L. Chen, C.-J. Gao, Preparation and characterization of surface-modified zeolite-polyamide thin film nanocomposite membranes for desalination, Desal. Water Treat. 34 (2011) 6-12.

[81] P.S. Goh, A.F. Ismail, Review: is interplay between nanomaterial and membrane technology the way forward for desalination?, J. Chem. Technol. Biotechnol. 90 (2014) 971-980.

[82] A. Subramani, N. Voutchkov, J.G. Jacangelo, Desalination energy minimization using thin film nanocomposite membranes, Desalination 350 (2014) 35-43.

[83] C.Y. Tang, M. Reinhard, J.O. Leckie, Effects of hypochlorous acid exposure on the rejection of salt, polyethylene glycols, boron and arsenic (V) by nanofiltration and reverse osmosis membranes, Wat. Res. 46 (2012) 5217-5223.

[84] Y. Yu, C. Zhao, Y. Wang, W. Fan, Z. Luan, Effects of ion concentration and natural organic matter on arsenic (V) removal by nanofiltration under different transmembrane pressures, J. Environ. Sci. 25 (2013) 302-307.

[85] R. Harisha, K. Hosamani, R. Keri, S. Nataraj, T. Aminabhavi, Arsenic removal from drinking water using thin film composite nanofiltration membrane, Desalination 252 (2010) 75-80.

[86] X. Wei, S. Wang, Y. Shi, H. Xiang, J. Chen, Application of positively charged composite hollow-fiber nanofiltration membranes for dye purification, Ind. Eng. Chem. Res. 53 (2014) 14036-14045.

[87] 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. Interf. 5 (2013) 6649-6656.

[88] T. Matsuura, Reverse osmosis and nanofiltration by composite polyphenylene oxide, in: G. Chowdhury, B. Kruczek, T. Matsuura (Eds.) Polyphenylene oxide and modified polyphenylene oxide membranes, Gas, vapor and liquid separation, Springer Science+Business Media, New York, 2013, pp. 181-212.

[89] Y.-L. Lin, J.-H. Chiou, C.-H. Lee, Effect of silica fouling on the removal of pharmaceuticals and personal care products by nanofiltration and reverse osmosis membranes, J. Hazard. Mater. 277 (2014) 102-109.

[90] J. Radjenović, M. Petrović, F. Ventura, D. Barceló, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment, Wat. Res. 42 (2008) 3601-3610.

[91] K. Wong, P. Goh, A. Ismail, Gas separation performance of thin film nanocomposite membranes incorporated with polymethyl methacrylate grafted multi-walled carbon nanotubes, Int. Biodeter. Biodegr. 102 (2015) 339-345.

[92] L.F. Sotoft, K.V. Christensen, R. Andrésen, B. Norddahl, Full scale plant with membrane based concentration of blackcurrant juice on the basis of laboratory and pilot scale tests, Chem. Eng. Process. Process Intensification, 54 (2012) 12-21.

[93] M. Sivakumar, D.R. Mohan, R. Rangarajan, Studies on cellulose acetate-polysulfone ultrafiltration membranes: II. Effect of additive concentration, J. Membr. Sci. 268 (2006) 208-219.

[94] D. Edwards, A. Donn, C. Meadowcroft, Membrane solution to a “significant risk” Cryptosporidium groundwater source, Desalination 137 (2001) 193-198.

[95] R. Jurenka, S. Martella, R. Rodriguez, Water treatment primer for communities in need, Denver: Bureau of Reclamation, 2001.

[96] J.G. Jacangelo, S. Adham, J.-M. Laîné, Membrane filtration for microbial removal, American Water Works Association, 1997.

[97] A. Mohammad, N. Hilal, H. Al-Zoubib, N. Darwish, N. Ali, Modelling the effects of nanofiltration membrane properties on system cost assessment for desalination application, Desalination 206 (2007) 215-225.

[98] U. Lachish, Optimizing the efficiency of reverse osmosis seawater desalination, 2002.

[99] 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.

[100] N. Ma, C. Liu, P.J. Wang, C.Y. Tang, Study on nanocomposite membranes with enhanced performance for forward osmosis, Adv. Mater. Res. 900 (2014) 191-196.

[101] C. Klaysom, S. Hermans, A. Gahlaut, S. van Craenenbroeck, I.F. Vankelecom, Polyamide/polyacrylonitrile (PA/PAN) thin film composite osmosis membranes: Film optimization, characterization and performance evaluation, J. Membr. Sci., 445 (2013) 25-33.

[102] X.-N. Chen, L.-S. Wan, Q.-Y. Wu, S.-H. Zhi, Z.-K. Xu, Mineralized polyacrylonitrile-based ultrafiltration membranes with improved water flux and rejection towards dye, J. Membr. Sci. 441 (2013) 112-119.

[103] K. Parashuram, S. Maurya, H. Rana, P. Singh, P. Ray, A. Reddy, Tailoring the molecular weight cut off values of polyacrylonitrile based hollow fibre ultrafiltration membranes with improved fouling resistance by chem. modification, J. Membr. Sci. 425 (2013) 251-261.

[104] Z.-D. Fei, L.-S. Wan, W.-M. Wang, M.-Q. Zhong, Z.-K. Xu, Thermo-responsive polyacrylonitrile membranes prepared with poly (acrylonitrile-g-isopropylacrylamide) as an additive, J. Membr. Sci. 432 (2013) 42-49.

[105] X. Li, K.Y. Wang, B. Helmer, T.-S. Chung, Thin-film composite membranes and formation mechanism of thin-film layers on hydrophilic cellulose acetate propionate substrates for forward osmosis processes, Ind. Eng. Chem. Res. 51 (2012) 10039-10050.

[106] J. Su, R.C. Ong, P. Wang, T.S. Chung, B.J. Helmer, J.S. Wit, Advanced FO membranes from newly synthesized CAP polymer for wastewater reclamation through an integrated FO-MD hybrid system, AIChE J. 59 (2013) 1245-1254.

[107] H.-H. Tseng, G.-L. Zhuang, Y.-C. Su, The effect of blending ratio on the compatibility, morphology, thermal behavior and pure water permeation of asymmetric CAP/PVDF membranes, Desalination 284 (2012) 269-278.

[108] M.A.H. Asgarkhani, S.M. Mousavi, E. Saljoughi, Cellulose acetate butyrate membrane containing TiO_2 nanoparticle: Preparation, characterization and permeation study, Korean J. Chem. Eng. 30 (2013) 1819-1824.

[109] A. Asmadi, Asmadi A. Synthesis, characterizationa performance of polysulfone/cellulose acetate phthalate/polyvinylpyrrolidone (PSf/CAP/PVP) blend ultrafiltration membranes, Doctoral dissertation, Universiti Malaysia Pahang, 2013.

[110] T.-S. Chung, K. Wang, Forward osmosis membrane and method of manufacture, US Patent 13/984,454, 2012.

[111] A. Ahmad, A. Abdulkarim, S. Ismail, B. Ooi, Preparation and characterisation of PES-ZnO mixed matrix membranes for humic acid removal, Desal. Water Treat., 54 (2015) 3257-3268.

[112] A. Rahimpour, M. Jahanshahi, S. Khalili, A. Mollahosseini, A. Zirepour, B. Rajaeian, Novel functionalized carbon nanotubes for improving the surface properties and performance of polyethersulfone (PES) membrane, Desalination 286 (2012) 99-107.

[113] A. Sotto, A. Rashed, R.-X. Zhang, A. Martínez, L. Braken, P. Luis, B. Van der Bruggen, Improved membrane structures for seawater desalination by studying the influence of sublayers, Desalination 287 (2012) 317-325.

[114] B. Vatsha, J.C. Ngila, R.M. Moutloali, Preparation of antifouling polyvinylpyrrolidone (PVP 40K) modified polyethersulfone (PES) ultrafiltration (UF) membrane for water purification, Phys. Chem. Earth, Parts A/B/C, 67 (2014) 125-131.

[115] J. Huang, K. Zhang, K. Wang, Z. Xie, B. Ladewig, H. Wang, Fabrication of polyethersulfone-mesoporous silica nanocomposite ultrafiltration membranes with antifouling properties, J. Membr. Sci. 423 (2012) 362-370.

[116] P. Moradihamedani, N.A. Ibrahim, W.M.Z.W. Yunus, N.A. Yusof, Separation of CO_2 from CH_4 by pure PSF and PSF/PVP blend membranes: Effects of type of nonsolvent, solvent, and PVP concentration, J. Appl. Polym. Sci. 130 (2013) 1139-1147.

[117] M. Safarpour, A. Khataee, V. Vatanpour, Thin film nanocomposite reverse osmosis membrane modified by reduced graphene oxide/TiO_2 with improved desalination performance, J. Membr. Sci. 489 (2015) 43-54.

[118] A. Peyki, A. Rahimpour, M. Jahanshahi, Preparation and characterization of thin film composite reverse osmosis membranes incorporated with hydrophilic SiO_2 nanoparticles, Desalination 368 (2015) 152-158.

[119] H. Zhao, S. Qiu, L. Wu, L. Zhang, H. Chen, C. Gao, Improving the performance of polyamide reverse osmosis membrane by incorporation of modified multi-walled carbon nanotubes, J. Membr. Sci. 450 (2014) 249-256.

[120] T. Tsuru, S. Sasaki, T. Kamada, T. Shintani, T. Ohara, H. Nagasawa, K. Nishida, M. Kanezashi, T. Yoshioka, Multilayered polyamide membranes by spray-assisted 2-step interfacial polym.ization for increased performance of trimesoyl chloride (TMC)/m-phenylenediamine (MPD)-derived polyamide membranes, J. Membr. Sci. 446 (2013) 504-512.

[121] 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.

[122] 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.

[123] Y. Zhang, Y. Su, J. Peng, X. Zhao, J. Liu, J. Zhao, Z. Jiang, Composite nanofiltration membranes prepared by interfacial polymerization with natural material tannic acid and trimesoyl chloride, J. Membr. Sci. 429 (2013) 235-242.

[124] C.C. Yu, H.W. Yu, Y.X. Chu, H.M. Ruan, J.N. Shen, Preparation thin film nanocomposite membrane incorporating PMMA modified MWNT for nanofiltration, Key Eng. Mater. 562 (2013) 882-886.

[125] D. Hu, Z.-L. Xu, Y.-M. Wei, Y.-F. Liu, Poly (styrene sulfonic acid) sodium modified nanofiltration membranes with improved permeability for the softening of highly concentrated seawater, Desalination 336 (2014) 179-186.

[126] P. Wang, J. Ma, Z. Wang, F. Shi, Q. Liu, Enhanced separation performance of PVDF/PVP-g-MMT nanocomposite ultrafiltration membrane based on the NVP-grafted polymerization modification of montmorillonite (MMT), Langmuir 28 (2012) 4776-4786.

[127] K.H. Mah, W.M. Hafizuddin, W. Yussof, M. Nizam, A. Seman, J. Nurul Ain, Study on factors affecting separation of xylose from glucose by nanofiltration using composite membrane developed from triethanolamine (Teoa) and trimesoyl Chloride (TMC), in: Proceedings of the 27th Symposium of Malaysian Chemical

Engineers (SOMChE 2014) in conjuction with 21st Regional Synposium on Chemical Engineering (RSCE 2014), 29-30 October 2014, Taylor's University Lakeside Campus, Subang Jaya., pp. 1-10.

[128] M.A. Seman, N. Jalanni, C. Faizal, N. Hilal, Polyester Thin Film Composite Nanofiltration Membranes Prepared by Interfacial Polymerization Technique for Removal of Humic Acid, in: R. Pogaku, A. Bono, C. Chu (Eds.) Developments in sustainable Chemical and Bioprocess Technology, Springer Science+Business Media, New York, 2013, pp. 111-117.

[129] S. Li, S. Zhang, Q. Zhang, G. Qin, Assembly of an unbalanced charged polyampholyte onto Nafion® to produce high-performance composite membranes, Chem. Commun. 48 (2012) 12201-12203.

[130] D. Hu, Z.-L. Xu, Y.-M. Wei, A high performance silica–fluoropolyamide nanofiltration membrane prepared by interfacial polymerization, Sep. Purif. Technol. 110 (2013) 31-38.

[131] A. Ghosh, R. Bindal, S. Prabhakar, P. Tewari, Composite polyamide reverse osmosis (RO) membranes–Recent developments and future directions, BARC Newsletter 321 (2011) 43-51.

[132] W. Lau, A. Ismail, P. Goh, N. Hilal, B. Ooi, Characterization methods of thin film composite nanofiltration membranes, Sep. Purif. Rev. 44 (2015) 135-156.

[133] T.N. Nilsen, I.L. Alsvik, Thin film composites, US Patent 13/701,520, 2011.

[134] 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.

[135] L.-F. Liu, Z.-B. Cai, J.-N. Shen, L.-X. Wu, E.M. Hoek, C.-J. Gao, Fabrication and characterization of a novel poly (amide-urethane@ imide) TFC reverse osmosis membrane with chlorine-tolerant property, J. Membr. Sci. 469 (2014) 397-409.

[136] S.G. Kim, S.Y. Park, J.H. Chun, B.-H. Chun, S.H. Kim, Novel thin-film composite membrane for seawater desalination with sulfonated poly (arylene ether sulfone) containing amino groups, Desal. Water Treat. 43 (2012) 230-237.

[137] A. Wang, H. Yin, M. Ren, X. Cheng, Q. Zhou, X. Zhang, Effects of different functional group-containing organics on morphology-controlled synthesis of silver nanoparticles at room temperature, Acta Metall. Sin. Engl. 19 (2006) 362-370.

[138] Y. Li, W. Gao, L. Ci, C. Wang, P.M. Ajayan, Catalytic performance of Pt nanoparticles on reduced graphene oxide for methanol electro-oxidation, Carbon 48 (2010) 1124-1130.

[139] J. Kim, B. Van der Bruggen, The use of nanoparticles in polymeric and ceramic membrane structures: review of manufacturing procedures and performance improvement for water treatment, Environ. Pollut. 158 (2010) 2335-2349.