# EXPLORING THE POTENTIAL OF NANOFILLERS FOR ADVANCED THIN FILM NANOCOMPOSITE FORWARD OSMOSIS MEMBRANES FABRICATION

MOHAMMAD GHANBARI

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Universiti Teknologi Malaysia

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## DEDICATION

*I dedicate this dissertation to my beloved family;*

*my dear father;*

*and my merciful mother. for her encouragement*

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# ABSTRACT

Novel and promising forward osmosis (FO) is a membrane-based separation with significant potentials for the desalination process. While this technology offers various benefits, overcoming its internal concentration polarization (ICP) and membrane fouling in polyamide (PA) skin layer remain as a challenge. In this study, three types of novel thin film nanocomposite (TFN) membranes were synthesized by either coating a typical PA film over the surface of substrate made of polysulfone–halloysite nanotubes (HNTs) or embedding HNTs and titanium dioxide ($TiO_2$)/HNTs nanocomposites into PA thin layer formed over a typical polysulfone (PSF) substrate. These approaches aim to reduce membrane fouling and/or ICP during FO applications. In the first stage of this study, both hydrophilicity and porosity of the substrate were increased using HNTs. The results obtained from filtration experiments showed that the TFN membrane prepared with incorporation of 0.5 wt% HNTs (TFN 0.5) demonstrated the most satisfactory results by exhibiting high water permeability and low reverse solute flux in both FO and pressure retarded osmosis (PRO) configurations. This improvement can be ascribed to the fact that the structural parameter (S value) of TFN membrane is much lower compared to that of control thin film composite (TFC) membrane (0.37 vs 0.95 mm), leading to reduced ICP effect. In the second stage of this study, both hydrophilicity and surface roughness of TFN membranes increased with incorporation of HNTs into PA layer. In the FO mode, the fabricated TFN FO membrane in this study exhibited significantly higher fouling resistance compared to the control TFC membrane. As an indication to reversibility of fouling in TFN FO membrane, it was also found that more than 96% permeate flux could be recovered after a simple water rinsing process. In the third stage of this study, $TiO_2$/HNTs nanocomposites synthesized via one-step solvothermal method were used as nanofillers in the preparation of TFN membranes for the FO application. With respect to separation performance, it was discovered that the TFN membrane incorporated with 0.05% (w/v) $TiO_2$/HNTs (TFN 0.05) exhibited the best performance due to its high water permeability and low reverse solute flux when tested using 10 mM sodium chloride (NaCl) feed solution and 2.0 M NaCl draw solution under two different membrane configurations. Compared to the control membrane (without $TiO_2$/HNTs incorporation), the fabricated TFN 0.05 membrane could offer up to 90% higher water flux and exhibited significantly better antifouling affinity against bovine serum albumin (BSA). The results revealed that fouling in the TFN 0.05 membrane was completely reversible. As a conclusion, it was found that modifying the PA skin layer of composite membrane using $TiO_2$/HNTs as nanofillers could give the most promising results, improving not only membrane permeability and selectivity but also its anti-fouling property.

# ABSTRAK

Proses osmosis hadapan (FO) yang novel adalah satu teknik pemisahan berasaskan membran yang berpotensi besar untuk proses penyahgaraman. Walaupun teknologi ini menawarkan pelbagai kelebihan, cabaran utama yang perlu diatasi adalah polarisasi kepekatan dalaman (ICP) dan kotoran membran pada lapisan aktif poliamida (PA). Dalam kajian ini, tiga jenis novel membran filem nanokomposit nipis (TFN) telah disintesis sama ada melalui kaedah penyalutan filem PA di atas permukaan substrat yang diperbuat daripada polisulfona- tiub nano haloisit (HNTs) atau menggabungkan HNTs dan titanium dioksida ($TiO_2$)/HNTs nanokomposit dengan lapisan nipis PA yang terbentuk di atas substrat polisulfona (PSF). Pendekatan ini bertujuan untuk mengurangkan kotoran membran dan/atau ICP semasa proses FO. Pada peringkat pertama kajian, kehidrofilikan dan keliangan substrat PSF telah meningkat selepas penambahan HNTs. Keputusan yang diperoleh daripada kajian turasan telah mendapati membran TFN yang diperbuat daripada 0.5% berat HNTs dalam substrat (TFN 0.5) menunjukkan fluks air yang tinggi dan fluks bahan terlarut yang rendah dalam konfigurasi FO dan konfigurasi tekanan osmosis terbantut (PRO). Peningkatan ini disebabkan oleh parameter struktur (nilai S) untuk membran TFN yang jauh lebih rendah berbanding dengan membran kawalan filem komposit nipis (TFC) (0.37 vs 0.95 mm), yang mengakibatkan kepada pengurangan kesan ICP. Pada peringkat kedua kajian, kehidrofilikan dan kekasaran permukaan membran TFN meningkat dengan penambahan HNTs ke dalam lapisan PA. Pada mod FO, membran TFN FO mempunyai rintangan kotoran yang lebih tinggi berbanding dengan membran kawalan TFC. Bagi membuktikan keboleh-balikan kotoran dalam membran TFN FO, hasil kajian menunjukkan bahawa lebih daripada 96% fluks boleh diperoleh semula selepas proses pembilasan air yang mudah. Pada peringkat ketiga kajian, nanokomposit $TiO_2$/HNTs yang disintesis melalui kaedah solvoterma telah digunakan sebagai pengisi-nano dalam penyediaan membran TFN untuk proses FO. Hasil kajian menunjukkan bahawa membran TFN yang digabungkan dengan 0.05% (berat/isipadu) $TiO_2$/HNTs (TFN 0.05) mempunyai prestasi yang terbaik dengan kebolehtelapan air yang tinggi dan fluks bahan larut balikan yang rendah apabila diuji menggunakan 10 mM natrium klorida (NaCl) larutan suapan dan 2.0 M NaCl larutan luaran pada dua konfigurasi membran yang berbeza. Berbanding dengan membran kawalan (tanpa $TiO_2$/HNTs), membran TFN 0.05 mampu menghasilkan fluks air 90% lebih tinggi dan sifat anti-kotoran terhadap serum bovin albumin (BSA) yang jauh lebih baik. Hasil kajian juga menunjukkan bahawa kotoran pada membran TFN 0.05 boleh berbalik. Kesimpulannya, pengubahsuaian lapisan aktif PA membran komposit menggunakan $TiO_2$/HNTs sebagai pengisinano boleh meningkatkan bukan sahaja kebolehtelapan dan kememilihan membran tetapi juga sifat anti-kotorannya.

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## LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| Sc | - | Schmidt number |
| Sh | - | Sherwood number |
| $C_P$ | - | Concentration polarization |
| CTA | - | Cellulose triacetate |
| ECP | - | External concentration polarization |
| FO | - | Forward Osmosis |
| FTIR | - | Fourier Transform Infrared Spectroscopy |
| HTI | - | Hydration Technologies Inc |
| HNT | - | Halloysite nanotube |
| ICP | - | Internal concentration polarization |
| XRD | - | X-ray diffractometer |
| $M_W$ | - | Molecular weight |
| NF | - | Nanofiltration |
| PA | - | Polyamide |
| PAI | - | Polyamide-imide |
| PAN | - | Polyacrylonitrile |
| AFM | - | Atomic force microscopy |
| DMAc | - | Dimethylacetamide |
| MPD | - | 1,3-Phenylendiamine |

| | | |
|---|---|---|
| PEG | - | Polyethylene Glycol |
| TMC | - | 1,3,5-enzenetricarbonyl Trichloride |
| PES | - | Polyether sulfone |
| PI | - | Polyimide |
| PIP | - | Piparazine |
| TEM | - | transmission electron microscopy |
| PRO | - | Pressure retarded osmosis |
| PSF | - | Polysulfone |
| PS | - | Polystyrene |
| FESEM | - | Field Emission Scanning Electronic Microscope |
| PVP | - | Polyvinylpyrolidone |
| Re | - | Reynolds number |
| RO | - | Reverse osmosis |
| SEM | - | Scanning Electron Microscope |
| sPEEK | - | Sulfonated poly(ether ether ketone) |
| sPSf | - | Sulfonated polyethersulfone |
| TFC | - | Thin-film composite |
| TEA | - | Triethylamide |
| UF | - | Ultrafiltration |

## LIST OF SYMBOLS

| | | |
|---|---|---|
| A | - | Water permeability coefficient ($m^3/m^2.s.Pa$) |
| B | - | Solute permeability coefficient (m/s) |
| C | - | Concentrationof salt (mol/l) |
| $C_{F,b}$, $C_{D,b}$ | - | Salt concentration of the bulk feed and draw solution |
| $C_{F,i}$, $C_{D,i}$ | - | Concentration of feed and draw solution near membrane surface inside porous supports |
| $C_{F,m}$, $C_{D,m}$ | - | Concentration of feed and draw solution near membrane surface |
| D | - | Solute diffusion coefficient ($m^2\ s^{-1}$) |
| IP | - | Interfacial polymerization |
| Js | - | Reverse salt flux ($g\ m^{-2}\ h^{-1}$) |
| Jw | - | Water flux ($m^3 m^{-2}\ s^{-1}$) |
| K | - | Water transport coefficient ($m.s^{-1}$) |
| L/t | - | Thickness( $\mu$ m) |
| M | - | Molality (M) |
| MWCO | - | Molecular weight cut-off (kDa) |
| P | - | Pressure (bar) |
| p | - | Material density ($g.cm^{-3}$) |
| R | - | Solute rejection (%) |

| | | |
|---|---|---|
| S | - | Membrane structural parameter (m) |
| T | - | Membrane thickness (m) |
| W | - | Power ($W/m^2$) |
| $W_d$ | - | Dry membrane weight(g) |
| $W_w$ | - | Wet membrane weight (g) |
| $\pi$ | - | Osmotic pressure (Pa) |
| $\pi_{F,b}$, $\pi_{D,b}$ | - | Osmotic pressure of the bulk feed and draw solution (Pa) |
| $\pi_{F,m}$, $\pi_{D,m}$ | - | Osmotic pressure of feed and draw solution near membrane surface (Pa) |
| $\pi_{F,i}$, $\pi_{D,I}$ | - | Osmotic pressure of feed and draw solution near membrane surface inside porous supports (Pa) |
| $\Delta P$ | - | hydraulicpressuredifference (bar) |
| $\Delta\pi, \Delta\pi_{eff}$ | - | Osmotic pressure difference and effective osmotic pressure difference (Pa) |
| $\varepsilon$ | - | Membrane porosity |
| $\sigma$ | - | Reflection coefficient |
| $\tau$ | - | Pore tortuosity |

## LIST OF APPENDICES

# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background

Scarcity of fresh water caused by social, economic, and technological developments has become a major concern for many countries. Increment in population and development of countries have resulted in pollution of drinking water sources like rivers, lakes and groundwater. This phenomena cause increase in salinity of the water resources or diminishment of some safe resources. Emerging water shortage problems may push the world toward a very disastrous situation. As a result, water related problems are currently very important issues all over the world and two main solutions are proposed to solve this problem. They are water recovery and water desalination. However, it should be emphasized here that quality of recovered water is not high enough to be used in human water drinking section. In fact, this kind of water is suitable for applications like irrigation, plant cooling water and groundwater regeneration. On the other hand, water desalination technique is a trustable method to produce high quality fresh water for human drinking. Also, it is necessary to remind that brackish and seawater are infinite resources which can be used in desalination processes (Greenlee *et al.*, 2009).

In the desalination process, the saline water is cleaned from salts and non-ionic minerals in such extent that allows it to be used in customary drinking. Sharp increase in population of the world and the subsequent need for supplying fresh water have motivated researchers to utilize new methods for providing clean water. Various methods are applied to clean inland brackish water as well as seawater. The total dissolved solids (TDS) in the former and latter are 10,000 and 35,000 mg/L, respectively. Current desalination methods are based on membrane or thermal desalination. The most important thermal methods include multi-effect distillation (MED), multistage flash (MSF) and vapour condensation (VC) whereas reverse osmosis (RO) is the most used membrane method. In thermal distillation method, after boiling the polluted water at low pressure, the resultant vapour is collected and distilled to gain fresh water. In RO processes, however, the water molecules are forced to diffuse into a membrane by applied hydraulic pressure while passage of salts molecules is not possible. From economical point of view, a high amount of energy is needed to evaporate water from salty solution and this makes the thermal methods more expensive in comparison with RO ones which use only electricity. Membrane methods are associated with different advantages including low energy consumption, suppression of chemical usages and smaller operation space. Due to these benefits, membrane methods are replacing conventional thermal techniques in water purification industry (Greenlee *et al.*, 2009).

In 1970 when RO process was used widely in water purification industry, a new method named forward osmosis (FO) appeared for salt removal over the last decade (Zeng *et al.*, 2013; Zhang *et al.*, 2011). A brief literature review shows that the concept of FO was first developed theoretically by some researchers rather than being found experimentally. FO is a process in which osmotic pressure gradient forces water molecules to pass through a semi permeable membrane from the feed solution side toward draw solution side. The former solution has low osmotic pressure while the latter has high osmotic pressure (McGinnis and Elimelech, 2007). In the recent years, FO membranes are widely used in different areas like wastewater treatment, seawater/brackish desalination, food processing and power generation (McCutcheon *et al.*, 2005). The most important advantages which resulted in flourishing of FO are low energy consumption, low fouling and high water recovery. Other pressure-driven membrane processes like RO, nanofiltration (NF) and ultrafiltration (UF) do not benefit from such advantages. Most of these pros are originated from low hydraulic pressure demand of FO membranes (McGinnis and Elimelech, 2007).

Recently, thin film composite (TFC) FO membranes are introduced in two different forms including flat sheet and hollow fiber. Elimelech's group was the first research team who synthesized TFC FO membrane by the use of interfacial polymerization (IP) of phenylenediamine (MPD) and trimesoyl chloride (TMC). The polymerization was carried out on the surface of porous polysulfone (PSF) support layer cast on a polyester nonwoven fabric (Qiu *et al.*, 2011). Their investigations showed that substrate greatly affects TFC FO membrane performance (Tiraferri *et al.*, 2011b). The research in this area was continued by Wang *et al.* (2010b) where they fabricated hollow fiber FO membranes. They similarly performed interfacial polymerization of TMC and MPD on both inner and outer surface of porous polyethersulfone (PES) substrate (Chou *et al.*, 2010; Wang *et al.*, 2010b). According to their results, a preferred FO membrane structure includes a thin, highly porous substrate possessing very small part of sponge-like layer (Chou *et al.*, 2010). In addition, this group fabricated flat sheet TFC FO membrane which had a special morphology. The morphology consisted of finger-like pores under a thin sponge-like skin layer of PSF. It was concluded that the impact of substrate structure on the performance of FO membrane is great. Comparing straight finger-like pore morphology with the spongy pore structure of the support layer, the former shows lower internal concentration polarization (ICP) (Wei *et al.*, 2011b). In 2012, this group made a hollow fiber membrane for power generation through pressure retardant osmosis (PRO) process (Chou *et al.*, 2012).

By the use of IP method, TFC FO membranes containing sulfonated material were made by Widjojo *et al.* (2011). They reported that presence of sulfonated material can affect support layer significantly. As sulfonated material content increases, more sponge-like structure will develop. This positively affects permeate flux. In addition, it is widely reported that hydrophilicity of the substrate plays a critical role in FO performance because higher hydrophilicity facilitates diffusion of water molecules across the membrane (Widjojo *et al.*, 2011; McCutcheon and

Elimelech, 2008). By introducing sulfonated PES, Wang's group tried to increase hydrophilicity of the substrate and thereby improve FO membrane performance (Wang *et al.*, 2012b). Recently, Song *et al.* (2011) produced nanofiber TFC FO membrane through electrospinning and interfacial polymerization technique. This membrane has low tortuosity and high porosity which reduced membrane structural parameter and finally increased water flux. Ultimately, it was observed that water flux of nanofiber TFC FO membrane is three times higher than typical TFC FO membrane (Bui *et al.*, 2011).

Very recently, Emadzadeh *et al.* (2014b) modified the substrate of TFC FO membrane by addition of titanium dioxide ($TiO_2$) nanoparticles into PSF substrate . Experimental results verified that the FO membrane incorporated with 0.5 wt% $TiO_2$ demonstrated the most satisfactory results by exhibiting high water permeability and low reverse solute flux in both FO and pressure retardant osmosis (PRO) configurations. The flux improvement was around 90% and 71.5% comparing with the control TFC membrane for PRO and FO modes, respectively. Ma *et al.* (2013) studied effect of zeolite NaY nanoparticles on substrate of TFC membrane used for FO processes. Similar to $TiO_2$, it was reported that 0.5 wt% was the optimum value of zeolite NaY loading into nanocomposite substrate to simultaneously achieve high water flux and good solute rejection. This group also added NaY zeolite nanoparticles into a polyamide (PA) layer obtained by IP of MPD and TMC monomers to prepare a thin film nanocomposite (TFN) membrane for FO application (Ma *et al.*, 2012). Their investigations showed that by addition of only 0.1 wt/v% zeolite into PA layer, the best permeable TFN membrane with significantly higher water permeability than that of usual TFC membrane could be obtained. The improved water permeability is ascribed to the sub-nanometer pores existing in the zeolite particle. These pores create narrow size channels for transportation of water molecules.

## 1.2 Problem Statement

FO processes based on membrane technology have drawn attention of many scientific communities as a potential candidate for desalination processes (Chou *et al.*, 2010; Wang *et al.*, 2010b; Cath *et al.*, 2006). Low water permeability and salt rejection are two important drawbacks of the commercial FO membranes which limit their extensive application. On the other hand, TFC FO membranes containing porous support layer and a thin PA selective layer show higher water flux and better solute rejection in comparison with commercial FO membranes (Wei *et al.*, 2011b; Wang *et al.*, 2010b). Although various advantages of TFC membranes are mentioned here, they also suffer from some main challenges. These include low water flux, reverse solute diffusion, membrane fouling and internal concentration polarization. Considering these drawbacks, this research aims to prove performance of TFC FO membranes by tailoring both membrane selective layer and porous support layer.

In both FO and PRO processes, osmotic pressure difference is the driving force. In these membranes, features of the support layer strongly influence efficiency of the process. Here water molecules chemically diffuse across the membrane in both FO and PRO processes. As a result, decrease in flux can be expected due to internal concentration polarization (ICP). ICP refers to dilution of the draw solution in the porous substrate which leads to dramatic decrease in driving force across the FO membrane. It is concluded that ICP in FO process will be minimized if substrate layer has a small structural parameter, *S*, (McCutcheon and Elimelech, 2006). Moreover, substrates with higher hydrophilicity show lower resistance against water passage and allow more water productivity.

Various approaches have been considered for improving the performance of TFC FO membranes via modification of substrate. In this regard, different nanomaterials such as carbon nanotubes (CNTs) and $TiO_2$ have been incorporated in the substrate of TFC FO membranes to improve their performance and efficiency in minimizing ICP (Emadzadeh *et al.*, 2014b; Wang *et al.*, 2013). Among all these nanomaterials, halloysite nanotubes (HNTs) are much cheaper, possess a unique structure and can be easily harvested and obtained in all over the world (Ghanbari *et al.*, 2015b; Pan *et al.*, 2011). Presence of hydroxyl groups on the surface of HNTs has made them highly hydrophilic in nature. Moreover, HTNs benefit from high stability, exhibit acceptable rejection against organic solvents and can be easily disposed or reused, which are crucial factors for fabrication of a membrane suitable for water recovery applications (Wang *et al.*, 2011).

Another major issue faced by the most membrane based water separation processes including FO is extensive membrane fouling by which membrane performance declines in a long run. Due to their hydrophobicity and nanoscale "ridge-and-valley" morphology, fouling is an existing challenge for the aromatic TFC PA membranes used in FO processes (Lu *et al.*, 2013). While fouling mechanisms and antifouling surface modifications of TFC FO membranes has been extensively studies, poor attention has been given to investigate fouling-resistant TFN FO membranes. Therefore, it is important to study and analyse the fouling behaviour of TFN FO membranes under extensive experimental conditions. It can be expected that the presence of hydrophilic HNTs in PA selective layer of TFN FO membranes could significantly improve fouling resistant of such membranes in long filtration time. Implications of these porous nano materials are discussed with respect to the requirement for improved fouling resistant FO membranes in desalination and water purification.

Developing FO membrane with nanomaterials embedded within the thin PA selective layer could be a novel strategy to tailor the technical obstacles of FO membrane, owing to the unique characteristics of nanomaterials to match with the thickness of PA layer. Recently, advancements in nanotechnology have made it possible to fabricate desirable porous nano-materials suitable for FO membranes making (Zhao *et al.*, 2014). Among the nanomaterials available, nano-sized $TiO_2$ nanoparticles have been used widely to improve the characteristics of membranes owing to superhydrophilicity and potential of exhibiting antifouling behaviours (Cao *et al.*, 2006; Bae and Tak, 2005). However, it should be noted that commercial crystalline $TiO_2$ nanoparticles possess high surface energies and direct use of them as nanofillers for TFN membranes fabrication may cause significant particle aggregation. This agglomeration can further negatively affect the potential antifouling abilities of $TiO_2$ particles and result in surface defects in PA layer (Razmjou *et al.*, 2011). Supported technology, which relies on deposition of $TiO_2$ nanoparticles on the platform of supported nanomaterials with large surface area, is a promising and effective method for avoiding $TiO_2$ nanoparticles aggregation. The presence of hydroxyl radicals enable HNTs to be directly used as a support for $TiO_2$ nanoparticles. It can be concluded that the unique tubular structure of HNTs coupled with the excellent anti-fouling features of $TiO_2$ have made $TiO_2$/HNTs nanocomposites a reliable material with a bright perspective in improving the antifouling affinity of conventional thin film composite membranes for FO applications.

## 1.3 Objectives of the Study

Based on the aforementioned problem statements, the objectives of this study are:

i. To synthesize, characterize and evaluate TFN FO membrane with an optimized PSF-HNTs substrate for water desalination.

ii. To synthesize, characterize and evaluate TFN FO membrane with an optimized polyamide-HNTs selective layer for water desalination.

iii. To synthesize, characterize and evaluate TFN FO membrane with an optimized polyamide-$TiO_2$/HNTs selective layer for water desalination.

## 1.4 Scope of the Study

In order to achieve the objectives, the following scopes have been considered:

i. Synthesizing TFN FO membranes with top selective layer formed via interfacial polymerization of 1,3-phenylendiamine (MPD) in aqueous solution and 1,3,5-benzenetricarbonyl trichloride (TMC) in hexane solution over substrates made of different PSF-HNTs nanocomposite.

ii. Fabricating TFN FO membranes with different characteristics of polyamide selective layer by adding various concentrations of HNTs (zero-0.1 wt/v %) into TMC-cyclohexane solution.

iii. Synthesizing $TiO_2$/HNTs nanocomposites via one step solvothermal method and using them as nanofillers in the preparation of TFN membranes for FO application.

iv. Characterizing the properties of synthesized $TiO_2$/HNTs, PSF-HNTs TFN , PA-HNTs TFN and PA-$TiO_2$/HNTs TFN membranes using electron microscope (FESEM), atomic force microscope (AFM), transmission electron microscope (TEM), X-ray diffractometer (XRD), Fourier transform infrared spectroscope (FTIR), X-ray photoelectron spectroscope (XPS) and contact angle goniometer.

v. Evaluating the performances of synthesized TFN membranes in terms of water flux and reverse draw solute at different membrane configurations, i.e. FO (active layer facing feed solution) and PRO (active layer facing draw solution) mode.

vi. Comparing the performances of two well-known commercial FO membranes, i.e. HTI-ES and CTA-HW with synthesized TFN membranes in various process conditions.

vii. Determining S parameter values to evaluate the propensity of internal concentration polarization in the synthesized TFC/TFN membranes.

viii. Studying the organic fouling properties of synthesized TFC/TFN membranes through operation time in FO mode.

## 1.5 Organization of the Thesis

This thesis which consists of seven chapters describing synthesis of TFN membranes which will be used for water desalination through FO process. The first chapter gives a concise introduction to the desalination process and points out to the history of the research. The problem statement which determines the research direction is also illustrated in this chapter. Considering problem statement, the objective and scope of the research are explained. In chapter two, a literature review regarding FO systems for desalination is presented. FO is compared with other membranes used for desalination and its advantages are highlighted. Afterward, the challenges experienced during development of the FO membranes are described. Moreover, current investigations concerning development of TFC FO membranes are discussed. In chapter three, synthesis and characterization of $TiO_2$/HNTs and TFN FO membranes are discussed in details.

In chapter four, by addition of different quantity of halloysite nanotubes (HNTs) into PSF support, nanocomposite substrates are fabricated. Thin PA layers are formed over the substrates by performing interfacial polymerization. The resulting TFN membranes are used for water desalination in FO application. Chapter five introduces new antifouling HNTs-PA TFN FO membranes which are used for water desalination. In chapter six, synthesized $TiO_2$/HNTs are applied as nanofillers in preparation of high performance TFN membranes for water desalination. Finally, concluding remarks obtained from this research and general suggestions for future investigations are proposed in chapter seven.

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