THIN FILM NANOCOMPOSITE MEMBRANE INCORPORATED WITH SILVER-CARBON NANOTUBE HYBRID FOR DESALINATION

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DEDICATION

“My dearest family, lecturers and friends”

This is for all of you.

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ABSTRACT

Addressing water scarcity is an essential of the sustainable development's goal. One potential solution for new water resource is desalination. Forward osmosis (FO) desalination, utilizing the concept of osmotic pressure difference between high and low salinity streams across semipermeable membrane is of interest in the membrane research community in recent years. Nevertheless, practical application of FO desalination has been limited by the unsatisfactorily membrane performance to simultaneously offer high permeability and excellent anti-fouling properties. Hence, the overall goal of this study was the development of high-performance thin film nanocomposite (TFN) membrane with consistent water flux, high salt rejection and good biofouling resistance. Hybrid nanofiller, silver-functionalized carbon nanotubes, Ag-fCNTs synthesized via hydrothermal method was blended with PES dope solution and TFN membranes were fabricated by varying nanofiller loading (0.1, 0.3 and 0.5 wt%) using phase inversion followed by interfacial polymerization technique. Different characterizations such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and transmission electron microscope (TEM) confirmed the successful formation of Ag-fCNTs. The effects of Ag-fCNTs on the membrane properties and physical characteristics such as, chemical functionality, morphologies, surface roughness and surface hydrophilicity were analyzed. The resultant TFN membranes exhibited enhanced hydrophilicity, porosity and surface roughness, which in turn improved the overall membrane performance. Evaluation using dead-end reverse osmosis revealed that TFN membranes enhanced the water permeability without trade-off in salt rejection and the structural parameter (S) was reduced, indicating the suppression of internal concentration polarization. Furthermore, FO performance significantly improved e.g., the water flux of the optimum blending ratio, TFN0.3 achieved 27.99 l/m^2h in pressure retarded osmosis (PRO) mode by using 2.0 M NaCl/RO water as the draw/feed solution, while the specific salt flux was acceptable at 0.15 g/m^2h. However, antibacterial assessment and antibiofouling filtration experiments of pristine TFC and TFN membranes against the Gram-negative bacteria, *E. coli* demonstrated no noticeable antibacterial activity. This could be related to the small amount of Ag nanoparticles used (1:5 ratio) for Ag-fCNTs hybridization. Despite showing poor anti-biofouling properties, the promising water flux and salt rejection improvement implied the potential of the newly developed TFN for practical FO desalination application.

ABSTRAK

Mengatasi kekurangan air merupakan matlamat utama pembangunan mampan. Salah satu penyelesaian yang berpotensi untuk sumber air baru adalah penyahgaraman. Osmosis hadapan (FO) yang menggunakan konsep perbezaan tekanan osmotik antara aliran kemasinan tinggi dan rendah merentas membran separa telap telah menarik perhatian yang sangat besar dalam komuniti penyelidikan membran beberapa tahun kebelakangan ini. Namun begitu, aplikasi praktikal FO untuk penyahgaraman telah dibatasi oleh kekurangan prestasi membran untuk menawarkan kebolehtelapan yang tinggi dan ciri-ciri anti-kotoran yang baik. Oleh yang demikian, matlamat keseluruhan kajian ini adalah pembinaan membran filem nipis nanokomposit (TFN) prestasi tinggi dengan aliran air yang konsisten, penolakan garam yang tinggi dan rintangan kotoran yang baik. Bahan nano hibrid yang terdiri daripada zarah nano silver (Ag) dan nanotiub karbon berfungsi (fCNT) disintesis menggunakan kaedah hidroterma telah dicampur dengan larutan dop polieter sulfon (PES) dan membran TFN direka dengan pemuatan nanofiller yang berbeza-beza (0.1, 0.3, dan 0.5 wt%) dengan menggunakan teknik penyongsangan fasa diikuti dengan teknik pempolimeran antara muka. Pencirian yang berbeza seperti spektroskopi inframerah transformasi Fourier (FTIR), difraksi sinar-X (XRD) dan mikroskop elektron penghantaran (TEM) mengesahkan kejayaan pembentukan Ag-fCNT. Kesan Ag-fCNT pada sifat dan ciri fizikal membrane seperti fungsi kimia, morfologi, kekasaran permukaan dan hidrofilik permukaan telah dianalisis. Membran TFN yang dihasilkan menunjukkan peningkatan hidrofilik, keliangan dan kekasaran permukaan, yang seterusnya meningkatkan prestasi membran keseluruhan. Penilaian menggunakan osmosis terbalik (RO) menunjukkan membran TFN meningkatkan kebolehtelapan air tanpa menjejaskan penolakan garam dan parameter struktur (S) menurun menunjukkan berlakunya pengurangan pempolimeran kepekatan dalaman. Tambahan pula, aliran air bagi sampel nisbah pengadunan optimum, TFN0.3 mencapai 27.99 l/m^{2}h di bawah mod PRO dengan menggunakan 2.0 M NaCl /air RO sebagai larutan pengambilan/suapan, sementara fluks garam spesifik menunjukkan nilai yang dapat diterima iaitu 0.15 g/m^{2}h. Namun, penilaian antibakteria dan eksperimen penapisan antibiokotoran membran TFC dan TFN terhadap bakteria Gram-negatif, E. coli tidak menunjukkan aktiviti antibakteria yang ketara. Ini berkaitan dengan sejumlah kecil nanopartikel Ag yang digunakan (nisbah 1: 5) untuk penghibridan Ag-fCNTs. Walaupun menunjukkan sifat anti-biofouling yang tidak baik, penambahbaikan yang dijanjikan dalam aliran air dan penolakan garam mempunyai potensi dalam pembentukan TFN yang baru untuk aplikasi desalinasi FO praktikal.

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LIST OF ABBREVIATIONS

AFM - Atomic Force Microscopy
AL-DS - Active Layer Facing Draw Solution
AL-FS - Active Layer Facing Feed Solution
ATR-FTIR - Attenuated Total Reflectance-Fourier Transmission Infrared Spectroscopy
BSA - Bovine Serum Albumin
CN - Carbon Nitride
CNF - Carbon Nanofibers
CP - Concentration Polarization
DMF - Dimethylformamide
DS - Draw Solution
ECP - External Concentration Polarization
FESEM - Field Emission Scanning Electron Microscopy
FO - Forward Osmosis
FS - Feed Solution
FTIR - Fourier Transform Infrared Spectroscopy
ICP - Internal Concentration Polarization
IP - Interfacial Polymerization
MMM - Mixed Matrix Membrane
MOF - Metal Organic Framework
MPD - 1,3-phenylenediamine
NaCl - Sodium Chloride

NMP - N-methyl-2-pyrrolidone

NPs - Nanoparticles

PA - Polyamide

pCN - Protonated Carbon Nitride

PES - Polyethersulfone

PSf - Polysulfone

PVP - Polyvinylpyrolidone

RO - Reverse osmosis

SEM - Scanning electron microscopy

TEM - Transmission electron microscopy

TFC - Thin film composite

TFN - Thin film nanocomposite

TMC - Trimesoyl Chloride

XRD - X-ray Diffractometer

LIST OF SYMBOLS

A - Water permeability coefficient ($m^3/m^2.s.Pa$)

B - Solute permeability coefficient (m/s)

J_s - Reverse solute flux ($g.m^{-2}.h^{-1}$)

J_w - Water flux ($m^3.m^{-2}.s^{-1}$)

M - Molarity

P - Pressure

R - Salt Rejection

S - Membrane Structural Parameter

Π - Osmotic Pressure

ΔP - Hydraulic Pressure Difference

w/v - Weight over Volume

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Water scarcity is being driven by two converging phenomena which are growing freshwater use and depletion of usable freshwater resources. It can be a result of two mechanisms which are physical water scarcity and economic water scarcity (Wang *et al.*, 2018). Physical water scarcity is a result of inadequate natural water resources to supply a region's demand while economic water scarcity is a result of poor management of the sufficient available water resources. Due to water scarcity, technologies to produce clean water have received worldwide attention. Besides, the factors which caused the water scarcity might be climate change, such as altered weather patterns including droughts or floods, increased pollution and human demand, and overuse of water (Greenlee *et al.*, 2009).

Nowadays, addressing water scarcity issue is a goal of many countries and. Thus, the applications of desalination have received considerable interest in the recent decade (Chung *et al.*, 2015). Desalination is a process which converts saltwater into fresh water. Desalination has been developed and already being used for centuries to solve the water scarcity issues. The process consists of two main categories which are thermal distillation processes and membrane separation processes. Depending on the geographical conditions and availability of natural resources, both processes have received equal attention as a reliable source for drinking water production. The basic thermal approaches are multiple effect distillation (MED), multi-stage flash (MSF) and vapor compression distillation (VCD) while for membrane separation process, the methods involve nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED) (Misdan *et al.*, 2012). In comparison to membrane desalination technology, the conventional thermal desalination process was not competent in terms of energy consumption and create thermal and mechanical problems like tube clogging (Shatat and Riffat, 2014). Among available water treatment, desalination using membrane technology has attracted increasing research interest owing to low energy consumption, suppression of chemical usages and smaller operation space (Greenlee *et al.*, 2009).

Since 1960, RO has become one of the most prominent technology in desalination industry to produce high quality water from unusable water sources due to its low process cost as well as using latest membrane technology (Goh *et al.*, 2016). However, the growth of the RO technology has limited by a few restrictions such as relatively low water recovery factors, biofouling and high cost of electrical energy. This hence call for widespread applications of forward osmosis (FO) as a promising alternative membrane separation technology (Akther *et al.*, 2015). It is a process which involves the selective permeable membrane where osmotic pressure difference based on the concentration gradient of feed solution (FS) and draw solution (DS) is the driving force of water molecules to diffuse across the membrane (Goh *et al.*, 2013). The selective permeable membrane allows water to cross but blocks the unnecessary item like salt ions. In FO, the draw solution represented by the high salinity solution where it has a higher osmotic pressure than the feed solution thus encourages water flow across the selective permeable membrane from the feed to the draw. Therefore, compared to RO, FO needs less energy to transfer a net water flow across the membrane (Chung *et al.*, 2015).

The primary stumbling block for the progress of FO technology is the availability of membranes with desired properties such as promising separation performance in terms of water flux and salt rejection. Additionally, as membrane generally shows the tendency to be attached with various form of foulants which present in the water supply, the quality of the feed water is known to be influential to the membrane performance. The most commonly used configuration of FO membrane is thin film composite (TFC) membrane. Generally, TFC membranes have an asymmetric porous support and a top selective skin where the mechanical strength is provided by the micro-porous support and the separation are done by the selective skin layer (W. Xu *et al.*, 2017). Compared to the asymmetric cellulose acetate membrane counterpart, TFC demonstrated some advantages such as higher chemical resistant.

However, the major issue with TFC FO membrane is still the internal concentration polarization (ICP). ICP is caused by a dilution of the DS which consequently, reduced the osmotic pressure difference across the membrane active layer (AL). Unlike external concentration polarization (ECP) which occurs outside the membrane, ICP occurs inside the porous support hence cannot be mitigated by increasing the water flow rate or turbulence (Lee and Kim, 2016). TFC flat sheet membranes has been modified via various physical and chemical routes to reduce the ICP of membrane. Modification is performed on the TFC flat sheet membrane by introducing various additives such as bulky monomers and surfactants in reacting solutions to improve the intrinsic free volume of the rejecting layer and water permeability (Cui *et al.*, 2014).

Like any other membrane processes, FO also suffers from membrane fouling problem, although the fouling is generally less severe than RO fouling. Membrane fouling is a process which takes place in membrane surface or membrane pores whereby a solution or a particle is deposited (Li *et al.*, 2018). Membrane fouling can cause severe flux decline and affect the quality of the water produced. Some fouling problems may need intense chemical cleaning or membrane replacement and this will increase the operating costs of a treatment plant. Biofouling is one of the most challenging problems in membrane separation processes which hinders wider applications of the membrane. Biofouling starts with the bacterial adhesion on the membrane surface where once it attaches to the membrane surface, a bio-film will be produced. They are difficult to be removed and often causes irreversible damage to the membrane structure with the decline of water flux (Liu *et al.*, 2015). Silver compounds and silver ions have been known to exhibit strong inhibitory and bactericidal effects as well as a broad spectrum of anti-microbial activities (Ben-Sasson *et al.*, 2014). Due to their excellent biocidal properties and low toxicity towards mammalian cells, silver nanoparticles (AgNPs) have been widely applied in desalination membrane modification.

Based on the findings of previous studies, it has been suggested that membrane modification through incorporation of functional nanomaterials is a straightforward strategy to simultaneously address the issues related to ICP and membrane fouling (Ma *et al.*, 2018; Islam *et al.*, 2020). Therefore, this study focuses on developing thin film nanocomposite (TFN) membranes for FO desalination where Ag-fCNT hybrid is introduced into the membrane substrate to attain the desired membrane's physico-chemical performance and desalination performance.

1.2 Problem Statement

The performance of FO process largely depends on the membrane characteristics. Recent findings demonstrated that the membrane performance in terms of flux and anti-fouling behaviour are two crucial factors that dictate the ability of the FO system to desalinate seawater. Comparing both configurations, AL-FS and AL-DS, published articles on desalination reported AL-DS configuration showed higher water flux. However, pronounced water flux drop was observed over time due to the more severe membrane fouling (Tang *et al.*, 2010). This outcome also implies the importance for the development of a new FO membrane with an antifouling as well as antibacterial properties so that fouling can be minimized to boost FO performance.

Particularly, membrane fouling has severe negative impact on the performance of FO process due to the water flux decline after a period of operation. Early works on the FO process fell short to attain promising results due to the ineffective of the semi-permeable membrane. Thus, biofouling represents the major concern for industries that exploit membrane technology including water, food and pharmaceuticals (Al *et al.*, 2017). As an alternative to disinfectant application, nanotechnology has impacted on the design and fabrication of nanocomposite membranes with the potential for creating self-cleaning and antimicrobial surfaces.

Another issue related to membrane performance is reverse solute diffusion (RSD) and ICP. Loss of draw solute during FO operation occurs via reverse solute flux, which refers to the back permeation of draw solutes from the bulk draw solution through the membrane active layer and goes into the feed. The ability of an FO membrane to minimize reverse draw solute is critically important because the loss of draw solute is economically unfavourable and can have negative impacts upon release of some toxic draw solutes, such as ammonia to the environment. Detrimentally, it can lead to severe fouling and scaling in the feed solution. The semipermeable membrane used in FO desalination should not allow the permeation of draw solute into the feed solution and the early water flux models assumed the reverse salt flux to be negligible.

Furthermore, RSD is also a reason behind ICP phenomenon in FO desalination. Since FO is an osmotically driven membrane process, obviously the concentration polarization is strongly affecting the water flux of the system. Basically, the occurrence of ICP and ECP related to polarized salt concentration profiles across the porous support layer of the FO membrane. ICP in the support layer is greatly affected by the physicochemical properties of the solution facing the support layer. The ICP phenomenon will be more severe hence resulting in low water flux once the solution against the support layer has a lower aqueous diffusivity but larger ion/molecule size and higher viscosity. Such problem not only give bad impact on the water flux but also affect the water recovery, the permeate quality and shortened membrane life. According to the classical model of ICP developed by Loeb *et al.*, (Loeb *et al.*, 1997) structural parameter (S) is an exponential function of ICP. Generally, membranes with higher permeability have lower S-value which results in lower ICP and better FO performance (Amini *et al.*, 2013; Wei *et al.*, 2011). This study aims to develop FO membrane having both optimized PA layer and membrane support layer.

Unfortunately, no membrane is perfectly semipermeable, and a small amount of draw solute will permeate across the membranes from the draw to the feed solution owing to the difference in solute concentrations. According to McCutcheon and Elimelech, 2006, if the substrate layer of membrane owns a small structural parameter, S, then the ICP in FO process could be minimized. Besides, substrates which performed higher hydrophilicity show lower resistance against water passage and allow more water productivity. ICP phenomenon is actually influenced by the thick substrate layer and high S value that contributes to a huge decline in the effective osmotic driving force as well as the flux. Other than ICP, fouling is also being a serious issue in FO membranes, thus they can be solved by constructing a substrate with its interior pores highly interconnected by understanding that the mechanism on ICP is essential in order to innovate membrane design and synthesis. Hence, this study aims to develop FO membrane with high water permeability by incorporating Ag-fCNTs hybrid within the membrane substrate in order to have a low S parameter membrane for minimizing concentration polarization. The fabrication of FO membrane with nanomaterials embedded into the membrane substrate can improve the characteristic of membranes owing to their super hydrophilicity and potential of exhibiting antifouling behaviours (Lee *et al.*, 2020). The Ag nanoparticles can serve as an effective anti-microbial agent to mitigate the issues related to membrane biofouling. On the other hand, the presence of the fCNTs in the TFN is expected to render fast water transport hence improve the water permeability.

1.3 Objectives of Study

The aim of this study is to fabricate and evaluate the potential of TFN membrane embedded with Ag-fCNTs hybrid for FO desalination. The specific objectives of this study are listed below:

(i) To synthesize hydrophilic and antimicrobial Ag-fCNTs hybrid nanomaterials.

(ii) To fabricate and characterize TFN FO membranes incorporated with different loadings of Ag-fCNTs hybrid (0.1, 0.3 and 0.5%) within the PES substrate.

(iii) To evaluate the desalination performance of the TFN FO membrane in terms of flux, rejection and antibiofouling properties in AL-DS mode.

1.4 Scopes of Study

In order to achieve the objectives, the following scopes have been derived.

(i) Preparation and surface modification of Ag-fCNTs hybrid with w/w ratio of 1:5 (fCNTs to Ag) via one step hydrothermal method using $AgNO_3$ as precursor and by using acid treatment with hydrochloric acid (HCl) in 0.03M NaCl solution as solvent.

(ii) Characterization of the morphology and crystallinity of Ag-fCNT hybrid using transmission electron microscope (TEM) and x-ray diffraction analysis (XRD).

(iii) Preparation of membrane substrate via interfacial polymerization using dope formulation of 17 wt% PES, 1 wt% PVP and 82 wt% NMP.

(iv) Preparation of TFC membrane via interfacial polymerization (IP) of amine monomer; 2% (w/v) 1,3-phenylenediamine (MPD) in aqueous solution and acyl chloride monomer; 0.15% (w/v) 1,3,5-benzenetricarbonyl trichloride (TMC) with nanomaterial in n-hexane solution over a polyethersulfone (PES) support membrane.

(v) Preparation of TFN membrane by incorporating Ag-fCNT hybrid's loading ranging from 0.1-0.5 wt% of nanomaterial into the PES substrate via physical blending.

(vi) Characterization of fabricated TFC and TFN membranes using field emission scanning electronic microscope (FESEM) for morphology analysis, atomic force microscopy (AFM) for surface topography analysis; zeta potential and contact angle meter goniometer for surface charge and hydrophilicity, respectively.

(vii) Evaluation of the water permeability performance and NaCl rejection of TFC and TFN membranes in dead-end RO filtration system using RO water and brine water of 2 g/L (2000 ppm) NaCl, respectively as feed solution.

(viii) Performance evaluation of synthesized TFC and TFN membranes in terms of water flux, antifouling, flux recovery and reverse draw solute in FO system in AL-DS modes.

1.5 Significance of Study

Diminishing trade-off effect between water permeability and salt rejection is a great concern for membrane properties and have attracted many researchers' attention in their studies. The application of Ag-fCNTs hybrid in TFN membrane is to enhance water permeability which later improve water flux without sacrificing the rejection of FO rejection. On the other hand, the surface modification on nanomaterial can provide a suitable charge that significant to encounter particle agglomeration and decrease defects in the PA structure, thus improve water permeability and salt rejection performance in FO and RO system. This study is the first attempt of preparing Ag-fCNTs to simultaneously improve the flux and anti-microbial activities of the membrane to heighten the FO in PRO mode performance.

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