Carbon nanotube-enhanced membrane
for advanced water treatment

A thesis submitted in fulfillment of the requirements for the
degree of Doctor of Philosophy

By

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Declaration

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgment has been made in the text.

Jieun Lee

March 2016
“For at the proper time we will reap a harvest if we do not give up” Galathian 6:9

愚公移山，孔子
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Abstract

Membrane technology has been extensively used in advanced water treatment as a response to the global demand for drinking water due to the global water shortage. Driven by its separation performance, membrane technology is able to apply to municipal/wastewater treatment, drinking water treatment and seawater desalination. Despite its benefits such as energy efficiency and high performance in separation, the challenging issue in currently used polymeric membrane is a trade-off between permeate flux and separation efficiency, and vulnerability to fouling. Such drawbacks made progress on developing membrane material for the purpose of advancing membrane process. For example, incorporation of nanomaterials into a membrane matrix has brought attention to its favorable characteristics. There have been many studies on the development of membrane materials using nanomaterials such as carbon nanotubes (CNTs), metal organic frameworks (MOFs) or silver. Among those candidates, CNTs possess advantages such as high adsorption capacity for contaminant removal and hydrophobicity for slippage effect in the water channel. Further, CNTs as a nanofiller in the polymer matrix are able to engineer the membrane structure to the way in which is favorable to the flux and selectivity. However, dispersion in a polymer matrix to maximize the benefits of CNTs still remains a challenge which prevents its wide application to the membrane process.

First, we synthesized multiwall carbon nanotubes/polyaniline (MWCNTs/PANI) complex by in-situ polymerisation and successfully introduced it to the membrane matrix. Doping process during MWCNTs/PANI complex synthesis via chemical oxidation transformed the charge of PES polymer to a positive one. The MWCNTs/PANI enhanced membrane exhibited remarkably enhanced performance compared to the conventional polyethersulfone (PES) membrane. The
significance of this research is that the membrane removed natural organic matter 4 fold (80 %) which cannot be effectively removed by currently used low-pressure driven membranes, as well as delivering 30 times higher water product (1400 LMH/bar) than the PES membrane. Further research on physical/chemical properties of the membrane revealed that the hydroxyl functionalized MWCNTs/PANI complex increased the hydrophilicity, porosity and slip length of the membrane by improving the membrane structure. It also altered the surface charge of the membrane, which contributed to the increase electrostatic interaction between the membrane surface and the negatively charged organic matter, compared that currently used polymeric membranes are negatively charged. Due to the positively charged surface, this membrane can open up an opportunity for recovery of valuable cationic macromolecules in bioprocess/pharmaceutical industries. Examination of removal mechanism and fast water flux would be of great importance for enhancing the performance of UF membrane which is widely used in water treatment. The membrane exhibited 100 % UPW permeability recovery and 65 % total fouling ratio after acid/base cleaning.

A second part of the research targeted to the application for enhanced organic matter removal in seawater pre-treatment. The research was aimed to enhance UF membrane coupled with adsorption system which can prevent performance decline in RO membrane desalination plant. By enhanced natural organic matter removal and delivering high permeate flux, the MWCNTs enhanced membrane contributed to minimizing sludge volume generated from seawater desalination plant as removing organic matter in seawater. Compared that conventional PES membrane required 1.5 g/L PAC, the MWCNTs membrane coupled PAC adsorption system exhibited enhanced removal efficiency at 0.5 g/L PAC, and 4 fold increased permeate flux. The
ionic strength was found to influence reduced organic removal and permeate flux enhancement in MWCNTs membrane. Lastly, protein fouling behavior in the MWCNTs membrane was examined under different solution chemistry (pH and ionic strength) for the wide application of MWCNTs membrane in wastewater reclamation and recovery of bioprocess industry. MWCNTs membrane showed high permeate flux at different pH and ionic strength compared to the commercial PES membrane. Four different fouling models were used to explain the flux decline with protein deposition during membrane filtration. For MWCNTs membrane, two dominant fouling mechanisms—standard blocking and cake filtration operated simultaneously under different pH and increasing ionic strength throughout the entire filtration. In a single protein filtration test, Lys filtration caused more strong fouling potential than BSA filtration due to its comparable size to the pore diameter of the membrane. Low pH condition alleviated standard blocking and cake layer formation on the membrane due to increased electrostatic repulsion between the membrane surface and Lys. Further, increasing ionic strength lessened the protein deposition because of ion shielding effect on the model protein. For oppositely charged BSA filtration, membrane fouling potential was weakened at pH 4.7 and 10.4 due to the decreased electrostatic interaction at these points. Increasing ionic strength seemed to contribute to fouling mitigation, but not comparable to the pH effect. For mixed protein filtration, severe pore blocking and cake layer formation were observed at their IEP (4.7 and 10.4), presumably due to the enhanced bridging effect of neutralized proteins with their counter proteins, compared to the intermolecular interaction (Lys-BSA) at pH 7. Consequently, protein fouling of MWCNTs membrane was found to be alleviated by controlling electrostatic interaction with charged proteins via solution chemistry (pH and ionic strength).
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Chapter 1 Introduction

1. Introduction

1.1 Background

Water shortage is an emerging issue due to a significant gap between available water supply (4,200 billion m$^3$) and water demand (6,900 billion m$^3$) in 2030 as shown in Fig 1.1(a). To address the issue for the future, it is imperative to find new water resources and recycle current one by increasing water quality. In such a way, seawater/brackish water desalination and recycling of waste/municipal water will be the critical resources to produce clean water (Fig 1.1(b)).

Membrane technology has been widely applied for the water/wastewater treatment and desalination due to its separation performance and energy intensiveness over the last decade. Low pressure driven membrane such as microfiltration (MF) and ultrafiltration (UF) is an effective process for drinking water and membrane bioreactor in municipal/wastewater treatment at a relatively low cost. Reverse osmosis membrane is increasingly adopted in a large number of desalination plants due to its highly competitive performance, energy efficiency and cost saving among various desalination technologies [1, 2].

Despite its benefits, such membrane processes still have several drawbacks in the application to water treatment. Natural organic matter (NOM) is the major pollutant which causes serious membrane fouling and performance decline. Further, NOM generates disinfection by-products (DBPs), carcinogen when it reacts with chlorine residual in tap water. However, conventional MF/UF membranes such as polyethersulfone (PES), polysulfone (PSf) and polyvinylidene
fluoride (PVDF) is limited to NOM removal due to its relatively larger pore size than humic/fulvic acid (<1 nm), exhibiting only 20 -50 % rejection. Moreover, RO membrane in desalination plants such as polyamide (PA) and cellulose acetate (CA) has two challenges to be overcome. The first challenge is concentrate recycling. RO desalination plants generate increasing amount of concentrate from the process, which contains a high concentration of salts, process chemicals and effluent organic matter [3]. Another issue on RO membrane is the need for the capital and energy-intensive pretreatment due to the vulnerability in membrane fouling [4, 5]. Seawater contains low molecular organic matter such as humic/fulvic acids, carboxylic acid and extracellular polymeric substances (EPS). Such contaminants result in serious membrane performance decline by irreversible membrane fouling. While MF/UF membrane hybrid system coupled with coagulation/adsorption seems to have effective removal efficiency, it generates a large amount of chemical sludge due to a usage of the high amount of coagulant/adsorbent.

UF membranes have been increasingly applied to secondary effluent from municipal and wastewater plant. However, effluent organic foulants containing proteins, humic/fulvic substances cause serious membrane fouling and flux decline via pore blocking and/or pore constructions. Such drawbacks then lead to frequent membrane replacement and increase in chemical cleaning, which will have a negative impact on the environment. The protein fouling is strongly affected by solution chemistry such as solution pH, ionic strength and its concentration [6-8]. For this reason, UF membrane in municipal/wastewater treatment is severely fouled by feed water pH and ionic strength.

The attempt to address those challenging issues makes progress on developing membrane material by nanomaterial incorporation [9-12]. Of nanomaterials, carbon nanotubes (CNTs) are
one of the favored candidates to the membrane for advanced water treatment due to its unique properties such as an excellent adsorption capacity by high specific surface area, electro-conductivity, slippage effect on permeate flux by the molecular smoothness of nanotube wall (hydrophobicity) and easiness to functionalization [13-16]. In addition to its intrinsic characteristics, incorporation of CNTs alters physical/chemical properties of the polymeric membrane, which is the key parameter to influence significantly separation performance such as porosity, pore size, membrane structure, surface roughness, hydrophilicity and surface charge of the membrane [17].

However, the main challenge to inhibit its benefit from outperforming conventional polymeric membrane performance is CNTs aggregation in the polymer matrix. Moreover, CNTs nanocomposite membrane fouling remains as challenges due to the trade-off between high removal efficiency and adhesion of foulants on the membrane. For the successful application of the robust CNTs membrane to the municipal/wastewater treatment, it is suggested to examine protein fouling behavior under different solution chemistry (pH, ionic strength).
1.2 Scope and purpose of the study

This research highlights on the fabrication of multi walled carbon nanotubes (MWCNTs) enhanced membrane which can overcome current issues on UF membranes such as low NOM removal, a large volume of sludge generation in seawater pretreatment. For the purpose of advancing membrane process, the focus is on in-depth of study in protein fouling behavior under different solution chemistry which represents various conditions in municipal/wastewater treatment and seawater desalination. Fig 1.2 presents an overview of the research.

This study has three principal objectives:

1. Fabrication of MWCNTs membrane for efficient NOM removal and examination of the removal mechanism and its fast water flux
2. Application to the UF membrane hybrid system in the seawater pretreatment and examination of salinity effect on membrane performance

3. Examination of protein fouling behavior under different solution chemistry (pH, protein charge, and ionic strength)

(a) MWCNTs-enhanced membrane for UF membrane process.

(b) MWCNTs membrane coupled with PAC adsorption with a high permeate flux, organic reduction in seawater filtration to lessen the sludge volume in pretreatment.

Fig 1.2 Application of MWCNTs-enhanced membrane to the membrane processes.
1.3 Thesis overview

The thesis is set out in 6 chapters:

*Chapter 1* introduces the background and establishes objectives of this research.

*Chapter 2* provides a comprehensive review of the progress and challenges of carbon nanotube membranes for water treatment. A potential of carbon nanotubes (CNTs) membranes in the water treatment has highly been strengthened during last decade. The performance of CNTs membrane is highly likely dependent on the fabrication method. The intrinsic properties of CNTs could be a key factor of applicability to membrane process. This chapter provides an explicit and systematic review on CNTs membranes addressing the current epidemic—whether the CNTs membranes can tackle current challenges in the pressure and thermally driven membrane process, and efficacy of CNTs hybrid nanocomposite membrane to complement current CNTs enhanced membrane. This chapter was submitted to the *Critical Reviews in Environmental Science and Technology*.

*Chapter 3* presents the experimental procedure of the membrane fabrication.

*Chapter 4* builds up 1) the fabrication of MWCNTs enhanced UF membrane and 2) investigates mechanism of its NOM removal efficiency and fast water flux.

The aim of Chapter 4 is to develop ultrafiltration (UF) membrane material by incorporating carbon nanotubes (CNTs) into the polymer matrix that can effectively remove natural organic matter (NOM) in water. Its physical/chemical properties are thoroughly analyzed for the purpose of determining the critical factor of fast water flux and NOM removal mechanism.

The significance of the CNTs-enhanced membrane is to overcome the challenge in conventional UF membrane that cannot remove NOM efficiently and has relatively low water flux. Compared
that the conventional membrane can only remove 30 – 50 % of NOM, the CNTs-enhanced membrane in this research can remove up to 80 % of NOM. Further, the membrane achieved greatly enhanced water permeability (1400 LMH/bar), which is 30 times faster than the conventional PES UF membrane. The significant achievement is attributed to the synergetic effect of the increased porosity, narrow pore size distribution and hydrophilicity. Relatively narrow pore size on much thinner skin later and well developed finger like structure led to the slippage effect. Positively charged surface charge of the membrane also contributes significantly to the high removal efficiency on NOM. The membrane contributes to the progress of the UF membrane material development by engineering physic-chemical properties of membrane via nanomaterial incorporation. This chapter was published in *the Separation and Purification Technology* (Elsevier).

*Chapter 5* discusses 1) the application of MWCNTs-enhanced UF membrane for seawater pretreatment in RO desalination and 2) examines the effect of salinity on the membrane performance.

Since RO membrane technology has been increasingly applied to the seawater desalination plant, attention has been on the energy-intensive pretreatment prior to the RO membrane system due to the performance decline driven by RO membrane fouling. Currently, low-pressure membrane coupled with adsorption/coagulation system seems to address the issue, but a large amount of sludge and the limitation on the poor removal efficiency on the low molecular weight organic matter remains challenges.

MWCNTs-enhanced membrane coupled with PAC adsorption achieved significantly enhanced permeability with an organic reduction in seawater pretreatment. The study in this chapter considerably contributes to lessening the sludge volume in the seawater pretreatment in the RO
Chapter 1 Introduction

desalination plant. Another significance of the research is an examination of the effect of ionic strength on the organic removal efficiency in seawater filtration. This in-depth study determines the feasibility of CNTs membrane and delivers the sustainable separation technology employing membrane in the seawater desalination for the future. This chapter was published to the Journal of Industrial Engineering and Chemistry (Elsevier).

Chapter 6 examines protein fouling behavior under different solution chemistry (pH, protein charge, and ionic strength) and fouling mechanism.

1) The protein fouling behavior was investigated in the filtration of the multiwall carbon nanotube (MWCNT) composite membrane and commercial polyethersulfone ultrafiltration (PES-UF) membrane. 2) The effect of solution chemistry such as pH and ionic strength on the protein fouling mechanism was systematically examined using filtration model such as complete pore blocking, intermediate pore blocking and cake layer formation.

This research demonstrates that MWCNT membrane fouling can be alleviated by changing pH condition and ionic strength based on the foulant-foulant interaction and the electrostatic interaction between the membrane and foulant. This chapter is currently under Review in the Chemical Engineering Journal.

Chapter 7 presents conclusions of this research which summarize results and conclusion derived from each of journal published chapters and suggests future work.
Chapter 1 Introduction

Reference


Chapter 1 Introduction


19. *GWI DesalData / IDA (2011-2012).*
Chapter 2 Literature Review

2.1 Introduction

Membrane technology has been extensively applied for water and wastewater treatment, and water desalination due to its separation performance and energy intensiveness over the last decade [1]. Low pressure driven membranes such as microfiltration (MF) and ultrafiltration (UF) are an effective method in drinking water and membrane bioreactors for municipal and wastewater treatment at a relatively low cost. Reverse osmosis (RO) membrane is increasingly adopted in a large number of desalination plants since it shows highly competitive performance, energy efficiency and cost saving [2].

Despite their many benefits, such membrane processes still have several drawbacks in the application to water treatment. For example, natural organic matter (NOM) is one of the major pollutants that contribute to serious membrane fouling and performance decline. NOM can stimulate microbial regrowth in the distribution system [3]. Further, NOM generates disinfection by-products (DBPs), and carcinogen when it reacts with chlorine residual present in water. However, conventional MF/UF membranes such as polyethersulfone (PES), polysulfone (PSf) and polyvinylidene fluoride (PVDF) are limited to NOM removal due to its relatively larger pore size than humic/fulvic acid (<1 nm), exhibiting only 20 - 50 % rejections. Polyamide (PA) and cellulose acetate (CA) membranes for RO desalination have several challenges to be overcome. They generate an increasing amount of concentrate from the process, which contains a high concentration of salts, process chemicals, and wastewater. In addition, PA-RO membranes are vulnerable to degradation by chlorine. Another issue on RO membrane is the need for capital and energy-intensive pretreatment due to the poor quality of feed water [4]. Seawater contains relatively low molecular weight (LMW) organic matter such as humic/fulvic acids, and carboxylic acid. Such contaminants result in serious
membrane performance decline by irreversible membrane fouling (i.e. organic and biological fouling). For these reasons, MF/UF membrane hybrid system coupled with coagulation/adsorption seems to have effective pretreatment with high removal efficiency of LMW organic matter [5]. However, it generates a large amount of chemical sludge due to the usage of the high amount of coagulant/adsorbent.

The attempt to address those challenging issues is making progress on developing membrane material by incorporating nanomaterials [6, 7]. Of nanomaterials, carbon nanotube (CNT) is one of the favored candidates to the membrane for advanced water treatment due to its unique properties such as an excellent adsorption capacity by high specific surface area [8, 9], electro-conductivity [10], slippage effect on permeate flux by the molecular smoothness of nanotube wall (hydrophobicity) [11] and easiness to functionalization [12]. In addition to its tunable physical, chemical and electrical properties, incorporation of CNT enables the alteration of physical/chemical properties of the polymeric membrane, which is the key parameter influencing significantly separation performance such as porosity, pore size, surface roughness, hydrophilicity and surface charge of the membrane [13, 14].

Current research on the CNT membrane is focusing on fabrication/modification of pressure driven membrane by incorporating CNT into the conventional polymer matrix in order to enhance permeate flux, rejection efficiency, and fouling resistance [15, 16]. However, the main challenge to inhibiting its benefit from outperforming conventional membrane performance is inconsistencies of performance due to CNT aggregation in the polymer matrix. Moreover, CNT nanocomposite membrane fouling remains a challenge due to the trade-off between high removal efficiency and adhesion of foulants on the membrane.

Although currently reported critical reviews focus on the summary of membrane fabrication, CNT functionalization for better adsorption capacity and performance evaluation in the
context of its properties for water treatment [17-19], very few studies have provided an in-depth insight on applicability of CNT membranes and the impact of CNT nanohybrid membranes on the membrane processes.

This review, therefore, highlights firstly, the applicability of CNT enhanced membranes for current systems from pressure to thermally driven membrane processes, secondly potential impacts of the CNT hybrid nanocomposite membranes, and finally currently encountered challenges and further research directions in the point of view of membrane material and fabrication.

2.2 CNT materials

Carbon nanotube (CNT) is allotropes of carbon with a cylindrical carbon network, and the one-dimensional analogs of zero-dimensional fullerene molecules. A nanotube visualizes a micrometer-scale graphene sheet rolled into a cylinder of nano-scale diameter and capped with a spherical fullerene (Fig 2.1). Graphene sheets are composed of a monolayer of sp²-bonded carbon atoms in the x-y plane. Due to the presence of delocalized π-electron in the z-axis, CNTs have unique electrical properties [20].

![Fig 2.1 Structure of CNTs: (a) a schematic representation of a graphene sheet and CNT roll-up vector, (b) a 3-D model of single-wall CNT (SWCNTs), and (c) hybridization states of carbon-based nanomaterials [21, 22].](image)
CNT is classified into two types: single-wall carbon nanotube (SWCNT) and multi-wall carbon nanotube (MWCNT) (Fig 2.2). SWCNTs, which are a cylinder of a single graphene sheet, consist of a planar array of benzene molecules with hexagonal rings with double and single carbon-carbon bonding. The MWCNT is multi-layers of rolled graphene sheets. The SWCNT is revealed as metallic or semiconducting nanowires according to the chirality and diameter [10, 23]. Table 2.1 summarizes the characteristics of carbon materials [24]. The electrical conductivity of SWCNT is in the wider range (10²-10⁶ S/cm) than that of MWCNTs. SWCNT have 3-fold thermal conductivity than MWCNT.

Fig 2.2 Schematic diagrams of (a) single-wall carbon nanotubes (SWCNTs), (b) multi-wall carbon nanotubes (MWCNTs), (c) double wall carbon nanotubes, and (d) peapod nanotubes consisting of SWCNTs filled with fullerenes (e.g. C60) [25].

<table>
<thead>
<tr>
<th>Property</th>
<th>Graphite</th>
<th>Diamond</th>
<th>Fullerene</th>
<th>SWCNTs</th>
<th>MWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity (g/cm³)</td>
<td>1.9-2.3</td>
<td>3.5</td>
<td>1.7</td>
<td>0.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Electrical conductivity (S/cm)</td>
<td>4000⁰, 3.3</td>
<td>10⁻²-10⁻¹⁵</td>
<td>10⁻⁵</td>
<td>10²-10⁶</td>
<td>10¹-10⁵</td>
</tr>
<tr>
<td>Electron mobility (cm²/(Vs))</td>
<td>2.0×10⁴</td>
<td>1800</td>
<td>0.5-6</td>
<td>~10⁵</td>
<td>10⁵-10⁵</td>
</tr>
<tr>
<td>Thermal conductivity (W/(m K))</td>
<td>298⁰, 2.2</td>
<td>900-2320</td>
<td>0.4</td>
<td>6000</td>
<td>2000</td>
</tr>
</tbody>
</table>

p: in-plane, c: c-axis
The high polarized π-electron clouds in CNT result in strong attractive forces, so-called van der Waals, between CNT and the weak inter-planar interactions of the graphene sheet. The physical properties of individual nanomaterials, such as the size, shape, and surface area of carbonaceous nanomaterials are highly dependent on aggregation state and solvent chemistry. The physicochemical properties attributed to secondary structures of nanomaterial aggregates are highly variable and poorly characterized [21]. Resolving these characteristics is imperative for application of carbonaceous nanomaterials to water purification-membrane filtration [26].

CNT is intrinsically hydrophobic, and such property has benefits to water treatment. Firstly, hydrophobicity and capillarity contribute to the adsorption behavior and orientation of sorbates in microporous carbons. Physio-sorption is the dominant mechanism of sorption for un-functionalized nanomaterials. In environmental applications, adsorptive capacity has broad implications for contaminant removal and hydrogen storage. For example, CNT for conventional drinking water treatment strongly depends on physicochemical sorption processes for the removal of an organic and inorganic contaminant, such as NOM and heavy metals [27-29]. Carbonaceous nanosorbents, which have high surface area to volume ratio, controlled pore size distribution, and manipulable surface chemistry, outperform traditional sorbents due to their rapid equilibrium rates, high adsorption capacity, and effectiveness over a broad pH range and consistency with Brunauer, Emmett and Teller (BET), Langmuir, or Freundlich isotherms. Secondly, the superhydrophobic CNT channel can also contribute to ultrafast water fluid transport. This will be elucidated in section 3.4.1.
2.3 Fabrication of CNT membranes

2.3.1 Mixed matrix membrane – CNT/polymer composite membrane

Mixed matrix CNT membrane was initially designed to advance the separation performance of polymeric membranes. Hence, the incorporation of CNT as inorganic fillers to polymeric membranes was introduced to tune the physical/chemical properties that significantly control permeability, rejection efficiency, and fouling resistance [13]. Recently, a good fabrication method of the CNT incorporation to UF membrane was summarized systemically [30]. The mixed matrix membrane led to fabrication with the relatively easy process and without extensive efforts regarding membrane formation and its separation. This fabrication process can be divided into two steps: i) CNT functionalization, and ii) UF membrane preparation by phase inversion. Fig 3.3a presents the procedure of CNT composite UF membrane fabrication via phase inversion. CNT is difficult to be incorporated uniformly into the polymer matrix due to the intrinsical aggregation (hydrophobicity) by van der Waals force between nanotubes. Van der Waals forces between nanotubes hinder the CNT dispersion in the polymer matrix as CNT is formed as tightly aggregated conformation and low dispersed in both polar and apolar solvents. Thus, dispersion of CNT is a necessary step in the fabrication. The dispersed CNT by hydrophilic functionalization enables to maximize the effect of nanomaterial and to have a large surface area for removal efficiency and to enhance the flux of membrane. There have been many efforts to improve CNT dispersion. Chemical oxidation by acid treatment is the most commonly used technique that attaches hydroxyl/carboxylic groups to CNT wall [31, 32]. Sonication is the physical treatment that breaks van der Waals force temporarily by physical shock. However, these methods could not completely disperse the CNTs in the polymer matrix.

The second stage of the membrane fabrication is the formation of support layer by UF membrane via phase inversion method (Fig 3.3a). The physical properties of the membrane
such as pore size, porosity, and thickness strongly influence the permeate flux. Such properties are strongly affected by the parameters that can be controlled and determined by the fabrication procedure: insertion of nanofiller, polymer and solvent proportion, etc [33, 34]. Thus, researchers have focused on nanomaterial incorporation into the UF membrane to enhance the membrane performance [16, 35, 36].

In addition, the fabrication process of CNT composite RO membrane can be divided into three steps: i) CNT functionalization, ii) UF membrane preparation by phase inversion and iii) the formation of polyamide (PA) thin film layer by interfacial polymerization. The highlight in this fabrication is the formation of selective layer (PA thin layer) on the top of UF membrane support layer via interfacial polymerization (Fig 3.3b). Less than 1 nm diameter of the pore on a 0.5 µm-sized support layer is formed by the interaction of m-phenylenediamine (MPD) with trimesoyl chloride (TMC), leading to the greatly enhanced selectivity and mechanical strength to high pressure [37]. The thin film composite (TFC) membrane is suitable for RO and forward osmosis (FO) membrane system due to the greatly enhanced selectivity for salts and minerals by the rejection layer on top of the membrane[37-39]. Here, CNT can be incorporated into both aqueous phase (MPD) [40] and an organic phase (TMC in Hexane or Isopar-G) [41], or deposited on UF membrane support layer before PA layer formation by interfacial polymerization [42] [43].
Fig 2.3 Schematic illustrations of the CNTs composite membrane fabrication procedure: (a) CNTs UF membrane by phase inversion [44] and (b) CNTs/PA NF/RO membrane by interfacial polymerization.
2.3.2 Horizontally aligned carbon nanotube (HACNT) membrane

Self-assembly CNTs membrane can be divided into two types of the fabrication method, determined by the structure and arrangement of CNT in the membrane: horizontally aligned CNT (HACNT) membrane (Fig 2.4a) and vertically aligned CNT (VACNT) membrane (Fig 2.4b).

![SEM images of HACNT and VACNT arrays](image)

**Fig 2.4** SEM images of (a) HACNT [45] and (b) VACNT arrays [46].

HACNTs membrane has a randomly arranged CNT structure. Its fabrication procedure is followed by i) CNT functionalization for homogenous CNT dispersion and ii) vacuum filtration for the proper membrane structure. Hydroxyl/carboxylic-functionalized CNT is dissolved in solvents (ethanol, propa-2-ol) by ultra-sonication. This homogenous suspension is vacuum-filtered through a membrane filter and then dried in the oven to remove all solvents and moistures from the film [47-49]. Due to the arrangement and fabrication procedure, its pore size varies from few nanometers to micrometer. It can be determined by adjusting the volume of the CNT suspension and selecting the types of CNT [50].

The advantages of the HACNT membrane are highly microporous structure, high adsorption capacity [51] and superior inactivation E-coli cells [52]. However, due to poor mechanical strength, which cannot be overcome during the fabrication process, this membrane may be inadequate for the high-pressure process.
2.3.3 Vertically aligned carbon nanotube (VACNT) membrane

In the VACNT membrane matrix, CNT is vertically aligned on the membrane substrate. The gap between nanotubes is filled with fillers such as epoxy, polystyrene, and/or parlyene for proper membrane structure.

VACNT membrane is prepared in two stages: i) growth of an aligned array of CNT and ii) infiltration with a matrix material in the gap between nanotubes. VACNT arrays are usually synthesized by chemical vapor deposition (CVD) method [53-55]. As shown in Fig 2.5, CNT is grown by the reaction between ethylene \([C_2H_4(g)]\) and ferrocene \([\text{Fe(C}_5\text{H}_5)_2]\) as a catalyst precursor and further grown in the furnace. Ferrocene is decomposed with Fe by heating, and CNT is grown on the Si wafer substrate coated with aluminum oxide (AAO). In this step, aluminum acts as a template for the growth of aligned CNT. In order to remove substrate, water etching and vacuum extraction are performed. Here, CNT diameter can be controlled by modulating feeding rate of catalyst-precursor in a floating system. This has opened a way for VACNT arrays to be a potential membrane for water treatment.

![Fig 2.5 Schematic of the synthesis and detachment of a VACNTs array [53]](image)

However, CNT array cannot be employed to water treatment directly since it does not have a proper nanoporous structure for water transport, nor can it introduce water molecule into the
nanochannel due to its hydrophobicity. Thus, gap infiltration needs to be carried out for water to pass through only the channel of CNT, after growth of aligned CNT array. Table 2.2 summarizes the fabrication procedures of VACNT membrane. It provides a classification of CNT synthesis and post-treatment for fine ordered membrane structure by substrate removal and tip opening. Fig 2.6 presents the typical fabrication procedure of VACNT membrane: Firstly, gap infiltration is done with polymers (epoxy, polystyrene, and parlyene, etc.) under the vacuum pressure. Then, the substrate is removed by NaOH etching and finally, a tip opening is carried out by mechanical polishing, ion etching or plasma etching.

![Fabrication procedure of VACNTs membrane.](image)

Fig 2.6 Fabrication procedure of VACNTs membrane.
<table>
<thead>
<tr>
<th>Type of VACNT</th>
<th>Internal Diameter</th>
<th>Length</th>
<th>Contact angle</th>
<th>Flux</th>
<th>Operating pressure</th>
<th>Test material</th>
<th>Re. (%)</th>
<th>Method of CNT synthesis/fabrication</th>
<th>Method of tip opening</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW (6,6) functionalized with $\text{SOO}^-$</td>
<td>1.1 nm</td>
<td>1.3 nm</td>
<td>-</td>
<td>1.51 LMH/bar</td>
<td>26.4 bar</td>
<td>NaCl</td>
<td>100</td>
<td>Catalytic chemical vapor deposition/ Silicion nitride (Si$_3$N$_4$) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>[56]</td>
</tr>
<tr>
<td>(5,5) armchair type tube</td>
<td>0.32 nm</td>
<td>~1.4 nm</td>
<td>-</td>
<td>1.2 LMH/bar</td>
<td>55 bar</td>
<td>NaCl</td>
<td>100</td>
<td>Catalytic chemical vapor deposition/ Silicion nitride (Si$_3$N$_4$) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>[57]</td>
</tr>
<tr>
<td>(6,6) armchair type tube</td>
<td>0.47 nm</td>
<td>~1.4 nm</td>
<td>-</td>
<td>2.1 LMH/bar</td>
<td>55 bar</td>
<td>NaCl</td>
<td>100</td>
<td>Catalytic chemical vapor deposition/ Silicion nitride (Si$_3$N$_4$) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>[57]</td>
</tr>
<tr>
<td>(7,7) armchair type tube</td>
<td>0.59 nm</td>
<td>~1.4 nm</td>
<td>-</td>
<td>3.2 LMH/bar</td>
<td>55 bar</td>
<td>NaCl</td>
<td>95</td>
<td>Catalytic chemical vapor deposition/ Silicion nitride (Si$_3$N$_4$) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>[57]</td>
</tr>
<tr>
<td>(8,8) armchair type tube</td>
<td>0.75 nm</td>
<td>~1.4 nm</td>
<td>-</td>
<td>4.9 LMH/bar</td>
<td>55 bar</td>
<td>NaCl</td>
<td>58</td>
<td>Catalytic chemical vapor deposition/ Silicion nitride (Si$_3$N$_4$) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>[57]</td>
</tr>
<tr>
<td>Double-wall Multi-wall</td>
<td>1.3 - 2 nm</td>
<td>1-5 μm</td>
<td>-</td>
<td>$2.2\times 10^5$ LMH/bar</td>
<td>0.82 bar</td>
<td>Ru$_2$+(bipy)$_3$, 1.3 nm of particle size</td>
<td>-</td>
<td>Catalytic chemical vapor deposition/ Silicion nitride (Si$_3$N$_4$) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>[26]</td>
</tr>
<tr>
<td>Single-wall</td>
<td>1.3 - 2 nm</td>
<td>1-5 μm</td>
<td>-</td>
<td>$0.9\times 10^5$ LMH/bar</td>
<td>0.82 bar</td>
<td>Colloidal Au 2 ± 0.4 nm of particle size</td>
<td>-</td>
<td>Catalytic chemical vapor deposition/ Silicion nitride (Si$_3$N$_4$) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>[26]</td>
</tr>
<tr>
<td>Double-wall</td>
<td>1.3 - 2 nm</td>
<td>1-5 μm</td>
<td>-</td>
<td>$1.3\times 10^5$ LMH/bar</td>
<td>0.82 bar</td>
<td>Colloidal Au 5 ± 0.75 nm of particle size</td>
<td>Na$_4$PTS, 96 %, K$_3$Fe(CN)$_6$, 90 %, K$_2$SO$_4$, 80 %, CaSO$_4$, 37 %, KCl, 37 %</td>
<td>Catalytic chemical vapor deposition/ Silicion nitride (Si$_3$N$_4$) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>[58]</td>
</tr>
</tbody>
</table>
Hinds’ group has firstly introduced CNT membrane fabrication using the polymer infiltration [59]. CNT was grown for 30 min on a quartz substrate by a CVD process. Then, polystyrene and toluene solution encapsulated CNT arrays in order to form a well-ordered nanoporous membrane structure. Lastly, H$_2$O plasma-enhanced oxidation process was performed to remove a thin layer of excess polymer from the top surface and open the tips for membrane structure. Interestingly, plasma process attached carboxylic groups on the tips of CNT, which could be the basis for gatekeeper-controlled chemical separations or ion channel mimetic sensors.

An encapsulation of VACNT with low-stress Si$_3$N$_x$ was developed by using a low-pressure CVD process [60]. After encapsulation, the membrane is etched in order to remove an excess Si$_3$N$_x$ from the tips of the CNT, followed by oxygen plasma to uncap the CNT. The VACNT membrane has less than 2 nm pores in diameter and consistent with diameters of as-grown nanotubes.

Another approach was the fabrication of hierarchically organized vertical CNT arrays by plasma-enhanced CVD (PECVD) with self-assembled block copolymer nano templates [61]. Conventional thermal CVD does not produce highly oriented vertical architecture due to thermal fluctuation and gas flow established within the chamber during the growth process. However, PECVD can enhance the vertical alignment of CNT by the electric field in the PECVD chamber due to the high electrical polarizability of the structures. The large dipole moments induced in CNT by the external electric field impose aligning torques on the growing CNT, resulting in the growth of highly oriented VACNT arrays. Polystyrene-block-poly (methyl methacrylate) (PS-b-PMMA) was used as a self-assembling polymeric material to form cylindrical nanostructure with center-to-center distanced between them of 72-34 nm as nano templates for the hierarchical organization of CNT. The cylinder cores were etched by UV radiation and wet method for polymeric nano templates with hexagonally packed
cylindrical nanopores. The iron catalysts were deposited, and lift-off process was conducted to control the size and lateral distribution of the catalyst particles. Next, PECVD process was applied to the growth of CNT. Heat treatment at 750°C for 1 min was carried out for size decrease of the catalyst particles from 21 to 14 nm. As a result, CNT diameter became half of the agglomerated catalyst particle size. In this research, the diameter of CNT is dependent on the size of the catalysts particles. The nanopores’ size (D) and center to center distance between nanopores (L) of the block copolymer template depend on the molecular weight of the block copolymer (M): D, L ∝ M^{\frac{2}{3}}

Beside polymer infiltration method, thermally infiltration was applied to fill the gap between the nanotubes [62]. For the controlled embedment of nanotube into polymer films, aligned CNT film grown on the SiO₂/Si substrate was held on the hot plate and heated up to a temperature above the melting point (T_m) and below decomposition temperature (T_c). The top of a CNT array was fully covered with a thin film of polystyrene (~50μm). The melted polystyrene (PS) layer was gradually infiltrated into the aligned nanotube forest.

VACNT membrane has several benefits for the advanced water treatment due to its intrinsic properties. Firstly, the membrane provides well-defined narrow pore size, due to the role of CNT channel as a water passage. In addition, the pore size of VACNT membrane can be controlled in the CNT synthesis step by selecting proper catalysts such as Cu and Al [63]. Its diameter can be tuned from few hundreds nanometer (nm) to less than 1 nm size, indicating that VACNT membrane could be an ideal candidate for membrane distillation (MD) and RO membrane system that requires narrow pore size and its size distribution.

2.3.4 Key factors affecting the ultrafast water permeability of VACNT membrane

2.3.4.1 Slip length

Super ultra-fast water flux is mainly induced by the slippage effect in CNT channel [56, 64]. The reduced viscosity near the superhydrophobic wall generates the slippage effect for the
fluid transport in the CNT channel. Here, this fluid slip is so called, “slip length.” Slip length is the distance inside the wall at which the extrapolated fluid velocity would be equal to the velocity of the wall. In other words, it is the ratio of the slip speed to the mean shear rate. Thus, slip length is proportional to shear rate. In order to explain water transport within CNT, the Navier-Stokes equations can be used, which are continuum fluid mechanics along with a slip boundary condition. As can be seen in Fig 2.7, the slip boundary condition occurs when liquid is interfaced on the non-wetting surfaces (e.g., water on hydrophobic surfaces).

![Diagram of slip length flow past a stationary surface](image)

**Fig 2.7** Slip length flow past a stationary surface [65].

The theory of calculation is well explained in Table 2.3.

Slip length measurement can be defined as the ratio of slip velocity to shear rate at the wall. It can be expressed as follow:

\[ \nu_b = b \frac{dv}{dz} \]

Where,

\( \nu_b \) = the slip velocity of the fluid on the surface

\( b \) = Slip length

\( \frac{dv}{dz} \) = Velocity gradient
Table 2.4 summarizes the measurement of slip length in the channel.

Rheometry experiment

Slip length is obtained by measuring torque through a rheological experiment. In the rheological system with the plate-and-plate arrangement, the driving torque applied to the clamp is recorded at each shear rate.

Even though this method is the most popular geometry because it produces the uniform shear rate over the sample [66], there is a difference between the apparent viscosities in the rheological experiment for CNT and the intrinsic viscosity due to the slippage effect [67]. Hence, calculated slip length is over-estimated, and the influence of the edge effect should be removed in the slip length calculation.

Particle image velocimetry (PIV)

This is based on the measurement of the velocity of fluorescent particles embedded water. First, the velocity profile of the liquid is measured, and the slip length is extracted from the equation in Table 2.3. It is a direct technique to measure the liquid flow close to solid surfaces. It allows direct access to the velocity profile and extraction of the slip length with high accuracy [66].

Pressure-drop experiments

This is the measurement of pressure drop as a function of the flow rate in Navier boundary condition. However, light exposed particles make it difficult to achieve good spatial resolution in the PIV measurement normal to the plane of the ultra-hydrophobic surface (z direction).
## Chapter 2 Literature Review

### Table 2.3 Theory of slip length calculation.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Note</th>
</tr>
</thead>
</table>
| ![Diagram](image) | **b_0 = \infty**  
**b_l = 0**  
*Philip – flow parallel to the stripe on the planar surface with one-dimensional features*  
*Lauga & Stone – Flow perpendicular to stripes stripe on planar surface with one-dimensional features*  
*Microstructured superhydrophobic surfaces*  
*Flow perpendicular to the slip*  
*Calculated by Navier-Stokes equation*  
*Agreement with Philip and Lauga & Stone* |

When \( R \to \infty \), the effective slip length is

\[
b_{\text{Philip}} = \frac{L}{\pi} \ln \left( \cos \left( \frac{\pi \phi_g}{2} \right) \right) \]

Where, \( L \) = the pitch of the pattern  
\( \phi_g \) = the gas fraction area = \((L-a)/L\)  
\( a \) = stripe width with zero slip length

\[
b_{\text{Lauga–Stone}} = \frac{L}{2\pi} \ln \left( \cos \left( \frac{\pi \phi_g}{2} \right) \right) \]

\[
b = \frac{V_s}{\dot{\gamma}} \]

Where, \( V_s \) = effective velocity slip on the surface  
\( \dot{\gamma} \) = Shear rate
Ybert et al. [71]

\[ b_{\text{eff}} = L \left( \frac{0.325}{\sqrt{\phi_s}} - 0.44 \right) \]

Where, \( \phi_s = \) solid fraction
(Surface area where the lip length vanishes)
\( \phi_s = 1 - \phi_g = a/L \)

Davis & Lauga [72]

\[ b_{\text{eff}} = L \left( \frac{3}{16} \sqrt{\frac{\pi}{\phi_s}} - \frac{3}{2\pi} \ln(1 + \sqrt{2}) \right) \approx L \left( \frac{0.332}{\sqrt{\phi_s}} - 0.421 \right) \]

A surface with two-dimensional patterning, regular lattice
Linear reg between ression
Table 2.4 Methods of slip length measurement.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Equation</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Measurement</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle image velocimetry</td>
<td>( b = \frac{\partial u_s}{\partial z} )</td>
<td>Measurement of the velocity of fluorescent particles in water</td>
</tr>
<tr>
<td></td>
<td>Where, ( u_s ) = the velocity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \frac{\partial u_s}{\partial z} = ) shear rate</td>
<td></td>
</tr>
<tr>
<td>Cone and Plate Rheometer</td>
<td></td>
<td>Torque measurement with rheometer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Uniform shear rate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Questions about the accuracy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Experimental error in the apparent viscosity with one measuring process</td>
</tr>
<tr>
<td>Indirect Measurement</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rheometry experiment</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( M = \frac{2\pi \Omega R^3}{3 \theta_0} \left[ 1 - \frac{3 b_{eff}}{2R \theta_0} + \frac{3 b_{eff}^2}{R^2 \theta_0^2} - \frac{3 b_{eff}^3}{R^3} \ln \left( \frac{R \theta_0 + b_{eff}}{b_{eff}} \right) \right] )</td>
<td>Where, ( M ) = Torque (Applied), ( R ) = radius</td>
</tr>
<tr>
<td></td>
<td>Where, ( \Omega ) = angular velocity, ( \eta ) = liquid viscosity</td>
<td>( \theta_0 ) = measured in the rheometer</td>
</tr>
<tr>
<td>Parallel Plate Rheometer</td>
<td></td>
<td>( \eta_a = ) apparent viscosity measured in the rheometer</td>
</tr>
<tr>
<td></td>
<td>( \frac{\omega c \eta R}{D} = \frac{2 \pi R^3 \eta_c}{3} \frac{\omega R}{D} )</td>
<td>( \eta_a = ) apparent viscosity measured in the final wetting state (Wenzel state)</td>
</tr>
</tbody>
</table>
Chapter 2 Literature Review

Pressure-drop experiment
[76, 77]

\[ q = \frac{H^3}{4\eta} \left( -\frac{dP}{dz} \right) \left( \frac{1}{3} \frac{b}{H + b} \right) \]

- \( b \): effective slip length
- \( dP/dz \): pressure gradient

\[ D_R = \frac{\Delta P_{\text{no-slip}} - \Delta P_{\text{SH}}}{\Delta P_{\text{no-slip}}} \]

- \( \Delta P_{\text{SH}} \): experimentally measured pressure drop
- \( \Delta P_{\text{no-slip}} \): Pressure drop for flow over a no-slip surface

Surface force apparatus experiment [78, 79]
Damping versus distance

Indirect Measurement

Atomic force microscope experiment [80, 81]
Dynamic mode AFM experiment
High accuracy
Controlling the gap of the flow

\[ 1 + \frac{\gamma_H}{\gamma_0} = -\frac{A_0}{A} \sin(\varphi) \frac{Q_0}{\sqrt{1 + Q_0^2} + 2 \left( \frac{A_0}{A} \right) \cos(\varphi) + A_0^2/A^2 \sqrt{1 + Q_0^2}} \]

\[ \gamma_H = \frac{6\alpha R^2 \eta}{d} f^* \quad f^* = \frac{1}{4} \left[ 1 + \frac{6b}{4b} \left( \frac{1 + \frac{D}{4b}}{\ln \left( 1 + \frac{4b}{D} \right) - 1} \right) \right] \]
There are three possibilities that can explain large slip length in CNT channel: Narrow pore diameter, reduced viscosity, and hydrophobicity.

First, molecular dynamic simulation by Holt et al. [26] demonstrates that CNT membrane has significantly higher slip length than the other polymer membranes due to its relatively smaller pore diameter compared to the pore length. Table 2.5 compares slip length of nanochannel with different sizes of diameter. The largest slip length of CNT membrane is 1400 nm, which is almost three orders of magnitude greater than the pore size and is on the order of the overall size of the system (pore length). In contrast, it reveals that the polycarbonate membrane with a pore size of 15 nm has a much smaller slip length of 5 nm. This clear comparison suggests that the slip flow through sub-2 nm CNT happens possibly due to the length scale confinement [82] or partial wetting of CNT’s surface [83]. The result raises the question whether Newtonian fluid could be used for determining water flow in CNT.

Table 2.5 Slip length of CNTs membrane.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Transport</th>
<th>Viscosity (Pa s)</th>
<th>Pore diameter (nm)</th>
<th>Expected flow</th>
<th>Slip length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT [84]</td>
<td>Water</td>
<td>8.94x10^-3</td>
<td>7</td>
<td>25 cm/s bar</td>
<td>39 – 54</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>1.074x10^-3</td>
<td></td>
<td>4.5 cm/s bar</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Iso-Propanol</td>
<td>1.945x10^-3</td>
<td></td>
<td>1.12 cm/s bar</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Hexane</td>
<td>294 x10^-3</td>
<td></td>
<td>5.6 cm/s bar</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>Decane</td>
<td>920 x10^-3</td>
<td></td>
<td>0.67 cm/s bar</td>
<td>3.4</td>
</tr>
<tr>
<td>DWNT 1 [26]</td>
<td>Water</td>
<td>8.94x10^-3</td>
<td>1.3 – 2.0</td>
<td>1500 – 8400</td>
<td>380 – 1400</td>
</tr>
<tr>
<td>DWNT 2 [26]</td>
<td></td>
<td></td>
<td></td>
<td>680 – 3800</td>
<td>170 – 600</td>
</tr>
<tr>
<td>DWNT3 [26]</td>
<td></td>
<td></td>
<td></td>
<td>560 – 3100</td>
<td>140 – 500</td>
</tr>
<tr>
<td>Polycarbonate [26]</td>
<td></td>
<td></td>
<td></td>
<td>15</td>
<td>3.7</td>
</tr>
</tbody>
</table>

*Feed temperature derived from viscosity: 20 °C

Another factor to control the slip length is viscosity. Frictionless surface at CNT wall (hydrophobic) was found to make fluid velocities high [84]. This result can explain why the slip length of CNT is remarkably long. The slip length decreases as solvents become more
hydrophobic, which indicates stronger interaction with the CNT’s wall. It is suggested that higher contact angle results in greater slip and more reduction in effective friction [85]. On the other hand, lower $\varepsilon_r$ (potential well depth ← relative energy parameter) and lower $\sigma_r$ (Atom size radius) tend to increase contact angle. Another explanation for the slip length is based on the fact that CNT is hydrophobic. The strength of attraction between water molecules is greater than the attraction between the hydrophobic solid and the water. Myers suggested the reduced viscosity model that is analogous to a slip model to provide the explanation [86]. The model provides a physical interpretation of the classical Navier slip condition and explains why slip length may be greater than the tube radius.

2.3.4.2 Modification of CNT membrane for channels of water and target molecules

Even though CNT channel has large slip length due to its frictionless hydrophobic nanochannel structure, it requires high pressure for water transport in the superhydrophobic channel in the pressure driven membrane process. In this way, hydrophobic VACNT channel requires being modified by attaching a specific hydrophilic functional group for enhanced selectivity and electrical and thermal property [87-90] (Fig 2.8a). Further, CNT functionalization can lead to highly selective separations caused by forcing a chemical interaction between permeate and functional molecules as the formation of hydroxyl and carboxyl groups on the surface of nanotubes [59, 91, 92].
Fig 2.8(a) Concept of tip functionalization of VACNT membrane and (b) oxidation process of CNTs using acid and oxidative gas [31].

Table 2.6 summarizes methods of hydrophilic functionalization in VACNT membrane.

Oxidation with acid treatment is one of the widely used methods that directly attach carboxylic groups and other oxygen-bearing groups, such as hydroxyl (-OH), carbonyl (C=O), ester, and nitro groups to ends and/or defect sites in the sidewalls of CNT [93-95] (Fig 2.8b). This method was employed in order to disperse nanotubes and purify amorphous carbon. This procedure is straight-forward, and commonly used for hydrophilic functionalization of CNT.
Plasma oxidation (during the membrane fabrication process) was reported to add carboxylic acid groups at the entrance of CNT [92]. These functional groups introduced water molecules to the CNT channels, which acted as a passage of water through the membrane. Therefore, water flux was enhanced by columbic attraction between surface modified CNT and water molecules. This approach increased not only water flux but also selectivity of the separation process. The charge state of carboxyl groups at the entrance to the CNT tips stimulated the attraction of ions into them [96]. It is due to the fact that the presence of polar water molecules, the cation-π effect by the ions, or an external electric field can alter the electronic structure of CNT and hence cause field-induced polarization. The presence of functional groups could also alter the electronic structure of the CNT. This coupled density functional theory of molecular dynamics approach resulting in an improved force field could explain such interactions.

A previous study on the relationship between functionalization and membrane performance was conducted by means of molecular dynamic simulation [97]. The concept of CNT functionalization was inspired by biomimetic modification – Aquaporin-4-channels in which four amino acids are added. Location of functional groups (CONH$_2$, NH$_3^+$, COO$^-$, and OH) in CNT channels was set out to the interior and or at the entrance of the channel. The result revealed that CNT with a wide diameter (1.35 nm) completely removed salt, delivering 150 – 170 % enhanced water flux compared to the unmodified (8,8) CNT [64]. Simulation of functional group location elucidated that the membrane exhibited a high rejection without sacrificing water flux when one functional group is attached to the tip and other four groups are added to the inside of the CNT channel.

Surface modification can be employed by an electrical method that offers a powerful, nondestructive, and selective way to achieve water transport through CNT membrane [98, 99]. Polarity and voltage-dependent wetting method could be used for various applications of
nanotube membranes. For example, VACNT membranes act as an anode (positive potential), and the Pt wire as the cathode (negative potential) [100]. Once critical voltage (1.7 V) is reached, the membrane is transferred from superhydrophobic to a hydrophilic state, and the water droplet rapidly passes through the nanotube arrays. The mechanism is that the sinking of the droplet is dependent on the presence of electrolysis in this system due to the electrochemical oxidation of the nanotube.
Table 2.6 Summary of hydrophilic treatments of CNTs.

<table>
<thead>
<tr>
<th>Method</th>
<th>Functional group</th>
<th>Effect</th>
<th>Condition</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma etching [101] [92]</td>
<td>COOH</td>
<td>Removal of amorphous carbon and one opened CNT tip</td>
<td>- For 30 min for removing amorphous carbon, - For 80 min for opening tip at 250 kHz, 30 W PH2O=0.62 Torr</td>
<td>(a) Before (b) After 80 min</td>
</tr>
<tr>
<td>H2O plasma-enhanced oxidation [59]</td>
<td>COOH</td>
<td>- Opening CNT tip, - Attaching COOH group, - Etching polymer matrix (CNT 10 - 50 nm above than PS matrix)</td>
<td>PH2O= 60 mtorr 2.5 W/cm² for 7 min</td>
<td>70 % of CNT tip open</td>
</tr>
<tr>
<td>HCl Treatment [59]</td>
<td>COOH</td>
<td>- Increasing ionic flux (Ru(NH3)6³⁺) 0.07 → 0.9 μmol/cm²hr⁻¹</td>
<td>-Immersing membrane in concentrate HCl for 24 hr at RT -Rinsing with DI water</td>
<td></td>
</tr>
<tr>
<td>Reactive Ion etching [26]</td>
<td>COOH</td>
<td>- Opening CNT tip for gas and water permeability</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td></td>
</tr>
<tr>
<td>Ag Catalyze oxidation [102]</td>
<td>Oxidized Carbon</td>
<td>Attaching Oxygen containing group - Epoxidation</td>
<td>Oxidation of 5 % Ag/CNTs for 105 min at 300 °C</td>
<td>CNT channels are wet by hydrophilic solvents</td>
</tr>
<tr>
<td>Wet chemistry method [103, 104]</td>
<td></td>
<td>Opening CNT tips</td>
<td>Selective oxidation by CO₂, O₂ above 600 °C</td>
<td>No results for hydrophilic group attachment on CNT tips</td>
</tr>
<tr>
<td>Oxidation method [31]</td>
<td>COOH, OH</td>
<td>- Opening CNT tips, - Attaching hydrophilic group to CNT walls</td>
<td>Oxidation of CNTs by boiling mixture of H₂SO₄ and HNO₃</td>
<td>Applied to HACNTs</td>
</tr>
</tbody>
</table>

36
| Acid oxidative | COOH | - Opening CNT tips,  
| (Sonochemistry) |   | - Attaching hydrophilic group to CNT walls  
| 105, 106 |   | - Oxidation by H$_2$SO$_4$/30% H$_2$O$_2$ solution  
|   |   | - Sonication for 5 min  

Acid sonicated CNTs show 1590 cm$^{-1}$ band of COO- groups increase
2.3.4.3 Challenges in VACNT membrane

VACNT membrane has many advantages for water treatment as discussed in the previous sections. The slippage effect derived from frictionless wall leads to the several orders of magnitude higher water flow than conventional fluid transport. However, it is possible only in the case that pore density is as compact as \((6 \pm 3) \times 10^{10} \text{ cm}^{-2}\) [59]. It indicates that low-density CNT array may not guarantee ultra-fast water flux. Moreover, it is imperative to synthesize highly ordered oriented vertical structure of CNT arrays, which may not be assured in conventional thermal CVD due to the thermal fluctuation and inconsistent gas flow in chamber. Even if VACNT membrane has many possibilities of tackling current challenges in membranes for water treatment, difficult fabrication, and synthesis of CNT arrays with optimal density for ultra-fast water flux procedure hinder its wide application to water treatment. In particular, further study on post-treatment such as hydrophilic functionalization on CNT tip would be a critical step for rejecting salt completely and realizing high water permeability. In addition, a scaled-up issue may be a key to making the progress of practical application of the VACNT membrane.
2.4 Application of CNT membranes in water treatment

2.4.1 NOM removal for surface water treatment and seawater pretreatment

2.4.1.1 Surface water treatment

NOM is a complex of particulate and soluble materials in surface water with varying molecular weight, mainly produced from the decomposition of plant and animal residues. It contains a heterogeneous mixture of humic substances, hydrophilic acid, protein lipids, carbohydrates, carboxylic acids, amino acids, and hydrocarbons. NOM in dissolved organic carbon can be divided into three segments: Hydrophobic (49 %), hydrophilic (30 %) and transphilic (21 %) [107]. Here, Humic substances are composed of 60 - 70 % of TOC in soil and 60 – 90 % of DOC in natural water. Due to the carboxylic and phenolic moieties, NOM carries a negative charge in the natural environment [108]. NOM generates carcinogen such as Trihalomethanes (THMs), Haloacetic Acids (HA) when it reacts with chlorine in distribution system [109]. Furthermore, it causes both severe reversible/irreversible membrane fouling in the presence of calcium [110], thus, leading to flux decline [111] and decreased rejection efficiency [112]. Such a foulant is hard to remove by low pressure driven membranes due to their relatively larger pore size.

An attempt to overcome this issue encouraged the enhancement of adsorption capacity of the membrane by developing nanocomposite membrane. In this way, CNT membrane can be extensively applied in the removing NOM due to its unique properties such as large surface area and hydrophobicity. CNT removes NOM by its adsorption capacity of organic chemicals [8]. The interaction between CNT and NOM includes π- π attractions, hydrophobic interaction, electrostatic interaction, and hydrogen bond. For example, π- π attractions appear between bulk π systems on CNT surfaces and organic molecules with C=C double bonds or
benzene rings. Hydrogen bonds occur between functional groups on CNT surfaces and NOM. Electrostatic interactions occur when CNT surfaces are charged.

**HACNTs membrane** removes NOM by adsorption mechanism. CNT directly contact to the organic contaminants due to their arrangement in membrane matrix. Such a fabrication facilitates hydrophobic interactions, $\pi-\pi$ interaction between CNT and organic chemicals. $\pi-\pi$ systems on CNT attracts with a cross-linked aromatic network of molecules on organics such as humic acids [113]. Thus, the adsorption capacity of CNT is proportional to the accessible surface area.

**CNT composite membrane.** Removal mechanism of CNT nanocomposite membranes is determined by system configuration (or application). It is noted that HA/FA with mean size less than 1 nm easily pass through low-pressure membranes such as MF/UF, exhibiting only 20 – 50 % rejection efficiency. However, NF/RO membrane can reject more than 90% NOM by the size exclusion. To increase removal efficiency in UF membrane, its adsorption capacity needs to be enhanced. Recently, MWCNT enhanced UF membrane has been reported to remove 80% HA removal rate by increasing electrostatic interaction between negatively charged HA and positively charged membrane surface. Compared that CNT incorporated membrane exhibits negative zeta potential, the CNT/PANI complex incorporated PES-UF membrane possesses positive zeta potential, which contributes greatly enhanced NOM rejection.

**VACNT membrane.** Currently fabricated VACNT membranes are classified in the UF or NF/RO membrane by their pore size (1 – 7 nm), rejection and applied pressure (2 and 20 bar) [114, 115]. Despite that application to NOM removal has not been reported, it is expected that VACNT membrane would have strong efficacy for the high NOM removal due to its mechanism driven by steric hindrance and adsorption capacity.
Table 2.7 compares HA removal efficiency of recently published CNT membranes with conventional polymeric membranes. In case of synthesized NOM filtration test, CNT composite membrane outperformed conventional polymeric membranes in UF membrane process, which cannot completely remove HA due to its separation performance (larger pore size than HA). As shown in Table 2.7, the CNT/PANI/PES membrane with 10 kDa MWCO exhibited 80 % of SRHA removal rate, compared that the ceramic and PES membrane (50 and 150 kDa, respectively) could remove 60 – 70 % SRHA. CA-UF membrane in the range of 3- 15 kDa removed 90 % of HA effectively. The notable thing is that the feed concentration in CNT/PANI/PES membrane is low (5 mg/L) than the one in ceramic and PES membranes (10 - 20 mg/L). Further, recently fabricated HACNT membrane reached to 90 % HA removal by facilitating adsorption capacity of CNT to the membrane matrix. However, in case of natural surface water filtration test, removal efficiency of PSf UF membrane (50 %) was comparable to CNT membrane (45 %). Based on current researches on NOM removal, MWCNT membrane seemed to have superior performance in synthetic NOM feed water compared to the conventional UF membrane, but did not outperform it in the low range of concentration of NOM such as natural surface water. The conventional UF membrane with small MWCO (< 10 kDa) showed high removal efficiency in the presence of high concentration HA filtration test.
**Table 2.7 Summary of HA removal efficiency by CNTs membranes.**

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>System</th>
<th>Composition</th>
<th>Proportion of CNTs (%)</th>
<th>MWCO (kDa) or Pore size</th>
<th>Water permeability (LMH/bar)</th>
<th>Model compound</th>
<th>Rejection efficiency (%, UVA 254 nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>Polysulfone (PSf)</td>
<td>-</td>
<td>-</td>
<td>68</td>
<td>-</td>
<td>NOM (From natural surface water)</td>
<td>50</td>
<td>[116]</td>
</tr>
<tr>
<td>Polymer</td>
<td>UF Ceramic</td>
<td>-</td>
<td>50, 150</td>
<td>-</td>
<td>-</td>
<td>SRHA* 20 mg/L</td>
<td>60</td>
<td>[117]</td>
</tr>
<tr>
<td>UF</td>
<td>PES</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>NOM 5 mg/L</td>
<td>70</td>
<td>[118, 119]</td>
</tr>
<tr>
<td>UF</td>
<td>Cellulose Acetate (CA)</td>
<td>-</td>
<td>3-15</td>
<td>10 - 60</td>
<td>HA 9 -10 mg/L</td>
<td>90</td>
<td>[118, 119]</td>
<td></td>
</tr>
<tr>
<td>HACNTs</td>
<td>HACNTs</td>
<td>100 %</td>
<td>(41 ± 10 nm)</td>
<td>-</td>
<td>HA 5 mg/L</td>
<td>90</td>
<td>[51]</td>
<td></td>
</tr>
<tr>
<td>RO</td>
<td>CNT-Polyamide</td>
<td>0 – 1</td>
<td>0.71 – 0.76</td>
<td>HA 10 mg/L</td>
<td>90</td>
<td>[120]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT nanocomposite</td>
<td>UF CNT- PES</td>
<td>0 – 4</td>
<td>25 - 27</td>
<td>2.4 – 21.8</td>
<td>NOM (From natural surface water)</td>
<td>45</td>
<td>[121]</td>
<td></td>
</tr>
<tr>
<td>UF</td>
<td>CNTs/PANI/PES</td>
<td>1.5</td>
<td>10 (4.6 nm)</td>
<td>500 - 1400</td>
<td>SRHA* 5 mg/L</td>
<td>80</td>
<td>[44]</td>
<td></td>
</tr>
</tbody>
</table>

*SRHA: Suwanee river humic acid, **: No data reported.
2.4.1.2 Seawater pretreatment

Removal of low molecular weight dissolved organic matters (LMW-DOMs) in seawater is a critical issue due to the decline in the membrane performance by irreversible membrane fouling. Colloidal issues such as humic substances and biopolymers (3-20 nm) mainly make membrane fouled through adsorption on the membrane surface or in the membrane pores. However, direct MF and UF membrane filtration with higher than 100 kDa MWCO cannot remove LMW-DOM (less than 350 Da) [122, 123]. An option to overcome the limit in pretreatment for seawater reverse osmosis (SWRO) is suggested to be the integration of filtration system with the adsorption or coagulation process [124, 125]. Recently developed membrane hybrid system coupled with adsorption with addition of powder activated carbon (PAC) demonstrated enhanced performance in the removal of LMW-DOM containing 75% of organic matter in seawater [126], mostly due to the fact that PAC (as an adsorbent) removes LMW-DOM with its affinity (covalent bonding) to the LMW organic compounds [127, 128].

Despite the outperformance of UF membrane hybrid system, a relatively high amount of adsorbent causes a large volume of chemical sludge from SWRO desalination plant, which brings serious environmental issues to the aquatic condition. Therefore, further study is suggested to focus on the reduction of chemical dosage by developing membrane material with enhanced removal efficiency and higher water flux.

For this reason, CNT composite membranes could be one of the favored approaches due to its unique characteristic of excellent adsorption capacity for organic matter. However, there are few existing research papers on the application of CNT membrane to seawater pretreatment for LMW-DOM removal. Thus, examination of CNT membrane for effective LMW-DOM removal in seawater pretreatment would considerably contribute to addressing the limit of MF/UF
membrane system for seawater pretreatment. Based on the recent progress of CNT nanocomposite membrane in water treatment, CNT membrane with greatly enhanced adsorption capacity is highly likely to contribute to the reduction of sludge volume by decreasing chemical dosage.

2.4.2 Salt rejection: from brackish water treatment to MD/RO concentrate recycling

VACNT applicability for seawater desalination has been investigated using molecular dynamics simulation. For example, Corry determined the optimal diameter of carbon nanotube for water desalination by molecular dynamic simulation [57]. Depending the effect of the different CNT’s sizes on the water flux and ion rejection, the optimal internal diameter of CNT for desalination was determined. Table 2.8 summarizes VACNT’s application in water treatment. CNT with up to 10 Å [(7, 7) armchair tube type] of C-C diameter removed nearly 100% of NaCl, with maintaining improved water flux. This result is comparable with FILMTEC SW30HR-380 commercial RO membrane [129]. It is notable that Na\(^+\) tends to pass through the pores of (6,6) membrane more readily than Cl\(^-\). Cl\(^-\) is not seen to pass through the (7, 7) membrane and five passes through the (8, 8) membrane in 25 ns compared to 23 Na\(^+\). This result can be similar to carbon nanotubes of different chirality as well as double or multi-walled ones. Donnan membrane equilibrium supports this phenomenon because electrochemical equilibrium is established when an ionic solution contacts a charged membrane and equilibrium partitioning of ions between the solution and the membrane phase under the constraints of electro-neutrality [58]. Electrostatic force repulses anions and attracts cations from the negatively charged CNT tips (-COOH group). The condition of the electro-neutrality prevents an independent migration of anions and cations. Then, two opposite electrostatic forces are balanced, thus leads to the overall rejection.
The ion rejection mechanism in CNT was assumed to be both steric hindrance and electrostatic repulsion. In order to understand the relative importance of these driving forces, Fornasiero et al. examined ion exclusion and selectivity as a function of solution concentration, pH, ion valence, and ion size [58]. Ion rejection in nanopores is mostly controlled by the electrostatic effect, which is demonstrated by Donnan membrane equilibrium model [130, 131]. CNT functionalized with COOH group were tested at two solutions having different pH values, one above the pKₐ of COOH group (pKₐ=5.5) and another below it. COOH groups are protonated (COO⁻) at high pH while neutral (COOH) at low pH. The research reported that there was more than 90% ion rejection above pKₐ of COOH (pH=7.2), indicating that major driving force for ion rejection is electrostatic interaction. In addition to pH effect, the valency of cationic (z⁺) and anionic (z⁻) species in solution affects ion rejection according to the Donnan equilibrium model. K₃Fe(CN)₆ having higher ion valance (3:1) was shown to have the highest rejection (> 90%), which is considered that overall rejection is determined by a valence between two opposite electrostatic forces and anion size. This is mainly due to the fact that the larger the anion valence relative to the cation valence the stronger the net repulsive force, and, therefore, the salt rejection.

Table 2.9 summarizes performance evaluation in NaCl filtration test in three types of CNT membrane. Overall, CNT composite membranes outperformed NaCl removal and permeate flux of commercial PA-RO membrane in molecular dynamic simulation. Compared that VACNTs membrane was proved to have high NaCl rejection and deliver several magnitude higher permeate flux than polymeric membranes by molecular dynamic simulation, the results from lab scale filtration has yet to be reported. A recent research demonstrated the applicability of HACNT membrane for NaCl rejection by much enhanced adsorption capacity of plasma modified long CNT [132]. This may contribute to point-of-use potable water purification in the
future. However, it is questionable for this type of membrane to be applied to recycling concentrate in high pressure driven process. It is suggested that the following be developed: 1) the HACNT membrane which can bear for high pressure, and 2) a suitable process for the practical application.
Table 2.8 Summary of VACNT in water treatment.

<table>
<thead>
<tr>
<th>Type of VACNT</th>
<th>Internal Diameter</th>
<th>Length</th>
<th>Contact angle</th>
<th>Flux</th>
<th>Operating pressure</th>
<th>Test material</th>
<th>Re. (%)</th>
<th>Method of CNT synthesis/fabrication</th>
<th>Method of tip opening</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW (6,6)</td>
<td>1.1 nm</td>
<td>1.3 nm</td>
<td>-</td>
<td>4.2</td>
<td>26.4 bar</td>
<td>NaCl</td>
<td>100</td>
<td>Catalytic chemical vapor deposition/ Silicon nitride (Si₃N₄) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>Corry (2011) [56]</td>
</tr>
<tr>
<td>(5,5) armchair type tube</td>
<td>0.32 nm</td>
<td>~1.4 nm</td>
<td>-</td>
<td>1.2</td>
<td>55 bar</td>
<td>NaCl</td>
<td>100</td>
<td>Catalytic chemical vapor deposition/ Silicon nitride (Si₃N₄) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>Corry (2008) [57]</td>
</tr>
<tr>
<td>(6,6) armchair type tube</td>
<td>0.47 nm</td>
<td>~1.4 nm</td>
<td>-</td>
<td>2.1</td>
<td>55 bar</td>
<td>NaCl</td>
<td>100</td>
<td>Catalytic chemical vapor deposition/ Silicon nitride (Si₃N₄) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>Corry (2008) [57]</td>
</tr>
<tr>
<td>(7,7) armchair type tube</td>
<td>0.59 nm</td>
<td>~1.4 nm</td>
<td>-</td>
<td>3.2</td>
<td>55 bar</td>
<td>NaCl</td>
<td>95</td>
<td>Catalytic chemical vapor deposition/ Silicon nitride (Si₃N₄) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>Corry (2008) [57]</td>
</tr>
<tr>
<td>(8,8) armchair type tube</td>
<td>0.75 nm</td>
<td>~1.4 nm</td>
<td>-</td>
<td>4.9</td>
<td>55 bar</td>
<td>NaCl</td>
<td>58</td>
<td>Catalytic chemical vapor deposition/ Silicon nitride (Si₃N₄) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>Corry (2008) [57]</td>
</tr>
<tr>
<td>DW MW</td>
<td>1.3 - 2 nm</td>
<td>1-5 μm</td>
<td>-</td>
<td>&lt; 2</td>
<td>0.82 bar</td>
<td>Ru²⁺(bipyrr)₃</td>
<td>-</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>Holt et al. (2006) [26]</td>
</tr>
<tr>
<td>DW</td>
<td>1.3 - 2 nm</td>
<td>1-5 μm</td>
<td>-</td>
<td>&lt; 3</td>
<td>0.82 bar</td>
<td>Colloidal Au 2 ± 0.4 nm of particle size</td>
<td>-</td>
<td>-</td>
<td>Catalytic chemical vapor deposition/ Silicon nitride (Si₂N₄) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
</tr>
<tr>
<td>SW</td>
<td>1.3 - 2 nm</td>
<td>1-5 μm</td>
<td>-</td>
<td>&lt; 3</td>
<td>0.82 bar</td>
<td>NaPTS</td>
<td>96 %</td>
<td>Catalytic chemical vapor deposition/ Silicon nitride (Si₂N₄) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>Fornasiiero et al. [58]</td>
</tr>
<tr>
<td>DW</td>
<td>1.3- 2 nm</td>
<td>1-5 μm</td>
<td>-</td>
<td>-</td>
<td>0.69 bar</td>
<td>K₂Fe(CN)₆</td>
<td>90 %</td>
<td>Catalytic chemical vapor deposition/ Silicon nitride (Si₂N₄) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>Fornasiiero et al. [58]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>K₂SO₄</td>
<td>80 %</td>
<td>Catalytic chemical vapor deposition/ Silicon nitride (Si₂N₄) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>Fornasiiero et al. [58]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CaSO₄</td>
<td>37 %</td>
<td>Catalytic chemical vapor deposition/ Silicon nitride (Si₂N₄) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>Fornasiiero et al. [58]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>KCl</td>
<td>37 %</td>
<td>Catalytic chemical vapor deposition/ Silicon nitride (Si₂N₄) encapsulation method</td>
<td>Reactive ion etching in an oxygen containing plasma</td>
<td>Fornasiiero et al. [58]</td>
</tr>
</tbody>
</table>
Table 2.9 Summary of salt removal efficiency by CNTs membranes.

<table>
<thead>
<tr>
<th>Type of membrane</th>
<th>Filler matrix</th>
<th>Fabrication procedure</th>
<th>System</th>
<th>Pure water permeability (LMH/bar)</th>
<th>Feed water (mg/L)</th>
<th>Salt rejection (%)</th>
<th>Removal mechanism</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs TFC membrane</td>
<td>MWCNTs/polyamide (PA)</td>
<td>Polymer grafting process</td>
<td>RO</td>
<td>0.71 ± 0.11</td>
<td>NaCl 4000</td>
<td>76 ± 1.10</td>
<td>Size exclusion</td>
<td>[120]</td>
</tr>
<tr>
<td></td>
<td>PA/CNTs</td>
<td>Interfacial polymerization</td>
<td>RO</td>
<td>3 (15.5)</td>
<td>NaCl 2000</td>
<td>95</td>
<td>Size exclusion</td>
<td>[40]</td>
</tr>
<tr>
<td>20% CNTs/PA</td>
<td>MWCNTs/polyamide (PA)</td>
<td>Zwitter ion functionalization of CNTs + Interfacial polymerization</td>
<td>RO</td>
<td>0.31 → 1.33 (36.5)</td>
<td>NaCl 1000</td>
<td>97.60 → 98.60</td>
<td>Steric hindrance + electrostatic repulsion</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>PA/CNT/PVA</td>
<td>Interfacial polymerization</td>
<td>RO</td>
<td>4.15 ± 0.99 (15.5)</td>
<td>NaCl 2000</td>
<td>98.40 ± 0.51</td>
<td>Size exclusion</td>
<td>[133]</td>
</tr>
<tr>
<td></td>
<td>CNT/PES</td>
<td>Phase inversion</td>
<td>NF</td>
<td>0.2 (4)</td>
<td>NaCl 500</td>
<td>17</td>
<td>Size exclusion</td>
<td>[134]</td>
</tr>
<tr>
<td>HACNTs membrane with support layer</td>
<td>Self-supported (Bucky paper)</td>
<td>Vacuum filtration</td>
<td>DCMD*</td>
<td>52.9 (With 22.7 kPa**)</td>
<td>NaCl 3500</td>
<td>99</td>
<td>Vapor pressure difference</td>
<td>[135]</td>
</tr>
<tr>
<td></td>
<td>Plasma modified ultra-long CNTs on the MCE support layer</td>
<td>Vacuum filtration</td>
<td>-</td>
<td>NaCl 3500</td>
<td>400% w/w</td>
<td>Adsorption</td>
<td>[132]</td>
<td></td>
</tr>
<tr>
<td>VACNTs membrane</td>
<td>Polystyrene-polibutadiene (PS-PB) copolymer</td>
<td>In-situ polymerization</td>
<td>UF</td>
<td>1100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[136]</td>
</tr>
<tr>
<td></td>
<td>Epoxy infiltration</td>
<td></td>
<td>UF</td>
<td>1100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[115]</td>
</tr>
<tr>
<td>Polymeric membrane</td>
<td>Polymide</td>
<td>RO</td>
<td>2 (20)</td>
<td>NaCl 580</td>
<td>90</td>
<td>Size exclusion</td>
<td>[137]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cellulose triacetate</td>
<td>FO</td>
<td>0.3</td>
<td>NaCl 580</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*DCMD: Direct contact membrane distillation, **Vapor pressure
2.4.3 Anti-fouling effect

Toxicity to bacteria/virus. CNT has toxicological effects, and its mechanism is to create reactive oxygen species (ROS) production by chemical interactions with CNT. As free radicals are formed by the interaction between CNT and virus and induce in vitro apoptosis, peroxidative products deplete cell antioxidants [138]. This toxicological perspective of CNT was introduced to antibacterial effects. Another research reported that diameter of CNT is the key factor for antibacterial effects [139]. SWCNT, which have higher surface area and shorter length than MWCNTs, were revealed to have higher toxicity by providing greater interaction with the outer membrane of cells.

Antifouling. Incorporation of CNT into polymer also influenced antifouling properties of CNT composite membrane by altering physical/chemical properties of the membrane. For example, CNT/PES composite membrane was reported to exhibit a lower irreversible fouling ratio for bovine serum albumin (BSA) and ovalbumin (OVA) and higher flux recovery ratio compared to pure PES membrane [140]. This research also indicated that protein fouling on CNT composite membrane could be overcome by simple washing. Recently, a publication on the HACNTs membrane has presented fouling resistance and enhanced permeability [141]. Iron oxide doped CNT membrane fabricated by sintering at higher temperature achieved 90% of sodium alginate (SA) as a model compound for EPS and minor flux decline after 4h of operation probably due to iron doped CNT’s role as increasing hydrophilicity. Fouling resistant CNTs/PES NF membrane by surface modification of CNT – amine functionalization were developed recently[142]. This paper demonstrated that decreased roughness, negatively charged membrane surface and increased hydrophilicity by insertion of amine functionalized CNT into polymer matrix led to enhanced fouling recovery ratio. In another study, MWCNT incorporated PES membrane had less amount of desorbed foulant than pure PES membrane, indicating that CNT/PES membrane could alleviate membrane fouling [121].
However, the trade-off between high adsorption and membrane fouling was not completely solved in the CNT enhanced membrane. For this reason, electrochemical system was introduced to the membrane process in which electrical potential is applied to remove foulant layer. Developing CNT membrane, which has enhanced electrical conductivity in the CNT synthesis step, was attempted for removing foulant layer from the membrane [143]. The mechanism of defouling/antifouling in electrically driven CNT membrane system is the removal of foulant layer by giving a shock to the foulant layer via applying electricity. Further, the electrically conductive membrane could contribute to decreasing foulant electromigration by applying electrical potential [144]. Interestingly, recent studies applied electrochemistry for anti-biofouling (electrostatic interaction between charged CNT membrane and bacteria) by CNT membrane. First, an anti-biofouling test was applied to the electrically conducting HACNT membrane in a dead-end filtration by applying electric potential. It showed 5.8 – 7.4 log removal value when 2 to 3 voltages were applied to CNT filter [145, 146]. As the electrical potential is applied, a positively charged CNT filter acted as an anode while negatively charged viral particles were oxidized on the MWCNT surface, and then it resulted in direct oxidation. The fouling behavior of HACNT membrane was investigated from large biomolecules to small molecules aromatics [147]. BSA and naphthalene were found to be major foulants due to solution coagulation and π-π stacking. SWCNT was found to be strong fouling resistant by size exclusion with BSA. The fouling mechanisms were oxidation and electrochemical etching of the CNT. It removed oxidized foulants by applying oxidation or reduction bias to the membrane as a working electrode. However, applying positive bias shortened CNT due to the etching effect.

In addition, the applicability of electrochemical system was expanded to the CNT composite membrane. Electrically conductive polymer RO and NF membrane was fabricated in CNT/PA nanocomposite by interfacial polymerization and applied to cross flow
configuration [148]. Due to the directly contacting rejection layer of CNT/PA on the top of PES support, the fabrication procedure conveyed conductivity of CNT to the PA membrane and showed up to 400 S/cm (20 orders of magnitude greater than PA polymer). The membrane achieved more than 95% of NaCl rejection and delivered a high water flux. To sum up, anti-biofouling and fouling mitigation were attributed to electrical conductivity and toxicology of CNT. Thus, how to introduce these properties to membrane matrix without a loss is challenging in CNT membrane fabrication and its application.

2.4.4 How the CNTs enhanced membrane contributed to the membrane system?

This section discusses the suitability of CNT membrane to the membrane processes – MF/UF, and RO. The membrane processes are classified via its performance and fabrication method as shown in Fig 2.9. Since dispersion of CNT in a polymer matrix to overcome its aggregation was achieved through many studies, incorporation of CNT into the polymer has been highly adopted to the membrane fabrication. From low-pressure (MF and UF) to high-pressure (NR and RO) driven membrane process, CNTs incorporation into the polymer membrane led to the superior outperformance, compared to that of conventional membranes which are presented in Fig 2.9.

![Fig 2.9 Classification of fabrication method in membrane process.](image URL)
**UF membrane system.** Altering physical/chemical properties of the membrane during membrane fabrication process (functionalized CNT incorporation into the polymer matrix) made considerable performance enhancement in low pressure driven membrane (i.e. UF membrane). It contributed to the flux enhancement by increasing pore size, porosity and/or hydrophilicity [149, 150]. Another benefit was enhanced anti-biofouling properties driven by increased surface roughness and decreased negative surface charge [121].

**NF/RO membrane system.** Progress of the CNT composite membranes in NF/RO system were made via the insertion of CNT into i) the selective layer, either MPD (aqueous phase) or TMC (organic solvent layer) via interfacial polymerization [40] and ii) UF support layer by dispersing in a polymer matrix [151]. The CNT inserted into the PA selective layer led to approximately 2 to 4-fold flux increase, enhanced salt rejection, antifouling effect and the durability and chemical resistance against salty water [41, 133]. In addition, CNT incorporation into the polymer matrix contributed to enhancing mechanical strength - bearable to high pressure (more than 10- 20 bar) [152]. Such outperformance appeared mainly due to the increased hydrophilicity and antimicrobial properties of CNT. CNT inserted into UF support layer mainly increased porosity, water uptake capacity and hydrophilicity of support layer, reducing the salt concentration polarization effect.
Table 2.10 Enhanced performance by the CNTs insertion in polymer membrane.

<table>
<thead>
<tr>
<th>System</th>
<th>Membrane type</th>
<th>Enhancement in performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF</td>
<td>CNT bridged 3D GO membrane</td>
<td>- Disinfection of pathogenic bacteria</td>
<td>[153]</td>
</tr>
<tr>
<td>MF</td>
<td></td>
<td>- Toxic heavy metal removal</td>
<td></td>
</tr>
<tr>
<td>MF</td>
<td></td>
<td>- Enhanced conductivity</td>
<td></td>
</tr>
<tr>
<td>MF</td>
<td>CNTs/PVDF hollow fiber membrane</td>
<td>- Increased permeability</td>
<td>[154]</td>
</tr>
<tr>
<td>UF</td>
<td>Hydrophilic CNTs coated membrane</td>
<td>- Improved antifouling properties</td>
<td>[15]</td>
</tr>
<tr>
<td>UF</td>
<td></td>
<td>- High permeability</td>
<td></td>
</tr>
<tr>
<td>UF</td>
<td>Dual layer of CNTs/PVDF membrane</td>
<td>- Electrical conductivity</td>
<td>[143]</td>
</tr>
<tr>
<td>NF</td>
<td>Polyelectrolyte complex/MWCNTs hybrid membrane</td>
<td>- Enhanced NF membrane performance</td>
<td>[155]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Water softening</td>
<td></td>
</tr>
</tbody>
</table>

2.4.5 Hybrid material with CNT as a new generation of membrane material

CNT composites have been tested for multi-functional effects for separation performance. In the attempts, CNT was blended with other nanomaterials such as graphene oxide (GO) and titanium dioxide (TiO$_2$) and conductive polymers such as PANI and Poly (3,4-ethylenedioxythiophene) (PEDOT).

2.4.5.1 CNT/GO and CNT/Graphene

CNT/GO complex was designed to supplement the limit of CNT membrane such as difficulty in assembling VACNT array in the polymer matrix and its aggregation due to Van der Waals force between CNT by incorporating with GO. Graphene-based material has many advantages such as two-dimensional structure, mono-atomic thickness, antibacterial properties, and high mechanical strength [156-158]. Several studies revealed that layered two-dimensional GO bridged with one-dimensional CNT could deliver the synergetic effect to the water treatment membrane. Research showed that 5:5 CNT/GO composite UF
membrane could contribute to enhancement in permeability and antifouling, compared to the CNT and GO membrane itself [159]. This enhanced dispersion of CNT/GO complex compared to individual one altered physical/chemical properties such as increased porosity and hydrophilicity, resulting in a 2.5-fold increase in permeate flux. Further, this membrane showed the enhanced antifouling effect and 98.8% flux recovery due to the fact that the affinity of hydrophilic low-dimensional CNT material hinders protein adsorption. In addition, CNT/GO incorporated RO membrane was reported to have much enhanced water flux, chlorine resistance, mechanical strength, durability compared to the pure PA-RO membrane and GO PA membrane (without CNTs) [160]. CNT/GO complex was inserted in MPD solution during the interfacial polymerization step. The enhanced performance could be mostly attributed to the effect of GO insertion to the increased dispersion of CNT in the aqueous solution and polymer matrix. A recent study also showed the progress in NF membrane by the synergetic effect of GO (for molecular sieving) and CNT (for expanding interlayer spaces between graphene sheets) [161]. These intercalated CNT/GO complex NF membrane achieved increased water flux (100%) and high dye rejection (> 96%) in comparison that GO membrane exhibited high permeate flux but low rejection efficiency. However, the membrane remains inferior BSA fouling resistance, suggesting that an in-depth study on engineering nanostructured membrane is required to overcome it. Furthermore, a 3D GO bridged with CNT membrane showed a high removal efficiency of toxic metal and E. coli O157: H7 bacteria simultaneously [153]. In this research, firstly CNT was conjugated with PGLa antimicrobial peptide and glutathione for the purpose of selective removal of toxic metals and then it was bridged with 2D GO. Finally, the 3D porous graphene-based membrane was developed.

Besides the effect of CNT/GO, the effort on the synthesis of CNT/Graphene hybrid material contributed to developing supercapacitor materials by the synergetic effect of both
nanomaterials [162-165]. For example, synthesis of CNT/Graphene led to the 3-dimensional hybrid nanomaterial with excellent electrical conductivities and high specific surface area (> 2000 m²/g) due to the covalent transformation of sp² carbon between the planar graphene and SWCNTs [166]. CNT/graphene hybrid material was designed for supercapacitor due to its highest energy density (188 Wh/kg) and high power density (200 kW/kg) [167]. Such properties of CNT/Graphene hybrid material may be employed for developing the next generation material of water desalination.

2.4.5.2 CNT/TiO₂

Photo-catalyst such as TiO₂ has been employed to the membrane for water purification with photocatalytic degradation of many organic pollutants such as persistent toxic substances, dyes, pesticides and pharmaceutical and personal care products (PPCPs) [168]. TiO₂ nanotube arrays having photo-catalysts property showed much enhanced photocatalytic activity due to the longer distance of electron transport and larger specific surface area [169-171]. Furthermore, CNT/TiO₂ has been developed in order to complement the limit from both nanomaterials and to have the synergetic effect of high surface area and high photoreactivity on decontamination process [172, 173]. Several studies focused on that CNT/TiO₂ hybrid materials have much enhanced photocatalytic activity compared to the TiO₂ nanotubes by minimizing recombination of photo induced electrons and holes [174-176]. TiO₂ was limited to the light absorption and rapid combination of electron-hole pairs. However, TiO₂ incorporated with CNT can be considered to be the robust hybrid material due to the excellent transporting electron properties and large surface area. Leveraged by the development of CNT/TiO₂ hybrid materials, a multifunctional membrane having superior adsorption capacity coupled with photocatalytic degradation has been thoroughly studied to aim at completely overcoming the fouling issue from the degradation of organic foulants. For example, 0.5/0.5 (wt%) of TiO₂ and MWCNT exhibited superior antifouling property and
nearly 60% TOC rejection, in comparison that pure PSf, and individually inserted TiO$_2$ and MWCNT to PSf membrane showed only less than 40% TOC rejection [177]. TiO$_2$/MWCNT membrane exhibited the lowest reversible/irreversible fouling ratio in both low (2 ppm) and high (700 ppm) HA filtration. This research reported that the superior performance was attributed to the synergetic effects of CNT and TiO$_2$ nanoparticle to engineer physical/chemical properties of membrane: 300% increase in mean pore size, increased hydrophilicity and surface roughness.

An attempt to highlight the synergetic effect of photocatalytic degradation with sieving mechanism is stimulated by the recent research on the fabrication of core web structured CNT/ZnO/TiO$_2$ nanocomposite membrane [178]. CNT/ZnO/TiO$_2$ nanocomposite was synthesized via hydrothermal and acid treatment coupled with ultrasonication. CNT/ZnO/TiO$_2$ membrane outperformed A07 degradation rate and permeability of single CNT and TiO$_2$ membrane by multi-channeled pores and increased specific surface area for photocatalytic degradation.

**2.4.5.3 CNT/PANI and CNT/PEDOT**

CNT/PANI nanocomposite has been developed for the purpose of enhancing the conductivity of both CNT and PANI [179-181], which can contribute to delivering the conductivity of CNT. Besides conveying the conductivities, PANI has been used as nanofiller to increase porosity and hydrophilicity of the membrane [182, 183]. Recent publications on CNT/PANI membrane demonstrate much enhanced water permeability and increased removal efficiency by altering physical/chemical properties of the membrane [44]. Further, SWCNT/PANI was synthesized by a flash welding method, and this membrane exhibited 10 factors of permeability and more than 90% of SiO$_2$ nanoparticle and around 20% of BSA rejection [184]. In addition, MWCNT/PANI magnetic composites fabricated by plasma induced
polymerization were applied for removal of Pb (II) due to its enhanced adsorption capacity of MWCNT [185].

2.5 Current challenges and future perspectives

The future research on membrane technology for water treatment is suggested to focus on overcoming trade-off between high removal efficiency and vulnerability to membrane fouling. CNT incorporation to the polymer matrix has been adopted to develop the nano-engineered membrane that can overcome the current challenges of polymeric membranes.

Despite the considerable contribution of CNT membrane to complementing the limitation of the conventional polymeric membranes, CNT membrane remains some challenging issues to be overcome. CNT nanocomposite membrane has significantly contributed to enhance separation performance in pressure driven membrane processes such as UF, NF and RO. However, it is only limited to the functionalized CNT properties. Further, there is lack of studies on the application of CNT enhanced membrane to seawater pretreatment that challenges in low pressure driven membrane system in desalination plant.

The attempts on complementing individual nanomaterials have inspired further research development on hybrid nanomaterials. These hybrid complexes could be an ideal candidate for a multifunctional membrane with enhanced fouling resistance, which could achieve superior performance without trade-off between high selectivity and highly adsorbed foulant in the membrane. For example, CNT/TiO$_2$ membrane driven by photocatalytic degradation could be an option of alleviating membrane fouling as delivering high performance. Electrically enhanced CNT/Graphene complex would be employed to the electrochemical membrane system, which removes foulant layer by applying electrical potential. Further, as a newly developed membrane material, CNT/Graphene has a potential to RO and/or MD for water desalination besides its benefits for supercapacitors in CDI. However, efforts on
developing membrane structure with such hybrid nanomaterial are required to a first place in order to facilitate their synergetic effect of two properties while simply blending those nanohybrid complexes with polymers.

Based on the research gap in conventional polymeric membranes and nanomaterial incorporated membranes, the research scope in this thesis is focused on the development of CNT composite membrane that can tackle the challenge in low pressure driven membrane such as low organic matter removal rate and permeate flux. Furthermore, lack of studies on the protein fouling in the various conditions of solution chemistry will be covered in depth so as that it will contribute to the understanding of fouling mechanisms in waste water treatment.
References


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**Chapter 2 Literature Review**


Materials and Methods

Chapter 3. Materials and Methods

3.1. Materials

The following chemicals were used for preparation of membrane casting solution: Aniline as a monomer in the PANI polymerization (VWR International), Ammonium peroxidesulfate (APS) as an oxidant in the PANI polymerization (Calbiochem, USA), PES (58,000 g/mol, Goodfellow Cambridge Ltd, UK), N-methyl-2-pyrrolidone (NMP) from Merck and 37 % HCl from VWR International. Suwannee River humic acid (SRHA) standard II was used as a model NOM compound (International Humic Substances Society). Latex particles (hydraulic diameter = 30 nm) were purchased from Sigma-Aldrich (L5155). Hydroxylated-MWCNT was supplied from BuckyUSA, and characterized by the company as follows: purity of 98 wt% a diameter of 5 - 15 nm and lengths ranging from 1 to 5 μm.

3.2. Fabrication of MWCNTs/PANI/PES membranes

Membrane fabrication was divided into two steps. The first step was a synthesis of the MWCNTs/PANI complex by in-situ polymerization; the second step was a fabrication of the MWCNTs/PANI/PES membrane by the phase inversion method. The MWCNTs/PANI complex was fabricated into MWCNTs/PANI/PES membrane

The first step is a synthesis of MWCNTs/PANI nanocomposite by in-situ polymerization, as shown in Fig 3.1 (a) [1, 2]. A solution of 3 mM aniline monomer and 0.8 mM APS was prepared in 1 M HCl and 99.5% NMP. MWCNTs were dispersed in 99.5% NMP solution by sonication (500 W) for one h. Three substances (i.e., aniline, APS and MWCNTs) were mixed in a glass vessel and stirred for 48 h at 4 °C.
Materials and Method

The dispersity of the MWCNTs/PANI composite was confirmed by observing UV absorbance (UV-2450, Shimadzu) as a function of time. MWCNTs/PANI complex was dispersed in an organic solvent (NMP). The absorbance at 295 nm was monitored every hour for 24 hours in order to quantify the dispersity of MWCNTs in the MWCNTs/PANI complex. The corresponding absorbance of MWCNTs dispersing in NMP without PANI was also monitored for comparison. In addition, synthesis of the MWCNTs/PANI charge transfer complex was proved by the peaks around 280-300 nm and 400-500 nm corresponding to the benzoid and quinoid band via UV/visible spectrophotometry [2]. Two peaks at 295, 450 nm correspond to the interaction between nanotubes and planar PANI [1, 3], corresponding to the π-π transition on the benzoid and quinoid excitation bands [4, 5].

In the second step, the MWCNTs/PANI/PES composite was blended in the PES solution and the membrane was fabricated by phase inversion (Fig 3.1 (b)) [6]. 15% PES was mixed with NMP for 1 h and then blended with the MWCNTs/PANI composite for 24 h to prepare the membrane casting solution. The resultant solution was cast on a glass plate using an applicator with 300 μm thickness. The casting film on the glass plate was immersed in the pure water bath, which allows the polymer to be transformed from a liquid to solid state by phase inversion (Fig 3.2). The membranes were stored in a deionized water bath for one day to remove residual solvents.
Fig 3.1 Synthesis of (a) MWCNTs/PANI nanocomposite and (b) fabrication procedure of MWCNTs/PANI/PES composite membrane.

Fig 3.2 Preparation of polymer membrane by phase inversion
REFERENCES


Chapter 4. Fabrication of carbon nanotube-enhanced membrane for natural organic matter removal

4.1. Introduction

In order to tackle the drawbacks of conventional polymeric UF membranes, nanomaterials have been recently introduced into the membrane fabrication [1-3]. Among various nanomaterials, CNTs possess excellent adsorption capacity for organic matter. Compared to the traditional adsorbents such as activated carbon, CNTs are superior adsorbents due to their mesoporous structure and less negative surface charge [4]. Furthermore, the \( \pi - \pi \) interaction between the aromatic group in NOM and CNTs contributes to the better adsorption behaviour of the CNTs [5]. Moreover, CNTs demonstrate excellent electrical and mechanical properties [6-8]. However, due to the van der Waals forces between carbon nanotubes, they are tightly bundled and insoluble in organic solvent. In order to maximize the use of CNTs over a large surface area and with high conductivity, their aggregation within the membrane casting solution has to be prevented [9-11]. There have been many studies on CNT dispersion in polymers and solvents [12-14]. The methods of CNT dispersion in these studies varied from physical treatment to chemical functionalization, which enhances compatibility between the polymer matrix and nanotubes. However, sonication disperses CNTs by breaking van der Waals forces temporarily and thus does not guarantee all CNTs are homogenously dispersed within the polymer matrix. Functionalization by chemical oxidation of CNTs is the most commonly used method, which breaks \( \text{sp}^2 \) hybrid carbon bonds on the sidewalls, and attaches carboxyl/hydroxyl groups to the CNTs [15]. Functionalized CNTs with the hydrophilic group have been reported as attributing to increased flux because hydrophilic modified CNTs can make membrane more permeable [16,
17]. Further, such increase to hydrophilicity is also a well-known approach to reducing membrane fouling [18, 19].

Another approach to enhance the separation properties of membranes is the incorporation of nanofillers [20, 21]. PANI is one of the favoured candidates due to its good environmental stability, miscibility with PES polymer and ease of synthesis [22]. Its synthesis procedure is considered as simple nonredox doping/dedoping chemistry under an acid/base reaction. PANI has been examined for potential applications for separation membranes [23], and biosensors [24] as a conductive nanofiller due to its electrical conductivity. PANI/PSf UF membranes were fabricated by an *in-situ* blending method and non-solvent induced phase inversion [25, 26], and exhibited the enhancement of water permeability due to the increase in hydrophilicity and pore size of the membrane.

Several studies reported that MWCNTs/PANI can form an electron transfer complex *via* donor-acceptor interaction by *in-situ* polymerization [27, 28]; this complex showed enhanced electrical and mechanical properties, and dispersions of CNT in polymer matrices [29]. These two integrated materials were found out to have strong potential for application in functional membranes [30], conductive films, capacitors [31] and biosensors. Such attempts to the integration of an MWCNTs/PANI composite with polymer matrix have opened up the new opportunities for advanced membrane materials for water treatment by overcoming MWCNTs aggregation and tuning membrane structure and its physicochemical properties which influences permeate flux and selectivity [32].

Even though the MWCNTs/PANI complex has a potential as a novel membrane material, the performance of the MWCNTs/PANI membrane for NOM removal and mitigation of fouling is
largely unknown. Therefore, it is desirable to develop MWCNTs/PANI composite membrane, which combines advantages of these two materials to complement the limitations of conventional UF membrane.

While currently a UF membrane fouling under different NOM foulant model has been investigated by the modification of membrane with functionalized MWCNTs [33], this study highlights CNTs composite membrane fabrication for advancing membrane process. We fabricated novel MWCNTs/PANI/PES membrane that showed enhanced removal efficiency and remarkably high flux compared to a PES membrane. An MWCNTs/PANI composite was synthesized by in-situ polymerization and introduced to a PES matrix. The significance of this research is the development of CNTs enhanced UF membrane for effective NOM removal with high water product that requires less operating pressure. In-situ polymerization was introduced to the fabrication procedure to overcome nanomaterial aggregation and tune the membrane structure and its physical/chemical properties. The study was aimed to determine key factors contributing to the enhanced performance, and examine the NOM removal mechanism. The chemical/physical properties of the membranes were thoroughly characterized regarding membrane morphology, pore size and its size distribution, porosity, zeta potential, and hydrophilicity. Flux decline with humic acid (HA) was conducted, and suitable cleaning methods were examined.
4.2. Materials and methods

4.2.1. Materials

Suwannee River humic acid (SRHA) standard II was used as a model NOM compound (International Humic Substances Society). Latex particles (hydraulic diameter = 30 nm) were purchased from Sigma-Aldrich (L5155).

4.2.2. Fabrication of membranes

The membranes were fabricated according to Chapter 3 Materials and methods - membrane fabrication.

4.2.3 Characterization of MWCNTs/PANI/PES membranes

Porosity ($\varepsilon$) was determined by the gravimetric method [34]. Each membrane was initially immersed in the propan-2-ol for 30 min and then deionized water for another 30 min at room temperature. Mass loss of wet membrane after drying was measured. The porosity of membrane was calculated by the following equation 1:

$$\varepsilon = \frac{(W_w - W_d)/\rho_{\text{water}}}{(W_w - W_d)/\rho_{\text{water}} + W_d/\rho_{\text{PES,PANI}}}$$ (1)

Where $W_w$ and $W_d$ are the weight of wet membrane and dry membrane, respectively, and $\rho_{\text{water}}$ and $\rho_{\text{PES,PANI}}$ are the water density (1 g/cm$^3$), PES and PANI density (1.36 g/cm$^3$), respectively.

The samples were degassed under vacuum before measurement.

Pore size and its size distribution were analysed using N$_2$ adsorption/desorption at –K (Micromeritics), and calculated by the Brunauer–Emmett–Teller (BET) method [35]. Contact angle measurements were performed using 4 – 8 µL sessile droplets of Milli-Q water with a Krüss Easy Drop goniometer. The zeta potential of membrane surface was measured by using
the streaming potential technique (Anton Paar electrokinetic analyzer). The experiment was run at an ionic strength of 0.001 M KCl and pH ranging from 2 to 10. Membrane morphology (cross-sectional image and MWCNTs dispersion within PES matrix) was obtained by field emission scanning electron microscopy (FE-SEM, Hitachi S4500 FE-SEM). To obtain cross-sectional images, samples were soaked in n-Hexane to preserve pore structure and fractured in liquid nitrogen. Mounted samples were sputter coated with gold before examined. Top down view of membranes was observed by FE-SEM (Zeiss ULTRA Plus).

4.2.4 Evaluation of filtration performance

Pure water flux was evaluated in a high-pressure stirred cell (HP 4750, Sterlitech) under 1-2 bar at a room temperature (23°C).

In order to examine key parameters of flux enhancement, flux was calculated by the Hagen-Poiseuille equation, which indicates the no-slip condition. The Hagen-Poiseuille equation well describes water flux \( (J) \) as a function of physical properties of the membrane. Thus, the effect of average pore size on water flux can be demonstrated by the theoretical flux calculated by the Hagen-Poiseuille equation (Eq.3).

\[
J = \frac{\varepsilon r^2 \Delta P}{8\eta L} \quad (3)
\]

Where \( \varepsilon \) is porosity, \( r \) is radius (m), \( \Delta P \) is the applied pressure (kPa), \( \eta \) is the viscosity of water (1mP.s), and \( L \) is the membrane thickness (m).

The Enhancement factor was calculated using the measured flux over calculated one by the Hagen-Poiseuille equation:
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\[ E = \frac{Q_{\text{measured}}}{Q_{\text{no-slip HP}}} \]  

(4)

where \( E \) is the enhancement factor, \( Q_{\text{measured}} \) is the flux measured by experiment, and \( Q_{\text{no-slip}} \) is the flux calculated by the Hagen-Poiseuille equation on the no-slip condition.

Slip length was calculated using the slip flow Hagen-Poiseuille equation.

\[ b = \frac{d}{8 \left( \frac{Q_{\text{measured}}}{Q_{\text{no-slip HP}}} - 1 \right)} \]  

(5)

where \( b \) is the slip length (m).

The impact of porosity on flux was examined by the Kozeny-Carmen equation.

\[ J_{K-c} = \frac{\varepsilon^3}{K\eta S^2(1-\varepsilon)^2} \frac{\Delta P}{\Delta x} \]  

(6)

Where \( J_{K-c} \) is flux calculated by Kozeny-Carmen equation (LMH). \( J_{K-c} \) was plotted as a function of porosity of membranes. \( \Delta x \) as a membrane thickness was measured with a digital caliper. All parameters except for porosity of membranes was fixed and presented in Table 4.1.

The removal efficiency of latex particle was measured in the HP stirred cell. Latex nanoparticles which have a uniform structure with a 30 nm diameter were selected for the removal test. A stock solution with latex particles (10 ppm) was prepared to confirm that membranes can retain > 90 % of the solute. The concentration of latex particles in the feed and membrane permeate was measured using a fluorometer (Turner Biosystems), and removal efficiency (R) was calculated by the equation (7) presented in supporting information. HA removal efficiency of the membrane was evaluated using a 5 ppm SRHA solution as a feed. The concentration of HA in the feed and
membrane permeate was measured using a UV/visible spectrophotometry (UV-2450, Shimadzu) at 254 nm. (All equations are explained in the supporting information.)

**Table 4.1** Parameters in the Kozeny-Carmen equation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$ = volume fraction of pores (porosity)</td>
<td>Variable</td>
</tr>
<tr>
<td>$K$ = Kozeny-Carman constant (shape of pores, tortuosity)</td>
<td>10.58</td>
</tr>
<tr>
<td>$S$ = internal surface area</td>
<td>33 m$^2$/g</td>
</tr>
<tr>
<td>$\eta$ = viscosity</td>
<td>1 mPa.s</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>1 bar</td>
</tr>
<tr>
<td>$\Delta x$</td>
<td>293 $\mu$m</td>
</tr>
</tbody>
</table>

4.2.5 Chemical cleaning efficiency

An efficient cleaning method was evaluated by 100 % recovery of flux and HA removal rate, and total fouling ratio. First, after HA filtration test, the fouled membrane was cleaned using five different cleaning methods presented in **Table 4.2**. The operation of cleaning is: (1) rinsing with 5 g/L NaOCl for 1 hr; (2) rinsing with 0.1 M NaOH for 1 hr; (3) rinsing with 0.1 M HCl for 1 hr; (4) rinsing with 0.1M NaOH, 1M HCl for 1 hour each; (5) rinsing with 0.1 M citric acid for 1 hr.

After determining the efficient chemical cleaning method, flux decline behaviour was examined by the HA removal test for approximately 200 minutes in total. The selected chemical cleaning was carried out at the point when HA permeability and removal rate dramatically dropped. The filtration test was repeated three cycles.

The flux recovery (FR) and total fouling ratio ($R_f$) were calculated as follows:

$$FR \, (\%) = \frac{J_{w,2}}{J_{w,1}} \times 100 \quad (7)$$
Where $J_{w,1}$ is the pure water permeability, $J_{w,2}$ is the water permeability of cleaned membrane with acid/base solution, and $J_p$ is the water permeability with 5 ppm HA solution. Here, high flux recovery (close to 1) and low total fouling ratio indicate a suitable cleaning method to improve the better antifouling properties of the membrane.

**Table 4.2 Chemical cleaning conditions.**

<table>
<thead>
<tr>
<th>Type</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>5g/L NaOCl for 1 h</td>
</tr>
<tr>
<td>(2)</td>
<td>0.1 M NaOH for 1 h</td>
</tr>
<tr>
<td>(3)</td>
<td>0.1 M HCl for 1 h</td>
</tr>
<tr>
<td>(4)</td>
<td>0.1 M NaOH for 1 h + 0.1 M HCl for 1 h</td>
</tr>
<tr>
<td>(5)</td>
<td>0.1 M Citric acid for 1 h</td>
</tr>
</tbody>
</table>
4.3. Results

4.3.1 Significance of in-situ polymerization as a membrane fabrication procedure

We introduced in-situ polymerization to the membrane fabrication procedure to advance membrane process by overcoming MWCNTs aggregation. Its effects on the membrane performance enhancement were investigated.

4.3.1.1 Dispersity of MWCNTs

MWCNTs/PANI complex synthesized by in situ polymerization were able to contribute to MWCNTs dispersion in the polymer matrix. PANI is well known for being miscible with a polymer such as PES and PSf. Further, MWCNTs forms a charge transfer complex with PANI. Consequently, during the membrane fabrication, MWCNTs/PANI complex is well mixed with PES polymer, which results in well dispersion of MWCNTs in PES polymer. After casting and phase inversion process, MWCNTs can be well dispersed in PES membrane structure. The effect of MWCNTs/PANI complex on reducing MWCNTs aggregation was evaluated by quantifying MWCNTS dispersion. The snapshot in Fig 4.1 shows the dispersed MWCNTs/PANI complex into NMP and its change in dispersity over 24 hours.

![Image: Dispersion of MWCNTs/PANI in NMP over 24 hours.](image)

**Fig 4.1** Snapshot shows dispersed MWCNTs/PANI in NMP over 24 h.
The MWCNTs/PANI complex maintained dispersion for 24 hours without any settlement. The stable dispersity of MWCNTs was approved by UV spectra of the MWCNTs/PANI complex at 200 - 700 nm wavelength and SEM images. For the MWCNTs/PANI complex, narrow and strong peaks appear with maxima at around 280 - 300 nm, and a broad band is seen at 450 nm. These two peaks at 295, 450 nm corresponds to the π-π transition on the benzoid and quinoid excitation bands [29, 36, 37], indicating an interaction between nanotubes and planar PANI [38, 39]. In comparison, not any sharp and strong peak were observed in the range of 280 – 300 nm and 450 nm when dispersing MWCNTs in NMP (Fig 4.2 (a)). The result suggests that MWCNTs formed a charge transfer complex with PANI, which results in evenly dispersed MWCNTs within the PES matrix. Here, MWCNTs act as an electron acceptor, and aniline as an electron donor. The absorbance at 295 nm was examined to quantify the dispersity of MWCNTs in the MWCNTs/PANI complex. As shown by the UV spectra of the MWCNTs/PANI complex in Fig 4.2 (b), the absorbance attributable to the CNTs remained constant over the course of 10 hours. However, for the MWCNTs dispersed in NMP without PANI, the absorbance dropped in 1 hour.
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**Fig 4.2** UV-Vis spectra of (a) the MWCNTs/PANI complex and MWCNTs in NMP, and (b) absorbance at 295 nm for 10 hours.

To confirm the effect of MWCNTs/PANI complex, dispersion of MWCNTs into PES matrix was also observed by SEM. **Fig 4.3** presents the SEM cross-sectional images taken at 3,000×, 5,000× and 10,000× magnification in both (a) MWCNTs/PANI/PES membrane and (b) simply blended MWCNTs/PES-1 membrane. In the SEM images of the MWCNTs/PANI/PES membrane (**Fig 4.3 (a)**), individual MWCNT (pointed by red arrows) is well dispersed into PES membrane matrix without any agglomeration. On the other hand, simply blended MWCNTs without PANI (pointed by circle and arrows) were aggregated in PES matrix, as shown in **Fig 4.3 (b)**. Moreover, **Fig 4.4** shows that MWCNTs were exposed on the top layer of simply blended MWCNTs/PES-1 membrane while no MWCNTs were observed on the surface of MWCNTs/PANI/PES membranes. It indicates that simply blended MWCNTs cannot overcome aggregation. Therefore, MWCNTs/PANI complex can contribute to MWCNTs dispersion within a polymer matrix as it reacts with MWCNTs in an electron transfer complex by *in-situ* polymerization.
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![SEM cross-sectional images of MWCNTs dispersion in PES polymer matrix: Cross-sectional images of (a) MWCNTs/PANI/PES membrane: MWCNTs are well-dispersed into the PES polymer and (b) MWCNT/PES-1 (simply blended) membrane: MWCNTs are aggregated in the PES matrix.](image)

**Fig 4.3** SEM cross-sectional images of MWCNTs dispersion in PES polymer matrix: Cross-sectional images of (a) MWCNTs/PANI/PES membrane: MWCNTs are well-dispersed into the PES polymer and (b) MWCNT/PES-1 (simply blended) membrane: MWCNTs are aggregated in the PES matrix.
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Fig 4.4 Top down views of MWCNTs/PES-1 (simply blended) membrane show that MWCNTs are protruded from PES matrix.

4.3.1.2 Effects of in situ polymerization fabrication on enhanced membrane performance

Ultrapure water flux behaviour and NOM removal efficiency of MWCNTs/PANI/PES membrane were compared with simply blended MWCNTs membrane (MWCNT/PES-1).

Fig 4.5(a) shows the flux behaviour of PES membrane with two MWCNTs composite membranes. No benefit was observed for the MWCNT/PES-1 membrane where MWCNTs were simply blended. Its water permeability was in the range of PES membrane. By contrast, the MWCNTs/PANI/PES membrane showed greatly enhanced water permeability. As can be seen, water permeability jumped from 20.4 to 490.8 LMH/bar by insertion of the MWCNT/PANI complex into PES matrix. By simply added PANI into PES matrix, the water permeability increased to 265.4 LMH/bar. Significantly enhanced removal efficiency of NOM (80 %) was observed in the MWCNT/PANI/PES-2 membrane which MWCNTs/PANI complex by in-situ polymerization was incorporated (Fig 4.5(b)). However, for simply blended MWCNT membrane (i.e., MWCNT/PES-1), its removal efficiency of NOM remained at 10 %. It is well known that
MWCNTs can only increase adsorption capacity of the membrane when it is well dispersed. When agglomerated, it only slightly modifies membrane property with less consistent pore size, resulting in lower HA removal efficiency. Further, selectivity to NOM is governed by the interfacial surface area of MWCNTs [5, 9]. Thus, MWCNTs in PES matrix by simply blending was not able to maximize adsorption ability of MWCNTs which is required for high removal efficiency.

As shown by the greatly enhanced performance of the MWCNTs/PANI/PES membranes compared to the poor removal/low flux of the MWCNTS/PES membrane, the MWCNTs/PANI/PES membrane did not only overcome nanomaterial aggregation but also contributed to significantly enhanced performance - water permeability and NOM removal.

![Fig 4.5](image)

**Fig 4.5** Effect of MWCNTs/PANI complex on the membrane performance – (a) water permeability, (b) HA removal (1- CNTs simply blended, 2 – membrane). MWCNTs/PANI membrane exhibited 30 fold enhanced water permeability and effective HA removal up to 80 %, compared to PES and PANI/PES membrane. MWCNTs simply blended in PES membrane did not show enhanced separation properties.
4.3.2 Membrane performance of MWCNTs/PANI/PES membranes by MWCNTs concentration

MWCNTs concentration in MWCNTs/PANI complex was increased, aiming to enhance water permeability and investigation of potential mechanism to the flux and HA removal.

**Fig 4.6** indicates that water permeability significantly increases with the increase of MWCNTs concentration in MWCNTs/PANI complex (PANI was adjusted to 50 \( \text{wt}\% \) in all range of MWCNTs/PANI/PES membranes). As 0.25 \( \text{wt}\% \) MWCNTs/PANI complex was incorporated into the polymer matrix, water permeability slightly increased from 265.4 to 376.9 LMH/bar. As MWCNTs increased up to 2 \( \text{wt}\% \), the water permeability dramatically increased from 376.9 up to 1498.1 LMH/bar. It is 15 - 30 times more permeable than the PES membrane while the results from the literature were reported to be 500 LMH/bar (2 times higher than pure PSf membrane) for CNTs blended PSf membrane and 560LH/bar for MWCNTs coated PES membrane [33, 40].

In addition to the effect on water permeability, MWCNTs/PANI complex was found to have a critical impact on enhanced HA removal efficiency (the average HA removal rate during one hr’s filtration). The MWCNTs/PANI/PES membrane removed up to 80 % of HA. As seen in **Fig 4.6(b)**, the PANI/PES membrane did not overcome the low HA removal efficiency of the PES UF membrane. However, insertion of MWCNTs as MWCNTs/PANI complex enhanced HA removal efficiency. As MWCNTs increased to 0.25 \( \text{wt}\% \), HA removal rate started to increase 2-fold. By increasing the amount of MWCNTs in MWCNTs/PANI complex to 1.5 \( \text{wt}\% \), MWCNTs/PANI/PES membranes exhibited enhanced HA removal efficiency up to 80 %, outperforming the previously published work (45 % removal by CNTs incorporation) [16].

However, slightly decreased HA removal was observed when MWCNTs increased up to 2 \( \text{wt}\% \). It may be presumably due to the fact that the highest permeate flux (1400 LMH/bar) causes
insufficient contact time of feed solution during filtration of 2 wt% MWCNTs for HA adsorption on the membrane.

**Fig 4.6** Effect of MWCNT proportion on (a) water permeability and (b) HA removal efficiency as a function of MWCNT concentration (%).
4.3.3 Physical and chemical properties of membrane

It is important to understand chemical and physical properties of the MWCNTs/PANI/PES membrane to explain the enhanced removal efficiency and high flux of the membrane. The results from membrane characterization reveal that the MWCNTs/PANI complex alters the physical properties of membranes: an increase in porosity, and change in pore size and its size distribution. In addition, MWCNTs mainly transform the chemical properties of the membranes: an increase in hydrophilicity and an alteration in the zeta potential of the membrane surface.

4.3.3.1 Physical properties: porosity, pore size and its size distribution

The insertion of hydroxyl-functionalized MWCNTs linking to PANI as pore former was found to change the physical properties of the membrane – porosity, pore size, its size distribution and morphology of membranes. Such parameters affecting permeation characteristics are governed by phase inversion process-polymer-solvent-nonsolvent system. Thus, incorporation of two material having different characteristics enables to tune physical characteristics of membranes during the fabrication process.

First, morphologies of membranes are shown in Fig 4.7. MWCNTs/PANI/PES membranes are observed to have well-developed finger like macrovoid while forming much narrower pores under top layer in comparison to the PES and PANI/PES membrane. This structure is more clearly observed as MWCNTs concentration increases. It can probably be accounted for by the effect of incorporation of hydrophilic and higher viscosity of MWCNTs/PANI complex to the PES casting solution in the solvent and nonsolvent exchange during phase inversion. Hydrophilic and relatively highly viscous MWCNTs/PANI/PES casting solution than PANI/PES and PES
casting solution delays solvent (NMP) diffusion from nonsolvent (water) bath-demixing process [41, 42]. It demonstrates that dense and thin skin layer and finger like macrovoid in the sub-layer structure are formed, resulting in high porosity and increased permeate flux.
Fig 4.7 SEM images of the PES membrane, PANI membrane and MWCNTs/PANI/PES membrane (a) Top down view, (b) Overall cross-sectional structure, (c) Cross section of top layer.

Table 4.3 and Fig 4.8 show porosity, pore size and its size distribution. As shown in Table 4.3, the average pore diameter of all membranes is in the range of 2 – 6 nm, and its size distribution varies 0.3 to 30 nm (Fig 4.8). Insertion of PANI or MWCNTs/PANI complex into PES polymer matrix resulted in different pore size and its size distribution. By the insertion of PANI (A membrane), average pore diameter and porosity of membrane increased to 5.1 nm and 82.2 % with broad pore size distribution (1.9 – 27 nm). This is mainly due to the fact that soluble PANI oligomer acts as pore former, resulting slightly higher porosity and bigger pore size. As expected, the change in physical characteristics of PES and [A] membrane is consistent with increased permeate flux. However, the insertion of 0.5 wt% MWCNTs/PANI complex on PES matrix ([B-2] membrane) appeared to form smaller average pore diameter (5.1 → 4.5 nm) and its relatively
narrow size distribution (0.9 - 1 nm) with decreased porosity, while its permeability increased. Overall, the trend in porosity seemed to increase by increasing MWCNTs concentration in MWCNTs/PANI complex up to 2 wt%. Compared to the initial porosity of PES membrane (78 %), membrane porosity increased up to 84.5 wt% by increasing amount of MWCNTs up to 2 wt%, which is consistent with the flux behaviour. Relatively broad pore size distribution in the range of 0.1 to 30 nm appeared when MWCNTs increased up to 2 wt%, which contributed to the great permeate flux enhancement. However, the average pore diameter slightly decreased with the narrowest pore size distribution (0.3 – 1 nm) when 1.5 wt% MWCNTs/PANI complex inserted ([B-4] membrane). The difficulty in tuning pore diameter may be due to the intrinsic fabrication process-phase inversion. In contrast, its permeate flux increased.

Based on the physical characteristics, MWCNTs/PANI complex was found to increase porosity and change sub-layer structure to finger-like macrovoid, resulting in enhanced permeability. Pore size and its size distribution seemed to be changed by MWCNTs/PANI complex but were shown to be inconsistent with flux enhancement.

Table 4.3 Porosity and pore size of membranes.

<table>
<thead>
<tr>
<th>Type of membrane</th>
<th>Porosity (%)</th>
<th>Pore size (nm)</th>
<th>Latex removal rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 % PES</td>
<td>78.0 ± 0.3</td>
<td>4.6</td>
<td>98.0 ± 0.2</td>
</tr>
<tr>
<td>[A]: 50 % PANI/ 15 % PES</td>
<td>82.2 ± 0.1</td>
<td>5.1</td>
<td>88.4 ± 2.4</td>
</tr>
<tr>
<td>[B-1]: 0.25 % MWCNTs/ 50 % PANI/ 15 % PES</td>
<td>80.3 ± 0.4</td>
<td>5.1</td>
<td>98.5 ± 0.3</td>
</tr>
<tr>
<td>[B-2]: 0.5 % MWCNTs/ 50 % PANI/ 15 % PES</td>
<td>80.8 ± 0.4</td>
<td>4.5</td>
<td>98.4 ± 0.2</td>
</tr>
<tr>
<td>[B-3]: 1 % MWCNTs/ 50 % PANI/ 15 % PES</td>
<td>83.2 ± 0.1</td>
<td>4.7</td>
<td>97.9 ± 0.4</td>
</tr>
<tr>
<td>[B-4]: 1.5 % MWCNTs/ 50 % PANI/ 15 % PES</td>
<td>83.8 ± 0.1</td>
<td>4.4</td>
<td>99.2 ± 0.1</td>
</tr>
<tr>
<td>[B-5]: 2 % MWCNTs/ 50 % PANI/ 15 % PES</td>
<td>84.5 ± 0.0</td>
<td>6.3</td>
<td>93.7 ± 1.3</td>
</tr>
</tbody>
</table>
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Fig 4.8 Pore size distribution of membranes. (PANI/PES membrane: [A], 0.25, 0.5, 1, 1.5 and 2 wt% MWCNT/PANI/PES membranes: [B-1], [B-2], [B-3], [B-4] and [B-5])
4.3.3.2 Chemical properties: hydrophilicity and zeta potential

Insertion of MWCNTs in the MWCNTs/PANI complex transformed the chemical properties of membranes—hydrophilicity. In Fig 4.9, the contact angle decreased from 73.5 to 67.4° as 0.25 wt% MWCNTs/PANI was inserted into the PES matrix. As MWCNTs were added up to 2 wt%, the contact angle of membrane decreased from 67.4° to 52.9°. It indicates that insertion of MWCNTs/PANI complex into PES matrix significantly increased the hydrophilicity of the membranes. This result corresponds to enhanced water permeability from 376.9 to 1498.1 LMH/bar.

![Graph showing contact angle vs. concentration of CNTs](image)

**Fig 4.9** Effect of MWCNTs concentration on the hydrophilicity of the MWCNTs/PANI/PES membrane.

The surface roughness of membranes is one of the potential effects which can influence the hydrophilicity of membrane surface. Atomic force microscopy (AFM) was used to investigate
the membrane surface roughness. No obvious correlation between surface roughness and increase in MWCNTs concentration in MWCNTs/PANI complex was found in this study. However, there might be potentially some macro surface structure difference for MWCNTs/PANI/PES membranes with different MWCNTs concentration. The difference of macro surface structure affects the contact angle values of the membrane, but might not be significantly enough to be picked up by AFM analysis.

It is important to discuss the zeta potential of the membrane surface since the surface charge property of a polymeric membrane depends on the chemical properties of the membrane and chemistry of the solution as membrane surfaces are electrically charged in the presence of water [43]. The inclusion of MWCNTs as an MWCNTs/PANI complex has contributed to the increased adsorption capacity by altering the surface charge of the membrane.

The reason for changing zeta potential by the insertion of MWCNTs/PANI complex into PES polymer matrix can be elucidated by the doping process during MWCNTs/PANI complex synthesis. Doping is the process of transforming a polymer to its conductive form via chemical oxidation [44-46]. Doping process can change the charge of polymer to positive or negative one. Thus, during the MWCNTs/PANI complex synthesis by the acid doping (chemical oxidation), MWCNTs PANI complex became positively charged (Fig 3.1(a)) [28]. For this reason, positively charged MWCNTs/PANI complex altered negatively charged PES membrane to the positively charged surface of the membrane.

The zeta potential of the MWCNTs/PANI/PES membrane changed from a negative value to a positive one by insertion of the MWCNTs/PANI complex in the polymer matrix, as shown in Fig 4.10. The zeta potential of the PES membrane is –20 mV at pH 5.6. As PANI was inserted to
Chapter 4 Fabrication of carbon nanotube enhanced membrane for natural organic matter removal

PES, it decreased to $-4.1$ mV at pH 5.6, but the membrane was still negatively charged. However as MWCNTs were inserted into the polymer matrix as the MWCNTs/PANI complex, the membrane became positively charged, varying from $+6.2$ to $+11.3$ mV at pH 5.6.

Due to the electrostatic interaction between negatively charged HA and positively charged surface of the membrane, adsorption of HA appeared on the membrane surface and pore inside [43]. It is supported by the results showing that enhanced adsorption capacity of NOM on carbons is governed by the cationic functional group on carbon surface since the net surface charge of NOM molecule is negative [47, 48]. Consequently, HA removal efficiency increased 4-fold in comparison to the PES membrane and PANI/PES membrane with a negative charge.

![Zeta potential of the membrane by streaming potential at pH 5.6 at a background electrolyte concentration of 0.001 M KCl (Zeta potential of 5 ppm HA solution = - 7.5 mV). Insertion of MWCNTs in the membrane altered to positively-surface charged membrane.](image)

**Fig 4.10** Zeta potential of the membrane by streaming potential at pH 5.6 at a background electrolyte concentration of 0.001 M KCl (Zeta potential of 5 ppm HA solution = - 7.5 mV). Insertion of MWCNTs in the membrane altered to positively-surface charged membrane.
4.4. Discussion

4.4.1 Why fast water flux through the MWCNTs/PANI/PES membrane?

The effects of physical/chemical properties and membrane morphology were systematically investigated to examine the potential mechanism affecting water flux behaviour.

In section 4.3.3.1, porosity was found to correspond to the flux enhancement. To systematically investigate the contribution of porosity on water flux enhancement, water flux as a function of porosity was calculated using the Kozeny-Carman equation, shown in Fig 4.11. Detailed information on parameters (Table 4.1) and equation are explained in the 2.4 section. It describes well the permeability-porosity relationship in organic membranes by phase inversion method having asymmetric structure [41]. Here, Kozeny-Carman constant (K) represents the shape of pores and tortuosity. Here $K = k_0 \tau^2$. $K_0$ is taken to be equal to 2 for a circular capillary. In Fig 4.11, theoretical water permeability shows an exponential function according to the increase in porosity, 2-fold. By contrast, the experimental results showed 4 – fold increase in water permeability. The notable thing is that porosity of the [B-1] and [B-2] membranes have an opposite trend with enhancement in water permeability. Even though [B-1] and [B-2] membranes are 1.5 – 2 % less porous than A membrane, their water permeability exceeded that of [A] membrane. It indicates that water permeability may also be governed by another characteristic – hydrophilicity, in this case.
The inclusion of hydroxyl-functionalized MWCNTs was observed to make the membrane surface more hydrophilic by the strong affinity between water molecules and membranes. Considering the slight increase in water permeability of the 0.25 wt% MWCNTs/PANI/PES membrane compared to the PANI/PES membrane, the decrease in porosity between the PANI/PES membrane and 0.25 wt% MWCNTs/PANI/PES membrane was compensated by the increase in hydrophilicity. The decrease in contact angle resulted in a slight increase in water permeability from 265.4 to 376.9 LMH/bar. As MWCNTs increased to 0.5 wt%, porosity and hydrophilicity rose to 80.8 % and 63.6 °, respectively. It correlates with a gradual increase in water permeability. However, as MWCNTs increased to 1 wt%, water permeability doubled. This sudden increase could be explained by the combination of porosity and hydrophilicity increase.
The porosity of the one wt% MWCNTs/PANI/PES membrane (83.2 %) exceeded that of PANI/PES membrane (82.2 %) as its hydrophilicity increased to 56. 1 °. The increase of both factors is consistent with a dramatically increased permeability.

The relationship between flux and physical properties such as pore size and its size distribution was investigated for a mechanistic understanding of membrane performance. In section 3.3.3.1, the discrepancy between flux enhancement and reduced pore size and its narrow size distribution was observed when MWCNTs/PANI complex inserted to PES polymer ([S], [A] vs. [B-1] – [B-5] membrane). As seen in Table 4.3, the pore size of all membranes by BET surface area is in the range of 2-6 nm. Given the conventional fluid flow by Haagen Poiseuille equation, decreased average pore size must result in the flux decline. However, compared to the flux calculated by Hagen-Poiseuille equation in this pore size range, experimental flux by MWCNTs enhanced membrane was reported 100 to 600 fold (Table 4.4). Considering the significant effect of pore size on the flux, the pore size of the MWCNTs/PANI/PES membranes is much smaller than the experimental water flux. Further, [B-4] membrane having high water flux was observed to have a smaller average pore size (4.5 nm) and narrow pore size distribution (0.3 – 1 nm). Such a discrepancy may be explained by the difference of hydrophilicity between membrane surface and channel within the membrane. The increase in hydrophilicity of membrane surface may introduce water molecules by a strong affinity of MWCNTs enhanced membranes. In membrane fabrication process, hydrophilic MWCNTs were formed on top of the membrane during diffusion/demixing process in a water bath by phase inversion due to its hydrophilicity. Thus, middle to bottom of membrane structure consisting of PES became less hydrophilic than the top part with hydrophilic MWCNTs. Here, slip length effect may be expected due to the smaller pore diameter in the range of 2 – 6 nm introducing water molecule into the relatively hydrophobic
channel within the membrane which is in the few micrometer range (Cross-sectional structure of each membrane are shown in Fig 4.7). It is assumed that top surface of the membrane with stronger affinity to water may seem to enhance water permeation, and relatively hydrophobic big channel (3 – 8 um) may attribute to dramatically enhanced flux by slippage effect. Therefore, the extremely low pure water flux for the PES membrane was due to the relatively small average pore diameter, broader pore size distribution, low porosity and less hydrophilicity which had been formed in phase inversion stage.

Based on the membrane characterization and theoretical/observed results, we may assume that the synergetic effect of porosity and hydrophilicity could mainly lead to the flux enhancement. Hydrophilic, narrow pore size on the top layer and relatively wide finger-like voids may contribute considerably to the enhanced permeability by inducing slippage effect.

Table 4.4 Enhancement factor and slip length of membranes.

<table>
<thead>
<tr>
<th>Type of membrane</th>
<th>Enhancement factor</th>
<th>Slip length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 % PES</td>
<td>7.2</td>
<td>3.6</td>
</tr>
<tr>
<td>[A]: 50 % PANI/ 15 % PES</td>
<td>189.6</td>
<td>120.2</td>
</tr>
<tr>
<td>[B-1]: 0.25 % MWCNTs/ 50 % PANI/ 15 % PES</td>
<td>698.0</td>
<td>183.0</td>
</tr>
<tr>
<td>[B-2]: 0.5 % MWCNTs/ 50 % PANI/ 15 % PES</td>
<td>195.5</td>
<td>109.4</td>
</tr>
<tr>
<td>[B-3]: 1 % MWCNTs/ 50 % PANI/ 15 % PES</td>
<td>374.1</td>
<td>219.2</td>
</tr>
<tr>
<td>[B-4]: 1.5 % MWCNTs/ 50 % PANI/ 15 % PES</td>
<td>511.0</td>
<td>280.5</td>
</tr>
<tr>
<td>[B-5]: 2 % MWCNTs/ 50 % PANI/ 15 % PES</td>
<td>290.7</td>
<td>228.1</td>
</tr>
</tbody>
</table>
4.4.2 NOM removal mechanism by the MWCNTs/PANI/PES membrane

The NOM removal mechanism can be explained regarding two factors – adsorption capacity and size exclusion. Due to the mean size (<1 nm) of HA, it easily passes through the low-pressure membranes such as MF and UF, but high-pressure membranes such as NF and RO can reject 90% HA. As previously discussed, MWCNTs/PANI complex slightly reduced the membrane surface pore size with latex removal rate. Based on Fig 4.8, very narrow pore size distribution was observed in the membrane B-2, B-3 and B-4, corresponding to the higher HA removal rate (80%). Such a narrow pore size distribution would be one of the key factors for high humic acid removal. However, that effect alone may not be able to change the humic acid removal efficiency due to the much smaller size of HA than the pore size of MWCNTs/PANI/PES membrane in the range of UF membrane. Even if MWCNTs/PANI/PES membrane has reduced pore size than PANI/PES membrane, HA removal is still beyond the separation ability of UF membrane with 2-6 nm of average pore size. Thus, the greatly enhanced separation property can be mainly due to the adsorption capacity of the membrane: an alteration of the zeta potential of the membrane surface.

The shift of the zeta potential of the membrane significantly affected the interaction between membrane and HA with a negative charge. Humic acid represents NOM, which contains negatively charged groups: 60 – 90% of groups are carboxylic (COO\(^-\)), methoxyl carbonyls (C=O) and phenolic (OH\(^-\)) groups [49]. As a result, HA is negatively charged when dissolved in water with the zeta potential value of -7.1 mV at pH 5.6. Such an electrostatic interaction by altering surface charge of the membrane leads to the great enhancement of HA removal efficiency. It is because HA removal mechanism is strongly governed by the interaction of membrane with feed [50, 51]. In addition to the electrostatic interaction, MWCNTs themselves
have adsorption capacity for organic matters [52]. The π-π system on the MWCNTs interacts with the cross-linked aromatic network of molecules on humic acid [53]. The insertion of MWCNTs may contribute to the increased NOM removal efficiency.

A filtration test with HA solution was run for 72 hours as shown in Fig 4.12. No decrease in HA removal (80 %) was observed in 1.5 wt% MWCNTs/PANI/PES membrane (B-4) while permeate flux declined. It indicates that, even after 72 hour’s filtration, HA adsorption has not reached its capacity yet. While membrane surface which was already covered by HA would potentially limit further the HA accessing due to the repulsion force among HA-HA, this might also result in higher HA removal rate. By comparison, the removal rates of PES membrane (S) further dropped with the filtration test lasted even though its initial removal rate was much lower than the 1.5 wt% MWCNTs/PANI/PES membrane (B-4).

![Graphs showing HA permeability and removal decline behaviour](image)

**Fig 4.12** (a) HA permeability decline behaviour and (b) HA removal decline behaviour of both the B-4 and the S membranes (684.9 L/m² filtration).
The removal mechanism is most probably the electrostatic interaction of positively charged membrane and negatively charged HA, resulting in enhanced HA adsorption capacity. Adsorption capacity driven by MWCNTs/PANI complex would result in higher HA rejection rate than that of PES membrane. When it reaches to the adsorption capacity, desorption may happen and reduce HA rejection. Some adsorption causes the membrane pores to be narrower by pore blocking and forms a cake layer on the membrane surface. So even after it reaches to adsorption capacity, the rejection rate only drops slightly.

4.5. Flux recovery by chemical cleaning
The HA adsorption inside the membrane pores may result in flux decline during long-term filtration test. The influence of cleaning method on the flux recovery in the presence of HA was examined in this section using five different cleaning methods. Table 4.5 summarizes pure water flux recovery, total fouling ratio and change of HA removal after cleaning. The MWCNTs/PANI/PES membrane completely recovered pure water flux after cleaning with both acid and base chemicals (method (4)). However, when using HCl or NaOH individually, its flux recovery did not reach 100 %. Moreover, cleaning with NaOCl without acid/base chemicals (method (1)) was found out to be ineffective as FR remained at 51.4 %. The effect of cleaning method (4) was confirmed by the change in HA removal before/after cleaning membranes. Membranes cleaned by acid/base chemicals removed 80 % HA while other methods decreased HA removal after cleaning. The mechanism of removing HA from the membrane surface can be explained regarding hydrolysis and solubilization [54]. First, NaOH dissolves HA with carboxylic and phenolic functional groups. HCl oxidizes HA forming soluble aromatic aldehydes and acids at NOM functional groups.
Table 4.5 The results shows a comparison of water flux discovery, total fouling ratio, and removal efficiency by cleaning method. By applying method 4, ultra-pure water flux recovery reached to 100 %, and its total fouling ratio was 65 %. Based on the results, cleaning method (4) is the most effective method for fouling mitigation.

<table>
<thead>
<tr>
<th>Cleaning method</th>
<th>pH</th>
<th>UPW Flux recovery (%)</th>
<th>HA Removal (%)</th>
<th>Total fouling ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 5g/L NaOCl 1 hr</td>
<td>9</td>
<td>51.4</td>
<td>80 → 50</td>
<td>81</td>
</tr>
<tr>
<td>(2) 0.1 M NaOH 1 hr</td>
<td>12</td>
<td>93.4</td>
<td>80 → 50</td>
<td>81</td>
</tr>
<tr>
<td>(3) 0.1 M HCl 1 hr</td>
<td>2</td>
<td>81.5</td>
<td>85.5 → 28.4</td>
<td>82</td>
</tr>
<tr>
<td>(4) 0.1 M NaOH 1 hr + 0.1 M HCl 1 hr</td>
<td>12 → 2</td>
<td>100</td>
<td>82 → 80</td>
<td>65</td>
</tr>
<tr>
<td>(5) 0.1 M Citric acid (1 hr)</td>
<td>4</td>
<td>79.5</td>
<td>86.4 → 65</td>
<td>76</td>
</tr>
</tbody>
</table>

Fig 4.13 shows HA flux decline and its removal behaviour during three cycles of the filtration test. As can be seen, its HA permeate flux was fully recovered after the selected chemical cleaning (method 4) for 3 cycles. 100 % HA removal recovery maintained in the second cycle. With a combination of acid/base cleaning, the membrane was able to exhibit 100 % water flux recovery and the lowest total fouling ratio, compared to that the previous research showed only 50 % flux recovery by incorporation of functionalized MWCNTs [2]. Even though HA was adsorbed in the membrane pores, the majority of the foulants was able to be removed by proper chemical cleaning.
Fig 4.13 HA permeate flux decline and its removal rate behaviour of [B-4] membrane with chemical cleaning during 3 cycles of filtration test: HA permeability was recovered for 3 cycles with the chemical cleaning (method 4 presented in Table 5). (The arrow indicates the time when chemical cleaning was conducted).

It is to note that high NOM adsorption normally would cause more significant fouling. However, for such a membrane, even with significant fouling or flux drop, the permeate flux is still quite high due to the extremely high initial flux. Moreover, the membrane has good cleanability properties. The fouling due to adsorption can be easily removed by acid/base cleaning with nearly 100 % flux recovery and 65 % total fouling ratio. This indicates that the flux decline of
MWCNTs/PANI/PES membrane can be overcome when a proper cleaning method involving acid and base is used.

4.6. Conclusion

The aim of this study is to advance the low pressure driven membrane process by designing nano-engineered material based membrane. MWCNTs enhanced membrane by incorporation of \textit{in-situ} polymerized MWCNTs/PANI complex achieved superior performance compared to the conventional PES UF membranes. The unique properties of MWCNTs/PANI complex successfully tuned the membrane structure and its physical/chemical properties, leading to the greatly enhanced water permeability and high HA removal rate which could not be effectively removed by the low-pressure membrane. In particular, positively charged surface of the membrane with MWCNTs/PANI complex contributed to the enhanced adsorption capacity by electrostatic interaction, compared that currently used polymeric membranes are negatively charged. Due to the positively charged surface, this membrane may open up an opportunity for recovery of valuable cationic macromolecules in bioprocess/pharmaceutical industries. Examination of removal mechanism and fast water flux would give a significant contribution to outperforming conventional UF membranes which are widely used in water treatment. Further research will be targeted to the application of the membrane for enhanced organic matter removal in seawater pre-treatment, aiming to zero discharge.
**REFERENCES**


Chapter 5. Application of carbon nanotube-enhanced membrane for seawater pretreatment and examination of salinity on the membrane performance

5.1 Introduction

Seawater reverse osmosis (SWRO) desalination technology requires an effective pretreatment to inhibit the decline in performance with irreversible fouling on membrane and degradation by frequent cleaning [1-3]. Such a drawback is derived from organic matter as a serious membrane foulant in seawater in RO desalination plants. Seawater organic matters include extracellular polymeric substances (EPS) or biopolymers, humics, fulvic acids, carboxylic acid and other low molecular weight dissolved organic matters (LMW-DOMs). Of these substances, colloidal matters in the range of 3 – 20 nm such as humic substances and biopolymers are the main membrane foulant to be adsorbed on the membrane surface or in the membrane pores. In most cases, LMW-DOMs account for 50% of the seawater organic matter (SWOM). Organic foulants are the precursor to the biological growth so it can also accelerate the biofouling on membrane. Low-pressure membranes such as microfiltration (MF) and ultrafiltration (UF) can be an option of seawater pretreatment as they can remove particulate, bacteria and large molecular weight organic matter. However, direct MF/UF filtration can overpass the technical limits of the process, resulting in RO membrane fouling [4]. In particular, a low-pressure membrane with cut off higher than 100 kDa was not able to remove LMW-DOMs (less than 350 Da) which can accelerate biofouling on RO membranes [5].

A solution to enhance the organic removal performance in MF/UF membrane system is the integration of the physico-chemical processes such as adsorption or coagulation/flocculation [6,
According to previous studies, ferric chloride (FeCl$_3$) as a coagulant forms flocs with organic matter by co-precipitation [8, 9]. Such a coagulation/precipitation system in seawater pretreatment has shown to be effective in total DOM removal, but basically, it cannot remove LMW-DOMs in seawater. Recently, to overcome the limitation of the physico-chemical process with low pressure membrane, membrane hybrid system coupled with adsorption (with the addition of powder activated carbon, PAC) has been reported to exhibit enhanced performance on the removal of LMW-DOMs containing around half of SWOM [10]. PAC (as an adsorbent) adsorbed organic matter by co-valence bonding [11], and removed LMW-DOMs with its affinity to them and by biological activity of microbial community developed [12].

Even though such an enhanced DOM removal was achieved by the membrane hybrid system in seawater pretreatment, a large amount of chemical sludge generated due to a usage of a relatively high amount of adsorbent. In this sense, an approach to the reduction of chemical dosage must be investigated, and a development of membrane with higher water flux and the anti-biofouling effect is desirable for sustainable pretreatment in SWRO.

Recently, there have been many attempts on enhancing UF membrane performance by incorporation of nanomaterials. Of the nanomaterials, carbon nanotubes (CNTs) are one of the favored approaches due to its unique characteristic of excellent adsorption capacity for organic matter [13]. In particular, the introduction of functionalized CNTs to the polymeric UF membrane has contributed to delivering increased permeate flux by changing membrane surface hydrophilicity [14-16], improved rejection of bovine serum albumin (BSA) and alleviated membrane fouling [17-20]. Even though development of the CNTs membrane has provided certain benefits to water treatment, there are few existing research papers on its application to seawater pretreatment for DOM removal. Therefore, feasibility study of CNTs membrane in
seawater pretreatment for effective removal of LMW-DOMs would be of great help for currently facing the limitation of a membrane system for seawater pretreatment. Based on the recent progress of nanocomposite membrane in water treatment, development of the membrane having an enhanced adsorption capacity can also contribute to lowering chemical dose, resulting in the reduction of sludge volume generated.

Seawater contains high concentrations of ions, and this ionic strength has been recognized to seriously affect DOM removal and fouling potential in membrane operation [21, 22]. Therefore, in-depth study on the effect of ionic strength on membrane performance would be of great importance in successful CNTs membrane application to SWRO pretreatment.

In this study, multi wall carbon nanotubes (MWCNTs) enhanced membranes fabricated by in-situ polymerization, since high water flux and effective natural organic matter (NOM) removal was previously reported with this membrane. The aims of this study were i) to test MWCNTs enhanced membrane in the seawater pretreatment with reducing PAC adsorbent dose by employing MWCNTs membrane with enhanced adsorption capacity of SWOM. Especially, it was to improve rejection efficiency of LMW-DOMs with high permeate flux in MWCNTs membrane filtration compared to the conventional UF membrane, and ii) to examine the effect of ion strength on organic removal and performance in the MWCNTs membrane filtration. Further, the effects of salinity and ion strength on the organic rejection efficiency and permeate flux were examined in MWCNTs enhanced membrane system.
5.2. Materials and methods

5.2.1 Materials

5.2.1.1 Seawater

Seawater was taken from Chowder Bay, Sydney in Australia. It was withdrawn 1 m below the sea surface level and passed through 140 µm the centrifuge filtration system to remove the large particles. Turbidity and pH of seawater used in this study were 0.5-0.7 NTU and 7.8-8.0, respectively.

5.2.1.2 Membranes

The fabrication procedure of 1.5 wt% of MWCNTs enhanced membrane was adopted from Chapter 3 Materials and method. Characteristics of membranes used in this study are given in Table 4.1. Detailed information is elucidated in Chapter 4.

Table 5.1 Characteristics of the membranes used in this study.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>UPW* permeability (LMH/bar)</th>
<th>Pore size by BET (nm)</th>
<th>MWCO** (kDa)</th>
<th>Contact angle (°)</th>
<th>Zeta potential*** (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNTs</td>
<td>1272 ± 103.8</td>
<td>5.0 ± 0.4</td>
<td>12</td>
<td>45.4 ± 0.1</td>
<td>9.8</td>
</tr>
<tr>
<td>PES</td>
<td>60±4.3</td>
<td>4.6 ± 0.3</td>
<td></td>
<td>57.6 ± 0.4</td>
<td>-21</td>
</tr>
</tbody>
</table>

*: UPW: Ultrapure water, **: MWCO: Molecular weight cut-off, ***: Zeta potential was measured at pH 5.6 at a background electrolyte of 0.001M KCl.
5.2.1.3 Powder activated carbon (PAC)

Coal-based PAC (MDW3545CB, James Cumming & Sons PTY LTD) was used as an adsorbent in this study. The mean diameter and the nominal size (80% min. finer than) of PAC were 19.7 μm and 75.0 μm, respectively. More details of PAC can be found in elsewhere [7].

5.2.2 Membrane filtration test

Performances of PES (a laboratory-prepared UF membrane) and MWCNTs enhanced membrane were evaluated in the membrane system with adsorption (PAC addition). For the membrane system with PAC adsorption, PAC (0.5 – 1.5 g/L based on feedwater volume) was added to seawater in the adsorption system. Then, pretreated seawater was undergone membrane filtration. Membrane filtration without adsorption pretreatment (PAC=0g/L) was also conducted to evaluate the performance of membrane filtration system itself. Membrane filtration was done in dead-end mode under 200 kPa with 0.00146 m² of effective membrane area. A 1L of seawater was filtered, and permeability was monitored over the time.

5.2.3 Dissolved organic matter measurement

Dissolved organic concentration (DOC) and the detailed organic fractions in feed/permeate were measured by liquid chromatography–organic carbon detection (LC-OCD) [23]. Hydrophilic organic fractions were separated into each fragment depending on their molecular size by the retention time in the size exclusion chromatography (SEC) column. Dual columns were applied in this study with 180 min retention time. Two different detectors (an ultraviolet detector (UVD) (absorption at 254 nm) and an organic carbon detector (OCD) (after inorganic carbon purging)) were utilized to measure the concentration of separated hydrophilic organic compounds. The eluted order of each fragment was biopolymers – humic substances/building blocks – LMW
organics (acids and neutrals). The amount of each organic fraction was calculated using a software program (ChromCALC DOC-LABOR, Karlsruhe, Germany) based on the chromatogram obtained from LC-OCD analysis. Detailed procedure is described in a previous study [24].

Removal efficiency (%) of organic matter was calculated by the following equation:

\[ R = \left( 1 - \frac{C_p}{C_f} \right) \times 100 \]

Where, \( C_f \) is the concentration (µg/L) of feed water and, \( C_p \) is the concentration (µg/L) of permeate (or membrane filtrate) from the membrane filtration system with PAC adsorption or membrane filtration itself.

### 5.2.4 Surface charge of membrane

The surface charge (in terms of zeta potential, mV) of membrane surface was measured by using the streaming potential technique (Anton Paar electrokinetic analyzer, USA). The measurement was conducted at different ionic strengths ranged between 0.001 and 0.010 M of KCl and pH 7.8.

### 5.2.5 Fouled membrane characterization

After filtering 1L of feed water (684.9 L/m² of seawater with or without PAC adsorption), membrane samples were taken and dried for 24h prior to analyses.

The morphology and chemical composition of fouled membranes were observed using scanning electron microscopy with an energy dispersive X-ray spectrometry (SEM-EDX, Zeiss Ultra, Germany). For SEM-EDX analysis, membranes then were coated with thin layer of gold. The contact angle was performed to measure the membrane hydrophilicity using 4 – 8 µL sessile droplets of Milli-Q water with a Kruss Easy Drop goniometer (Germany).
5.3. Results and discussion

5.3.1 Seawater filtration performance (without PAC addition)

5.3.1.1 Permeate flux

Fig 5.1 shows permeability (permeate flux) pattern of MWCNTs and PES-UF membrane in UPW and seawater filtration. MWCNTs membrane shows significantly increased UPW permeability (initial permeate flux was 1298.4 L/m²-h-bar (LMH/bar)) while initial permeate flux of PES-UF membrane was 66.2 LMH/bar. In seawater filtration, substantially declined permeate flux was observed with the MWCNTs membrane. In terms of initial permeate flux; it was 321.3 LMH/bar, which was almost 4 times dropped compared to UPW permeability. However, there was no significant change in permeate flux in seawater filtration by PES-UF membrane.
Fig 5.1 Permeability pattern of MWCNTs and PES-UF membrane in UPW and seawater filtration.

5.3.1.2 Organic reduction

A 5 mg/L of humic acid (HA) was dissolved in UPW, and it was firstly tested with two membranes. Especially, HA removal by MWCNTs membrane was superior (82±4%). However, in seawater filtration, there was a marginal reduction of HS (2.62 - 4.62%) by both membranes, even though HS concentration in seawater was only 0.496±0.012 mg/L (Table 5.2).

Table 5.2 Removal efficiencies of HS in seawater and 5 mg/L of HA in UPW by MWCNTs and PES-UF membrane filtration (HS and HA concentrations were measured using LC-OCD and TOC analyzer, respectively).

<table>
<thead>
<tr>
<th></th>
<th>HS in seawater (mg/L)</th>
<th>HS in permeate (mg/L)</th>
<th>R* (%)</th>
<th>HA in UPW (mg/L)</th>
<th>HA in permeate (mg/L)</th>
<th>R* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNTs</td>
<td>0.496±0.012</td>
<td>0.473±0.020</td>
<td>4.64±0.40</td>
<td>5.0±0.1</td>
<td>0.9±0.2</td>
<td>82±4</td>
</tr>
<tr>
<td>PES-UF</td>
<td>0.483±0.011</td>
<td>0.483±0.011</td>
<td>2.62±0.22</td>
<td>3.1±0.3</td>
<td>3.1±0.3</td>
<td>38±6</td>
</tr>
</tbody>
</table>

*R: removal efficiency
5.3.2 Effect of PAC addition

Fig 5.2 shows the permeability patterns in seawater filtration (before and after PAC adsorption) of MWCNTs and PES-UF membranes. When raw seawater was filtered, the initial permeability of MWCNTs membrane was to 300 LMH/bar. Interestingly, when PAC adsorption coupled, its permeability increased up to 600 LMH/bar. However, more rapid flux decline occurred in MWCNTs membrane filtration. It was probably due to more organic adsorption on the membrane surface by electrostatic interaction at the initial stage of filtration with higher organic loading by high permeate flux. When the lower dosage of PAC decreased to 0.5 g/L, the permeability of MWCNTs membrane still maintained in a high value, and there was no significant decline. However, no change in flux pattern was observed on PES membrane no matter how PAC was incorporated.

The removal efficiencies of the organic fraction by MWCNTs enhanced membrane coupled with or without PAC adsorption are given in Table 5.3. PES-UF membrane itself removed only 13% of DOC from raw seawater with 60% of biopolymers’ removal efficiency. DOC reduction by MWCNTs membrane (26%) was slightly higher than PES-UF membrane. PAC showed a high removal efficiency of hydrophilic organics, especially biopolymers and humic substances (high molecular weight organics). However, the removal of LMW neutrals was marginal. For example, around 50% of DOC was removed by 1.5 g/L of PAC. It is mainly due to the significant reduction of biopolymers and humic substances, which were 87% and 48%, respectively. Reduced PAC dose (0.5g/L) lowered DOC removal efficiency to 37%.

PES-UF membrane filtration with PAC adsorption increased DOC removal efficiency to 53% compared to PAC adsorption only (49%). In addition, DOC removal efficiency of MWCNTs membrane filtration significantly increased to higher than 60%, when it corporates with PAC.
adsorption (1.5g/L). In particular, the removal of LMW neutrals in MWCNTs membrane filtration increased by PAC adsorption to 34% from 8% (without PAC adsorption). It is alarming to note that there was an only small reduction of LMW neutrals by either MWCNTs membrane itself or PAC adsorption itself. Moreover, DOC removal by MWCNTs membrane, even though low PAC dose was used (0.5g/L), was comparable to that by PES-UF membrane filtration with 1.5g/L of PAC. It indicates that MWCNTs enhanced membrane had effective hydrophilic DOC removal efficiency when PAC adsorption was coupled.

Low HS removal efficiency of MWCNTs membrane filtration could be explained by reduced adsorption capacity of the MWCNTs membrane in feed water with high ionic strength. In previous research, NOM removal mechanism by MWCNTs enhanced membrane was found to be a greatly enhanced electrostatic interaction between a humic acid (HA) and positively charged MWCNTs enhanced membrane. However, ionic strength in seawater may probably weaken surface charge of both the membrane and humic substances. Negatively charged humic substances form metal ion-humic precipitation and aggregation in seawater with reducing surface charge of HA [25]. Thus, it may reduce the affinity of the MWCNTs enhanced membrane to the humic substances by reducing electrostatic interaction between HA (negatively-charged) and MWCNTs enhanced membrane (positively-charged). It is consistent with a previous research done by Jermann et al. [26]. They reported that metal ions neutralize the negatively charged foulants and the charge on the membrane. Further, salinity could weaken the surface charge of the membrane. It will be discussed in the section 5.3.4.1 via zeta potential measurement of the membrane under different ionic strengths. In addition to the reduced electrostatic interaction between humic substances and MWCNTs membranes, insufficient contact time may be considered as the main reason for low humic substances removal efficiency. Due to the rapid
permeate flux, MWCNTs enhanced membrane system had a short time for adsorption of humic substances. Based on that the removal mechanism of MWCNTs enhanced membrane is the enhanced adsorption by electrostatic interaction, contact time may also be a critical factor in the removing of LMW organic matter with reduced surface charge by salty water. Therefore, organics easily pass through MWCNTs membrane due to the fast permeate flux.

![Fig 5.2 Permeability decline pattern in MWCNTs and PES membrane filtration of seawater with different PAC doses.](image)
Table 5.3 Concentration and removal efficiency (R) of organic fractions by MWCNTs enhanced and PES-UF membrane with and without PAC adsorption.

<table>
<thead>
<tr>
<th>Membrane/treatment types</th>
<th>DOC (µg/L)</th>
<th>Hydrophilic DOC</th>
<th>Bio-polymers</th>
<th>Humic substances</th>
<th>Building blocks</th>
<th>LMW Neutrals</th>
<th>LMW Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw seawater</td>
<td>1,300</td>
<td>1,027</td>
<td>179</td>
<td>496</td>
<td>36</td>
<td>250</td>
<td>65</td>
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<tr>
<td>PAC1.5</td>
<td>658</td>
<td>529</td>
<td>24</td>
<td>256</td>
<td>2</td>
<td>241</td>
<td>6</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R (%)</td>
<td>49</td>
<td>48</td>
<td>87</td>
<td>48</td>
<td>94</td>
<td>4</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAC0.5</td>
<td>825</td>
<td>669</td>
<td>52</td>
<td>364</td>
<td>4</td>
<td>242</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>R (%)</td>
<td>37</td>
<td>35</td>
<td>71</td>
<td>27</td>
<td>89</td>
<td>3</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PES-UF</td>
<td>1,135</td>
<td>894</td>
<td>71</td>
<td>483</td>
<td>35</td>
<td>246</td>
<td>59</td>
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<td></td>
<td>R (%)</td>
<td>13</td>
<td>13</td>
<td>60</td>
<td>3</td>
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<td>2</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PES-UF-PAC1.5</td>
<td>607</td>
<td>474</td>
<td>16</td>
<td>204</td>
<td>19</td>
<td>233</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>R (%)</td>
<td>53</td>
<td>54</td>
<td>91</td>
<td>59</td>
<td>47</td>
<td>7</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MWCNTs</td>
<td>968</td>
<td>767</td>
<td>21</td>
<td>473</td>
<td>29</td>
<td>229</td>
<td>15</td>
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<td></td>
<td>R (%)</td>
<td>26</td>
<td>25</td>
<td>88</td>
<td>5</td>
<td>19</td>
<td>8</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MWCNTs-PAC1.5</td>
<td>439</td>
<td>386</td>
<td>14</td>
<td>193</td>
<td>8</td>
<td>165</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>R (%)</td>
<td>66</td>
<td>62</td>
<td>92</td>
<td>61</td>
<td>78</td>
<td>34</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MWCNTs-PAC0.5</td>
<td>529</td>
<td>452</td>
<td>14</td>
<td>226</td>
<td>16</td>
<td>189</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>R (%)</td>
<td>59</td>
<td>56</td>
<td>92</td>
<td>54</td>
<td>56</td>
<td>24</td>
</tr>
</tbody>
</table>
5.3.3 Effect of salinity and divalent cation on HA rejection

In Chapter 4, the MWCNTs enhanced membrane was found to have effective HA removal efficiency (> 80%). However, in section 5.3.1.2, low removal efficiency on humic substances was observed in seawater filtration where high salinity water samples were treated. It is noted that the low HS removal efficiency of MF/UF membranes in SWRO pretreatment can also cause irreversible RO membrane fouling [27]. For this reason, it is imperative to discuss which factor can seriously affect the HS removal efficiency of the MWCNTs enhanced membrane in seawater filtration to evaluate the performance of the MWCNTs membrane in SWRO pretreatment.

To examine the effect of salinity on humic acid (HA) rejection, membrane filtration was conducted with 5mg/L of HA under different NaCl concentrations. Further, the effect of ionic strength on membrane performance in HA rejection test was investigated under the presence of divalent cation (CaCl$_2$). Fig 5.3 and 5.4 show the permeate flux and HA removal under the different NaCl concentrations, respectively. Overall, salinity significantly contributed to the enhanced permeability and reduced HA removal efficiency in MWCNTs membrane. In contrast, PES-UF membrane performance was marginally affected by monovalent ion strength (NaCl).

As can be seen from Fig 5.3, permeate flux increased by 40 % when 0.01 M of NaCl was a presence with 0.5mg/L of HA compared to 5mg/L of HA without NaCl. Permeate flux decline at the initial stage (30 min) was overcome when NaCl increased to 0.1 M, showing the nearly same permeability as the one under 0.01 M NaCl. By contrast, HA removal efficiency was shown to reduce considerably under increasing concentration of ionic strength. Especially at the final stage, it decreased sharply (80 % to 30 %) as ionic strength increased. Such a result demonstrates that adsorption capacity of MWCNTs membrane reduced under higher concentration, and increasing concentration accelerated to reach HA adsorption capacity. It may appear due to the reduced electrostatic interaction between negatively
charged humic substances and positively charged membrane surface. As ionic strength increases to 0.1 M, it may weaken the surface charge of humic substances by forming a double layer on humic substances. Such a consequence can be interpreted to contribute to the flux enhancement by hindering adsorption of HA from the membrane surface, compared to the HA 5 ppm filtration without NaCl.

Divalent ion (CaCl₂) mostly affected to significantly reduced permeability in both MWCNTs and PES-UF membranes. In contrast, the addition of CaCl₂ considerably enhanced HA removal efficiency in both membranes. Permeate flux behavior and HA rejection efficiency under divalent cationic strength (CaCl₂) is shown in Fig 5.4. Severe flux decline was observed in MWCNTs enhanced membrane after 660 min filtration, in comparison to the flux under monovalent ionic strength (NaCl). PES membrane also exhibited much lower flux behavior (7.4 LMH/bar) from the initial stage. The removal rate of MWCNTs enhanced membrane in the initial stage increased by 12%, and no drop was observed during whole filtration period (filtered volume = 684.9 L/m²), compared that there was a sharp decrease in HA removal efficiency under increasing NaCl concentration by approximately 50 %. The enhanced HA removal efficiency is largely due to the increased HA aggregation under divalent cation such as Ca²⁺. It may make a compact network between HA by neutralizing negative charge on HA under around pH 6, resulting in larger size of HA. Even if the surface charge of MWCNTs enhanced membrane was weakened by salt ions, the synergetic effect of Ca²⁺ was able to contribute to the HA removal enhancement [28].

The synergetic effect of CaCl₂ mostly contributed to PES-UF membrane, which was shown to have low HA removal efficiency. PES-UF membrane exhibited higher removal efficiency (87 %) during the whole period. The notable thing is its removal rate increased by final stage. It appeared probably due to the fact that divalent cation increases HA aggregation by cross-linking of HA, which accelerated adsorption of humic acid on the membrane. In addition to the enhanced adsorption by the larger size of
HA, Ca ion has a bridge between HA adsorbed on the membrane surface and the one in feed water by reducing repulsion force among HA. Thus, relatively lower removal rate was observed at the initial stage (100 mL filtration) and increased at the final stage. Further, sufficient contact time of HA adsorption due to the severe flux decline by CaCl$_2$ combining with HA led to the increased HA rejection efficiency in PES-UF membrane.

![Permeability of membranes with HA 5mg/L (ppm) under the different NaCl concentrations.](image)

Fig 5.3 Permeability of membranes with HA 5mg/L (ppm) under the different NaCl concentrations.
Chapter 5 Application of Carbon nanotube enhanced ultrafiltration membrane for seawater pretreatment and examination of salinity on the membrane performance

Fig 5.4 HA rejection (%) of membranes with HA 5mg/L (ppm) under the different NaCl concentrations.

(a) Permeability

(b) HA rejection

Fig 5.5 Permeability and HA rejection (%) of membranes with HA 5 ppm under 0.01M of CaCl$_2$. 
5.3.4 Factors affecting membrane performance

5.3.4.1 Surface charge of membrane under different ionic strength – organic removal

According to the previous study (Chapter 3), the surface charge of the membrane was found to be the most critical factor of organic matter removal by a membrane. The surface charges of the membranes depending on ionic strength (under different background electrolyte, KCl) were examined to verify the effects of ionic strength on membrane performance. **Fig 5.6** shows that zeta potential of MWCNTs and PES-UF membrane under different KCl concentrations at pH 7.8. Zeta potentials of MWCNTs and PES-UF membrane at 0.001M of KCl were 9.8 and -21.0 mV, respectively. It indicates MWCNTs enhanced membrane charged positively while PES-UF membrane had negatively charged surface. Zeta potential of MWCNTs membrane significantly decreased when KCl concentration increased from 0.001 to 0.010 M. However, there was not a significant decline in zeta potential in PES-UF membrane despite increasing KCl concentration. It indicates that positively charged MWCNTs enhanced membrane is more strongly influenced by the ionic strength, in comparison to the negatively charged PES-UF membrane. Based on the results, it implies that organic matter removal efficiency of MWCNTs enhanced membrane could be lowered by increased ionic strength. It may be due to the weakened electrostatic interaction between membrane surfaces and mostly negatively charged SWOM such as humic substances.
Chapter 5 Application of Carbon nanotube enhanced ultrafiltration membrane for seawater pretreatment and examination of salinity on the membrane performance

**Fig 5.6** Zeta potential of membranes under different ionic strengths by streaming potential at pH 7.8 and different KCl (background electrolyte) concentrations (0.001, 0.005 and 0.010 M).

### 5.3.4.2 Chemical precipitation on membrane – filtration behavior

SEM-EDS analysis on the fouled membranes surface was performed to observe the morphology of membrane surface and chemical precipitation (elements). **Fig 5.7** presents SEM images and EDS results of each membrane surface (a: MWCNTs enhanced membrane and b: PES-UF membrane) before and after seawater filtration tests. Both virgin membranes (before filtration) were mainly composed of carbon (C), oxygen (O) and sulfur (S) since they were fabricated based on PES. As expected, organic/inorganic foulants oriented from seawater (or PAC) were observed on the fouled membranes with/without PAC adsorption. As shown in **Fig 5.7**, some crystals were found on the surface of fouled membranes. The main components of the crystals were carbon (C) and oxygen (O) as the components of foulants by organic matter [10]. Sodium (Na), chloride (Cl) and magnesium (Mg) were found to be other
components of these crystals, which are the main components of seawater. More crystals binding with organic contaminants were observed on the surface of MWCNTs enhanced membrane than PES-UF membrane. In particular, the proportion of inorganic foulants such as Na (7.85 %), Cl (15.53 %), S (6.14 %), Fe (5.79 %) and Mg (2.23 %) was shown to increase in crystal form when PAC adsorption was used, compared that only Na (3.40 %) and Cl (9.93 %) were detected on the surface MWCNTs enhanced membrane filtered with raw seawater (without PAC adsorption). The result explains flux behaviors in MWCNTs enhanced membrane filtration coupled with PAC adsorption. Deposition of accelerating crystallization on the surface of the membrane may cause rapid flux decline in MWCNTs enhanced membrane filtration with higher organic removal efficiency (due to more bonding with organics) although improved permeate flux compared MWCNTs enhanced membrane alone. In contrast, there was no increase of crystal bonded with organic foulants on the PES-UF membrane after PAC adsorption was integrated. It may be due to the fact that crystallization occurs in the interactions between crystals containing humic substances and salts, and membrane surface [11]. By the bridging effect of hydrophilic organic contaminants on salt and positively charged membrane surface, more crystallization deposited on the more hydrophilic surface of MWCNTs enhanced membrane, compared to the less hydrophilic PES-UF membrane.
Chapter 5 Application of Carbon nanotube enhanced ultrafiltration membrane for seawater pretreatment and examination of salinity on the membrane performance

(a) Virgin

Raw seawater

PAC 1.5g/L treated seawater

(b) Virgin
5.3.4.3 Membrane hydrophilicity (water contact angle)

Hydrophilicity of fouled membranes was measured in terms of water contact angle. Table 5.4 shows contact angle of fouled membrane before and after filtering of 684.9 L/m² of seawater samples (untreated and PAC treated). As can be seen from Table 5.4, MWCNTs enhance membrane has more hydrophobic membrane surface. After filtration of 684.9 L/m² of raw seawater, contact angles of PES-UF and MWCNTs enhanced membranes decreased from 57.6±0.4° to 53.9±1.9° and from 45.4±0.1° to 42.7±2.6°, respectively. It demonstrates that membrane surface became more hydrophilic and it may be due to the adsorption of hydrophilic contaminants in seawater onto the membrane surface. Such a result may occur due to the fact that organic matter in seawater forms ion-humic precipitation and agglomeration by the interaction between salt ions and negatively charged organic matters [25]. Such
precipitates are adsorbed onto the membrane surface during filtration test, resulting in contact angle increase of the fouled membrane. However, an interesting trend on contact angle was observed on MWCNTs enhanced membrane when it was filtered the PAC treated seawater. However, when pretreated seawater with PAC adsorption was used in MWCNTs enhanced membrane filtration, contact angle increased slightly to 45.9±2.1°, indicating that hydrophilic organic compounds were removed by PAC adsorption. It is fact that SWOM contains mostly hydrophilic organic compounds, which were effectively removed by PAC. However, for PES-UF membrane, there was not a significant change in contact angle when PAC adsorption incorporated. Such a result was confirmed by SEM-EDX observation indicating that there was not a significant crystallization formation on PES-UF membrane even though PAC adsorption was coupled.

Table 5.4 Changes of water contact angle of the membrane before and after filtration (filtered volume = 684.9 L/m²).

<table>
<thead>
<tr>
<th></th>
<th>PES-UF membrane (°)</th>
<th>MWCNTs enhanced membrane (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>57.6 ± 0.4</td>
<td>45.4 ± 0.1</td>
</tr>
<tr>
<td>Filtration of raw seawater</td>
<td>53.9 ± 1.9</td>
<td>42.7 ± 2.6</td>
</tr>
<tr>
<td>Filtration of 1.5 g/L PAC treated seawater</td>
<td>54.8 ± 3.2</td>
<td>45.9 ± 2.1</td>
</tr>
</tbody>
</table>
5.4. Conclusion

This study evaluated MWCNTs enhanced UF membrane for SWRO pretreatment. The results show that MWCNTs enhanced membrane can be an alternative SWRO pretreatment option. The MWCNTs enhanced membrane exhibited greatly enhanced permeate flux when PAC adsorption was coupled, compared to PES-UF membrane. It is mainly due to the increased porosity, hydrophilicity and finger-like structure having narrow pore size on top and relatively large micro-pores on sub-layer. There was no decline in permeate flux and removal efficiency even if PAC dosage decreased from 1.5 g/L to 0.5 g/L, which can substantially contribute to reducing sludge volume generated from SWRO pretreatment by reducing chemical usage. The salinity was found to affect greatly mainly enhanced permeate flux. However, it contributed to the considerably reduced organic matter removal efficiency. The detrimental effect on the organic matter removal efficiency in MWCNTs membrane could be most probably due to the significantly reduced electrostatic interaction between positively charged membrane surface and negatively charged SWOM. The salinity was proven to reduce surface charge of HS (negative charge) by HA filtration test under different ionic strengths. Further, it mainly reduced the surface charge of MWCNTs membrane (positively charge) via zeta potential measurement under different ionic strengths.
Chapter 5 Application of Carbon nanotube enhanced ultrafiltration membrane for seawater pretreatment and examination of salinity on the membrane performance

References


Chapter 6. Protein fouling behaviour under different solution chemistry (pH and ionic strength)

Chapter 6. Protein fouling in carbon nanotubes enhanced ultrafiltration membrane: fouling mechanism as a function of pH and ionic strength

6.1. Introduction

Ultrafiltration (UF)/nanofiltration (NF) membrane technologies have been increasingly used in the secondary effluent from wastewater treatment plant as well as been examined for whey protein fractionation on a laboratory scale [1-3], bioseparation [4-6] and cation macromolecule recovery in bioprocess [7] due to its superior separation performance. However, such applications appear to have several drawbacks in treating the feed waters containing effluent organic matters (EfOMs) such as protein, polysaccharides, humic and fulvic acids [8]. Protein fouling in UF membrane is attributed to proteins adsorption/deposition on the membrane surface or inside the pores via pore blocking and/or cake layer formation, causing significant flux decline, increased chemical cleaning, and membrane replacement [9].

The separation performance of UF/NF membrane can be significantly influenced by the solution chemistry such as ionic strength, concentration and solution pH [10-12]. It is mainly due to the fact that ionic strength and solution pH strongly influence membrane surface and protein interaction, protein, and protein interaction by shifting isoelectric point of protein and charge of the protein [13]. Thus, ionic compounds contained in wastewater lead to accelerating membrane fouling when the foulants are oppositely charged with the membrane and intensive chemical cleaning [14]. There have been numerous studies examining the effects of solution chemistry (ionic strength and solution pH) and model foulant in separation performance of UF/NF membrane [15-17]. Conventional polymeric membranes experience severe fouling by negatively charged protein at near to its isoelectric point (IEP) due to the decreased electrostatic repulsion between foulant-foulant, and foulant-membrane surface [18, 19]. Further, high ionic strength can induce membrane fouling due to electrical double layer
compression effect on the foulants [20, 21]. Such effects of solution chemistry on protein adsorption on the membrane surface and pores are governed by electrostatic interaction/repulsion [22], indicating that the protein fouling in the UF membrane could be reduced by controlling the electrostatic interaction [23, 24]. Like negatively charged polymeric membranes, positively charged conventional membrane showed reduced fouling to the same charged proteins (Lys) mostly due to the less adsorption on the membrane surface via electrostatic repulsion [25].

Recent progress on carbon nanotubes (CNTs) membrane fouling reveals protein-fouling resistance due to its modified surface properties [26-28]. Celik et al. [29] also studied the protein fouling behavior in CNTs composite membrane at different solution pHs and membrane properties (such as hydrophilicity). The challenge in protein fouling stimulated further development on positively charged nanohybrid UF membranes having antifouling properties due to electrostatic interaction with foulants. For example, poly (arylene ether sulfone) (PAES) block copolymers with carboxyl (COOH) functionalized CNTs incorporated UF hybrid membrane exhibited relatively low protein adsorption and irreversible protein fouling by increasing hydration of membrane surface and reducing the net charge density [30]. Further, currently fabricated positively charged graphene oxide (GO) nanosheet UF membrane presented enhanced antifouling properties due to the combined effect of hydrophilicity, surface charge and morphology of the membrane at different pH [31]. Recently fabricated CNTs/PANI composite membrane shows superior performance in natural organic matter (NOM) removal [32]. This membrane has unique physicochemical characteristics by incorporating the MWCNTs/PANI complex to UF membrane. It is positively charged below pH 9.2 (IEP) and removes NOM via electrostatic interaction with negatively charged NOM.

As such there have been numerous studies on protein fouling behavior in the positively charged membranes [33-35]. However, in-depth study on the influence of solution chemistry on protein fouling mechanism in a positively charged nanocomposite membrane has not reported in the literature. Therefore, this study is focused on the fouling behavior caused by positively/negatively charged
protein on the positively charged membrane (CNT/PANI membrane) under different ionic strengths and solution pHs. It would give useful information to the wide application of CNT engineered membrane for wastewater reclamation and bioseparation.

This study aims to i) investigate the influence of feed solution chemistry on protein fouling behavior in the positively charged membrane: flux pattern under different pHs and ionic strengths, and ii) evaluate protein fouling mechanism using filtration models.

6.2. Materials and methods

6.2.1 Materials

6.2.1.1 Model protein foulants and chemicals

Bovine serum albumin (BSA) and Lysozyme (Lys) were used as model protein foulants. BSA (powder, Sigma-Aldrich) was used as the negatively charged model protein foulant. Lys (powder, Sigma-Aldrich) was selected as the positively charged protein foulant. The molecular weight (MW) of BSA and Lys is reported to be 67 kDa and 14.3 kDa, respectively [12, 19]. The IEP of BSA and Lys 4.7 and 10.4, respectively. Each stock solution was prepared at a concentration of 1 g/L and stored in a glass bottle at 4 °C prior to use. The pH was adjusted using 1M-HCl and 1M-NaOH. The ionic strength of solution was adjusted by adding different concentrations of NaCl (VWR, ACS reagent). All stock solutions were prepared by ultrapure water (conductivity = 0.055 µS/cm).

6.2.1.2 Membranes

In this study, a multiwall CNT (MWCNT) enhanced membrane was tested and compared with a commercial polyethersulfone (PES) membrane (Nanostone Flat Sheet Membrane, PES UF OPE10HR).

Fabrication procedure of 0.5 wt% MWCNTs enhanced membrane was adopted from Chapter 3. Prior to use, all membranes were soaked in deionized (DI) water for 1-2 d to remove any impurities. Characteristics of membranes used in this study are summarized in Table 6.1.
Table 6.1 Information of the membranes used in this chapter.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>UPW* permeability (LMH**/bar)</th>
<th>Pore size by BET (nm)</th>
<th>MWCO*** (kDa)</th>
<th>Contact angle (°)</th>
<th>Isoelectric pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>490.8 ± 46.3</td>
<td>4.4-4.6</td>
<td>12</td>
<td>45.4 ± 0.1</td>
<td>9.2</td>
</tr>
<tr>
<td>PES</td>
<td>85.5 ± 8.5</td>
<td>-</td>
<td>10</td>
<td>57.6 ± 0.4</td>
<td>2.9</td>
</tr>
</tbody>
</table>

*UPW: Ultrapure water, **LMH: L/m²h; and ***MWCO: Molecular weight cut-off.

6.2.2 Fouling experiments

The protein fouling experiments were carried out in a dead-end filtration mode under 2 bar for 12 h. The effective membrane area was 0.00146 m². Constant pressure was applied during the filtration test using a compressed nitrogen gas cylinder. The flux data were continuously acquired using an electronic balance connected to a computer. Each feed solution was prepared under the following conditions:

- Concentration: BSA = 10 mg/L, Lys = 10 mg/L, and BSA-Lys mixture = 20 mg/L (10mg/L BSA + 10mg/L Lys)
- pH: 4.7, 7.0, and 10.4
- Ionic strength: NaCl in the concentration of 0.001, 0.01, and 0.1 M

6.2.3 Membrane characterization

The zeta potential of membrane surface was measured by using the streaming potential technique (Anton Paar electrokinetic analyzer). The zeta potential measurements were carried out as a function of pH (4.0-11.0) and ionic strength (with 0.001, 0.005, and 0.010 M KCl at pH 7.0).

6.2.4 Membrane fouling model

Protein fouling mechanism of the MWCNT membrane by protein was examined. Three types of membrane fouling model were used to explain the flux decline with protein deposition during
membrane filtration (standard blocking, and cake layer formation) [36, 37]. The equations of each fouling models are summarized in Table 6.2.

**Table 6.2 Fouling mechanism equations.**

<table>
<thead>
<tr>
<th>Fouling mechanisms</th>
<th>Equations</th>
</tr>
</thead>
</table>
| Completed blocking               | \[
|                                 | \frac{d(V)}{dt} = J_0 - k_b \frac{V}{A}      |
| Intermediate blocking            | \[
|                                 | \frac{dt}{d(V/A)} = \frac{1}{J_0 + k_i t}    |
| Cake layer formation             | \[
|                                 | \frac{t}{V/A} = \frac{1}{J_0} + \frac{k_c}{2} \frac{V}{A} |
|                                  |                                                 |

In these equations, \( t \) is the filtration time, \( V \) is the cumulative permeate volume, \( A \) is the effective filtration area (0.00146 m\(^2\)), \( J_0 \) is the initial flux, \( k_b \) (1/s), \( k_s \) (1/m), \( k_i \) (1/m) and \( k_c \) (s/m\(^2\)) are the coefficients of complete blocking, standard blocking, intermediate blocking, and cake filtration models, respectively. From these equations, three data plots have been proposed where the linearity of the filtration data in the plot of \( d(V/A)/dt \) vs \( V/A \), \( t/(V/A) \) vs \( t \), \( dt/d(V/A) \) vs \( t \) and \( t/(V/A) \) vs \( V/A \) offers proof of the complete blocking, intermediate blocking, and cake filtration model, respectively. Two pore blocking models (complete and intermediate) were applied at the initial stage of filtration (~2 h) because those two blocking models are expected to be dominant in both the MWCNT and PES-UF membranes with bigger pore size than the two model proteins. The initial stage of filtration was determined by the time when the initial permeate flux was declined by more than half and showed the highest value in all permeate flux profiles. At the later stage (2 – 12 h), cake layer filtration was applied. The dominant filtration model was determined by comparing correlation coefficient (R\(^2\)). The fouling potential of both membranes at different solution chemistry was examined by comparing the fouling coefficients (\( K_b \), \( K_i \) and \( K_c \)), which were derived from those equations.
6.3. Results and discussion

6.3.1 Effects of solution chemistry on surface charge of the membranes

It is essential to study the surface charge of the membrane for an understanding of protein fouling mechanisms on membranes. Zeta potentials of both MWCNT and PES membranes were analyzed by streaming potential measurement to evaluate the effect of solution chemistry on the membrane surface charge. Fig 6.1(a) shows the zeta potential of the MWCNT membrane, which varies from positive to negative value depending on the pH. The zeta potential of the MWCNTs membrane was shown to be highly positive (17.12 mV) under acidic condition (pH 4.7). Then, it slightly decreased to 10.9 mV when pH increased to 7.0. However, the membrane shifted to be a negative charge (-25 mV) at pH 10.4. Thus, it is noted that the isoelectric point (IEP) of the MWCNT membrane was 9.2 as shown in Table 6.1. On the other hand, the zeta potential of the PES-UF membrane remained in a negative value over the entire pH range, although its negative value slightly decreased (from -35 to -20 mV) as the pH decreased (pH 10.4 to 4.7). In addition to pH, ionic strength reduced the zeta potential of the MWCNT membrane as shown in Fig 6.1(b). The zeta potential of the MWCNT membrane dramatically dropped to the nearly zero (0) mV as the electrolyte (KCl) concentration increased to 0.01 M, indicating that the surface charge of the MWCNT membrane was strongly affected by ionic strength. Electrolyte ions could reduce the membrane surface charge density via charge neutralization. In contrast, there was no significant change in the negatively charged PES-UF membrane with the increase in electrolyte concentration. Meanwhile, the zeta potential at 0.1 M KCl could not be measured due to the limit of the equipment used. It is assumed that the zeta potential at 0.1 M would be almost zero (0) or near to negative.

Overall, solution chemistry, such as pH and ionic strength of feed solution, significantly influenced the surface charge of the MWCNT membrane while PES-UF membrane maintained being negatively charged regardless of solution chemistry.
**Fig 6.1** Zeta potential of MWCNT membrane and PES membrane (a) at different pHs (4.7, 7.0 and 10.4) and (b) different ionic strengths by adding different concentrations of KCl (background electrolyte) (0.001, 0.005 and 0.010 M) at pH 7.0.
6.3.2 Effects of pH on permeate flux with single proteins

6.3.2.1 Permeate flux behavior in positively charged protein (Lys)

6.3.2.1.1 MWCNT membrane

Fig 6.2 shows the flux decline of MWCNT and PES-UF membrane filtration with Lys under different pH levels. Overall, the MWCNT membrane was found to be sensitive to the feed properties both at the beginning of filtration and the corresponding filtration process. A rapid permeate flux decline was observed at the initial stage of the MWCNT membrane filtration with Lys, which is associated with the membrane pore size. In addition, flux pattern of the MWCNT membrane was considerably affected by pH. It is noted that the IEP of Lys is pH 10.4, which indicates that the charge of Lys is neutralized at pH 10.4. As can be seen in Fig 6.2(a), permeate flux was shown in the following order: pH 4.7 > pH 10.4 > pH 7.0. At pH 4.7, the initial permeate flux of MWCNT membrane was higher, and it was more than six times (from 50 to 340 LMH/bar). The high permeate flux at pH 4.7 in MWCNT membrane filtration may be due to less Lys adsorption on the membrane surface by the increased electrostatic repulsion between more positively charged membrane surface and positively charged Lys. Since MW of Lys (14.3kDa) was slightly larger than the pore size (12kDa) of the MWCNT membrane, feed solution with Lys had a possibility to block the pore of the membrane affecting the water transport through the membrane. In particular, at pH 4.7, the MWCNT membrane becomes more positively charged (17.12 mV) as shown in Fig 6.1(a), resulting in an increased electrostatic repulsion between membrane and Lys.
Chapter 6. Protein fouling behaviour under different solution chemistry (pH and ionic strength)

Fig 6.2 Comparison of permeate flux pattern of MWCNT and PES-UF membrane filtration with positively charged protein (Lys) and negatively charged protein (BSA) under different pHs (4.7, 7.0 and 10.4).

The higher flux at pH 10.4 than pH 7.0 can be explained by the foulant intermolecular interaction. As mentioned in the earlier section, the IEP is the pH at which a particular molecule carries no net electrical charge. The net charge on the molecule is affected by pH of its surrounding environment as the solution and can become more positively or negatively charged due to the gain or loss of protons (H\(^+\)). The IEP value can affect the solubility of a molecule at a given pH. Such molecules have a minimum solubility in water or salt solutions at the pH that corresponds to their IEP and often
Chapter 6. Protein fouling behaviour under different solution chemistry (pH and ionic strength)

precipitates out of solution. Hence, the weakened electrostatic repulsion between the membrane and Lys at pH 10.4 led to a higher flux of MWCNT membrane compared to at pH 7.0. It is probably due to the more aggregation between Lys molecules. It indicates that intermolecular interaction (Lys-Lys) could play a major role in permeate flux pattern in addition to the interaction between membrane and foulant.

Table 6.3 Comparison of the correlation coefficient ($R^2$) in the MWCNT membrane filtration with proteins under different solution chemistry at (a) the initial stage of filtration (2h) and (b) final stage of filtration (2 to 12h).

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Ion strength (NaCl) (M)</th>
<th>4.7</th>
<th>7.0</th>
<th>10.4</th>
<th>0.001</th>
<th>0.01</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lys (10 mg/L)</td>
<td></td>
<td></td>
<td>*</td>
<td>0.8694</td>
<td>0.9162</td>
<td>0.9910</td>
<td>0.8836</td>
<td>0.8554</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>**</td>
<td>0.9727</td>
<td>0.9644</td>
<td>0.9457</td>
<td>0.9129</td>
<td>0.9634</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>***</td>
<td>0.9983</td>
<td>0.9849</td>
<td>0.9978</td>
<td>0.8844</td>
<td>0.9954</td>
</tr>
<tr>
<td>BSA (10 mg/L)</td>
<td></td>
<td></td>
<td>*</td>
<td>0.9369</td>
<td>0.9205</td>
<td>0.9024</td>
<td>0.9162</td>
<td>0.9134</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>**</td>
<td>0.9664</td>
<td>0.9604</td>
<td>0.9349</td>
<td>0.9620</td>
<td>0.9520</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>***</td>
<td>0.9927</td>
<td>0.9830</td>
<td>0.9471</td>
<td>0.9457</td>
<td>0.9760</td>
</tr>
<tr>
<td>Lys + BSA (20 mg/L)</td>
<td></td>
<td></td>
<td>*</td>
<td>0.9213</td>
<td>0.9268</td>
<td>0.9273</td>
<td>0.9406</td>
<td>0.9462</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>**</td>
<td>0.9409</td>
<td>0.9571</td>
<td>0.9498</td>
<td>0.9896</td>
<td>0.9926</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>***</td>
<td>0.9990</td>
<td>0.9565</td>
<td>0.9930</td>
<td>0.9981</td>
<td>0.9847</td>
</tr>
</tbody>
</table>

* $R^2$ of complete pore blocking model, ** $R^2$ of intermediate pore blocking model, *** $R^2$ of cake layer filtration model.
Overall, complete pore blocking and intermediate pore blocking at the initial stage were dominant except for the pH 4.7 (The initial stage of filtration was determined to be 2 hours because severe permeate flux decline in most cases occurred in 2 hours, and $R^2$ did not vary in 2 ± 0.5 hours of filtration). Table 6.3 shows that the correlation coefficients ($R^2$) of complete and intermediate pore blockings are above 0.9 at pH 7.0 and 10.4. At the later stage, cake layer filtration was dominant, as seen in Table 6.3. The fouling potentials at different pH are presented in Table 6.4. For 10 mg/L Lys filtration, complete blocking and intermediate blocking appeared simultaneously at the initial filtration stage (2 h). Then, cake layer formation developed at the later filtration stage (2 h – 12 h). As seen in Table 6.4, $K_b$, $K_i$ and $K_c$ were high at pH 7.0 while they were low at pH 4.7. It indicates that severe pore blocking at the initial stage and cake formation at the later stage developed on MWCNT membrane at pH 7.0. Severe permeate flux decline with MWCNT membrane at pH 7.0 appeared possibly due to the pore blocking at the initial filtration stage (2 h) and developing cake layer form at the later stage. However, decreases in $K_b$, $K_i$ and $K_c$ at pH 4.7 indicate that pore blocking and protein adsorption was alleviated by increased electrostatic repulsion. Further, a decrease of $K_c$ at the final stage of filtration shows that protein deposition rate slowed down as filtration proceeds. It is noted that at pH 4.7, both membrane and Lys are strongly positively charged; thus, there is relatively strong electrostatic repulsion between the membrane and foulant. For this reason, at pH 4.7, the highest flux was observed due to less Lys adsorption by strong electrostatic repulsion (Fig 6.2). It is good agreement with the effect of electrostatic interaction on the fouling behavior. Fouling was also alleviated at the IEP of Lys (pH 10.4), but it was higher than that at pH 4.7 (Table 6.4). At pH 10.4, the membrane became negatively charged while Lys was neutralized. It may induce adsorption of Lys on the membrane surface by removing electrostatic repulsion, corresponds to slight increases of $K_{b,i}$ and $K_c$ compared to that at pH 10.4. Previous studies on protein fouling reported that severe fouling was observed at IEP of model protein due to decreased electrostatic interaction [38]. However, the MWCNT membrane showed low fouling potential at IEP of Lys. Such a discrepancy may be mainly
due to the change in zeta potential of the MWCNT membrane at IEP of the model protein (pH 10.4). More interestingly, a discrepancy occurs between the fouling coefficient and flux patterns in Lys filtration. Severe fouling appeared at pH 7.0 at which the membrane surface and Lys are still oppositely charged. Due to an electrostatic repulsion, its fouling should be reduced compared to that at pH 10.4 at which the electrostatic repulsion disappears due to neutrally charged Lys. It indicates that the fouling behavior of Lys filtration in the MWCNT membrane is also controlled by intermolecular interaction (Lys-Lys). Severe foulant aggregation occurs at its IEP (pH 10.4), resulting in the enhanced permeate flux due to its insolubility compared to at pH 7.0.

**Table 6.4** Comparison of fouling potential in the MWCNT membrane filtration with proteins under different solution chemistry at (a) the initial stage of filtration (2h) and (b) final stage of filtration (2 to 12h)

<table>
<thead>
<tr>
<th>Protein</th>
<th>pH</th>
<th>Ion strength (NaCl) (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.7</td>
<td>7.0</td>
</tr>
<tr>
<td>Lys (10 mg/L)</td>
<td>K_b</td>
<td>1.00×10^{-4}</td>
</tr>
<tr>
<td></td>
<td>K_i</td>
<td>1.63</td>
</tr>
<tr>
<td>BSA (10 mg/L)</td>
<td>K_b</td>
<td>1.00×10^{-4}</td>
</tr>
<tr>
<td></td>
<td>K_i</td>
<td>0.53</td>
</tr>
<tr>
<td>Lys + BSA (20 mg/L)</td>
<td>K_b</td>
<td>1.00×10^{-5}</td>
</tr>
<tr>
<td></td>
<td>K_i</td>
<td>19.50</td>
</tr>
<tr>
<td></td>
<td>K_c</td>
<td>2.15×10^{6}</td>
</tr>
</tbody>
</table>
Based on the synergetic effect of membrane-foulant interaction and foulant-foulant interaction (Lys-Lys), it is obvious that the permeate flux, at pH 7.0 at which both two interactions are dominant, was the lowest, and the fouling was greater.

### 6.3.2.1.2 PES-UF membrane

Permeate flux in the PES-UF membrane filtration was almost similar even at different pHs. However, there was no flux difference by pH level from 4.7 to 10.4 in the PES-UF membrane (the initial flux was around 70 LMH/bar). The dominant filtration mechanisms at the initial stage were found to complete and intermediate pore blockings (Table 6.5). There was no noticeable change in $K_b$ and $K_i$, indicating that adsorption rate of Lys particle was not affected by different pH. It may be interpreted that the electrostatic interaction between the membrane and Lys particle may not be the critical factor. Meanwhile, the relatively higher cake layer formation was observed at pH 7.0 while it was slightly reduced at IEP of Lys (pH 10.4). It is mostly due to the increase in the deposition of the neutrally charged Lys at the later stage of filtration. Consequently, the foulant-foulant interaction may have an important role in fouling in the PES-UF membrane filtration.
Table 6.5 Comparison of the correlation coefficient (R$^2$) in the PES membrane filtration with proteins under different solution chemistry at (a) the initial stage of filtration (2h) and (b) final stage of filtration (2 to 12h).

<table>
<thead>
<tr>
<th>pH</th>
<th>Ion strength (NaCl) (M)</th>
<th>4.7</th>
<th>7.0</th>
<th>10.4</th>
<th>0.001</th>
<th>0.01</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lys (10 mg/L) (a) *</td>
<td>0.9763</td>
<td>0.9871</td>
<td>0.9681</td>
<td>0.9888</td>
<td>0.9673</td>
<td>0.9981</td>
<td></td>
</tr>
<tr>
<td>Lys (10 mg/L) (b) **</td>
<td>0.9885</td>
<td>0.9954</td>
<td>0.9845</td>
<td>0.9855</td>
<td>0.9789</td>
<td>0.9890</td>
<td></td>
</tr>
<tr>
<td>Lys (10 mg/L) (b) ***</td>
<td>0.9995</td>
<td>0.9919</td>
<td>0.9993</td>
<td>0.9563</td>
<td>0.9946</td>
<td>0.9849</td>
<td></td>
</tr>
<tr>
<td>BSA (10 mg/L) (a) *</td>
<td>0.9488</td>
<td>0.9759</td>
<td>0.9536</td>
<td>0.9706</td>
<td>0.9684</td>
<td>0.9524</td>
<td></td>
</tr>
<tr>
<td>BSA (10 mg/L) (b) **</td>
<td>0.9928</td>
<td>0.9962</td>
<td>0.9881</td>
<td>0.9965</td>
<td>0.9937</td>
<td>0.9924</td>
<td></td>
</tr>
<tr>
<td>BSA (10 mg/L) (b) ***</td>
<td>0.9947</td>
<td>0.9950</td>
<td>0.9809</td>
<td>0.9925</td>
<td>0.9935</td>
<td>0.9947</td>
<td></td>
</tr>
<tr>
<td>Lys + BSA (20 mg/L) (a) *</td>
<td>0.9183</td>
<td>0.9681</td>
<td>0.9782</td>
<td>0.9159</td>
<td>0.9290</td>
<td>0.9318</td>
<td></td>
</tr>
<tr>
<td>Lys + BSA (20 mg/L) (b) **</td>
<td>0.9859</td>
<td>0.9858</td>
<td>0.9969</td>
<td>0.9817</td>
<td>0.9913</td>
<td>0.9844</td>
<td></td>
</tr>
<tr>
<td>Lys + BSA (20 mg/L) (b) ***</td>
<td>0.9990</td>
<td>0.9980</td>
<td>0.9950</td>
<td>0.9991</td>
<td>0.9943</td>
<td>0.9993</td>
<td></td>
</tr>
</tbody>
</table>

* R$^2$ of complete pore blocking model, ** R$^2$ of intermediate pore blocking model, *** R$^2$ of cake layer filtration model.

6.3.2.2 Permeate flux behavior in negatively charged protein (BSA)

6.3.2.2.1 MWCNT membrane

In the case of negatively charged protein (BSA), the BSA adsorption on the surface of membranes with a much smaller pore size (MW of BSA = 67kDa vs. membrane pore size = 10 kDa) caused a rapid decline in permeate flux of the MWCNT membrane at the initial stage of filtration (Fig 6.2(c)). Based on the flux decline, fouling by BSA on MWCNT membrane was less severe compared to that by Lys. BSA adsorption caused severe flux decline at around pH 7.0 where both the membrane and BSA are
oppositely charged. However, higher fluxes were observed at pH 10.4 where the membrane is negatively charged and at the IEP of BSA (pH 4.7). As shown in Fig 6.2(c), the permeate flux in MWCNT membrane was different depending on pH, and it had the following order: pH 10.4 > pH 4.7 > pH 7.0. Such a result could be interpreted due to the shift of electrostatic interaction between BSA and membrane. At below pH 10.4, the surface charge of the MWCNTs membrane shifted to negative charge while BSA was still negatively charged. Thus, BSA was less adsorbed on the membrane surface due to the electrostatic repulsion between BSA and membrane, indicating that BSA in feed solution at pH 10.4 did not seriously hinder the water transport. The comparable flux was observed at pH 4.7. It may be due to the zero charged BSA at its IEP. Similar as Lys, weakened interactions between BSA molecules by neutralized charge resulted in less adsorption of BSA-BSA foulant on the membrane surface. BSA molecules were aggregated each other, rather than adsorption of BSA onto the membrane.

Both complete and intermediate blockings were simultaneously dominant at the initial stage (Table 6.3). As shown in Table 6.4, fouling potentials were relatively weak, compared to those in Lys filtration. The severe fouling was observed at pH 7.0 while it was lessened at pH 4.7 and 10.4, corresponding to the flux pattern (Fig 6.2). It is probably due to the effect of pH on the electrostatic interaction between both charged membrane surface and BSA. At pH 7.0, as both membrane surface and BSA are oppositely charged, and it resulted in an increase in electrostatic interaction between the membrane and foulants. It induces the foulant adsorption on the membrane surface, leading to membrane fouling. However, at IEP of BSA (pH 4.7), due to the weakened electrostatic interaction, neutrally charged BSA became to be less adsorbed on the positively charged membrane surface compared at pH 7.0, leading to a slower fouling rate. Further, at pH 10.4, both membrane and BSA have the same charge (in negative), hindering BSA adsorption on the membrane surface via electrostatic repulsion.
6.3.2.2 PES-UF membrane

Overall, severer flux decline was observed with BSA than that with Lys. Although permeate flux in the PES-UF membrane filtration seemed to be affected by pH, its influence was much smaller than the MWCNT membrane. Permeate flux in the PES-UF membrane filtration at pH 10.4 was slightly higher than at other pH values probably due to the strong electrostatic repulsion between membrane and BSA (Fig 6.2(d)). Permeate flux at IEP (pH 4.7) of BSA was lower than that at pH 7.0 and 10.4 most probably due to deposition of BSA-BSA aggregates formed by surface charge neutralization. It showed that negatively charged PES-UF membrane was dominated by complete and intermediate pore blocking at the initial stage (Table 6.5). As shown in Table 6.6, K_i and K_c at pH 4.7 was the highest (6.25 and 3.09×10^5, respectively), indicating that rapid flux decline at the initial stage and building up the cake layer at the later stage occurred at the IEP of BSA. It is mostly due to the low electrostatic repulsion between BSA and the membrane. It is in agreement with the previous studies [19, 21].
Table 6.6 Comparison of fouling potential in the PES-UF membrane filtration with proteins under the different solution chemistry (a) at the initial stage (2h) and (b) later stage of filtration

<table>
<thead>
<tr>
<th>Protein</th>
<th>pH</th>
<th>Ion strength (NaCl) (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.7</td>
<td>7.0</td>
</tr>
<tr>
<td>Lys (10 mg/L) (a)</td>
<td>$K_b$</td>
<td>$3.00 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$K_i$</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td>$K_c$</td>
<td>$5.43 \times 10^4$</td>
</tr>
<tr>
<td>BSA (10 mg/L) (a)</td>
<td>$K_b$</td>
<td>$3.00 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$K_i$</td>
<td>6.25</td>
</tr>
<tr>
<td></td>
<td>$K_c$</td>
<td>$3.09 \times 10^3$</td>
</tr>
<tr>
<td>Lys + BSA (20 mg/L) (a)</td>
<td>$K_b$</td>
<td>$3.00 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$K_i$</td>
<td>2.15</td>
</tr>
<tr>
<td></td>
<td>$K_c$</td>
<td>$9.82 \times 10^3$</td>
</tr>
</tbody>
</table>

Based on the flux decline and fouling potential, the PES-UF membrane fouling is more affected by electrostatic repulsion with negatively charged protein (BSA).
Chapter 6. Protein fouling behaviour under different solution chemistry (pH and ionic strength)

6.3.3 Effect of ionic strength on permeate flux with single protein

6.3.3.1 Permeate flux pattern with positively charged protein (Lys)

6.3.3.1.1 MWCNT membrane

With positively charged protein (Lys), the permeate flux in the MWCNT membrane was also significantly influenced by ionic strength (in terms of NaCl) at pH 7.0. It is noted that at pH 7.0, MWCNT membrane charged positively and the charge of membrane gradually decrease to nearly zero as ionic strength decreases to 0.01 M. As can be seen in Fig 6.3(a), the permeate flux of MWCNT membrane when 0.001 and 0.01 M of NaCl were added to the solution, was much higher than zero ionic strength (without NaCl addition), and it was rather slightly increased in the presence of 0.1 M of NaCl. Slightly lower permeate flux at higher ion strength can be explained by the concentration polarization near to membrane. Overall, the low flux of the MWCNT membrane at pH 7.0 (Fig 6.2) was overcome in the presence of ionic strength (0.001–0.1 M). Such a flux enhancement may appear due to the charge shielding effect of chloride ion (Cl−) to the positive charged Lys (Lys+). It probably prevented deposition of Lys on the pores and surface of MWCNT membrane.

At 0.001 and 0.01 M NaCl, intermediate pore blocking was dominant, and both complete and intermediate pore blockings became simultaneously dominant at 0.1 M NaCl at the initial stage as presented in Table 6.3. Severe Lys fouling at pH 7.0 was reduced by the addition of ionic strength. As shown in Table 6.4, the coefficients (Kb, Ki and Kc) seemed to increase when NaCl increased from 0.001 M to 0.1 M, but overall, much lower than at pH 7.0 (without NaCl). Such a trend is consistent with the permeate flux pattern (Fig 6.3(a)). The flux had the following order: 0.001 M > 0.01 M > 0.1 M > 0 M.

It may appear probably due to the effect of ionic strength on Lys particles. Due to the presence of ionic strength, Lys-Lys interaction decreased via increasing repulsion hydrating forces between Lys-Lys [10]. Further, Cl− may interfere the interaction between the membrane and foulant by weakening
surface charge of both membrane and foulant, leading to fouling mitigation. It demonstrates that ionic strength mainly lessened fouling potential via charge shielding effect on the model proteins. The increased fouling potential at the increasing ionic strength can be explained according to the interaction between both neutralized foulants and the membrane surface. Under increasing ionic strength, both the membrane and Lys particle became neutralized, leading to the increase in Lys deposition on the membrane surface.

6.3.3.2 PES-UF membrane

In contrast to the MWCNT membrane, a different trend was observed in flux behavior of the PES-UF membrane by Lys fouling. The flux without ionic strength at pH 7.0 increased when 0.01 M of NaCl was added, but it showed a decreased flux with 0.001 and 0.1 M of NaCl. It indicates that there presented the critical point to neutralize the charge of Lys and PES-UF membrane. Ionic strength (NaCl) affected the charge of both Lys and membrane, especially negatively charged PES-UF membrane. However, at relatively high or low ionic strength, residual ions (Na$^+$ and Cl$^-$) after their reaction with Lys and membrane affected again to them. Thus, it is assumed that flux decline behavior in the PES-UF membrane is governed by complex mechanism due to the altered surface charge of both membrane and protein at different ionic strengths, which affects the interaction between protein and the membrane. Like as the MWCNT membrane, both complete and intermediate pore blockings were simultaneously dominant at the initial stage (Table 6.5). As shown in Table 6.6, $K_c$ increased as ionic strength increased, indicating that cake layer formation developed during the final stage of filtration (2h-24h). For this reason, ionic strength may induce the building up of deposition layer of Lys at the final stage of filtration.
6.3.3.2 Permeate flux behavior with negatively charged protein (BSA)

6.3.3.2.1 MWCNT membrane

Overall, ionic strength seemed to contribute considerably to permeate flux enhancement in the filtering of BSA with MWCNT membrane, but no significant difference was observed at the initial stage of filtration when the concentration of NaCl increased from 0.001 to 0.1 M. Then, there were minimal changes as increasing ionic strength at the final stage of filtration. As shown in Fig 6.3(c), permeate flux increased three times at the initial stage (2 h), continuing to have a stable flux for the rest filtration period (100-130 LMH/bar) when 0.001 – 0.1 M NaCl was added.

At the initial stage of filtration, both complete and intermediate pore blockings were simultaneously dominant (Table 6.3). The presence of ionic strength seemed to alleviate pore blocking and cake layer formation on the MWCNT membrane in the filtration of BSA, but the fouling potential induced at the increase in ionic strength. As shown in Table 6.4, $K_i$ at 0 M NaCl (4.10) decreased to 0.93 at 0.001 M NaCl, and then gradually increased (to 1.75) as the ionic strength increased to 0.1 M. Similarly, at the later stage, cake formation seemed to reduce in the presence of ionic strength. However, increase in ionic strength led to the building up the layer of BSA via protein adsorption, corresponding to the increase in $K_c$ as NaCl increased to 0.1 M. Overall, fouling was reduced mainly due to the charge shielding effects on the negatively charged BSA, resulting in a decrease of electrostatic interaction with positively charged MWCNT membrane. However, an increase in ionic strength lessened the charge of both membrane surface and BSA particle. Thus, it induced the neutralized BSA deposition on the less positively membrane surface at increasing ionic strength. Such trend corresponds to the permeate order: 0 M NaCl << 0.1 M < 0.01 M < 0.001M.
6.3.2.2 PES-UF membrane

Fig 6.3(d) shows that the permeate flux increased by nearly 30% at the initial stage (2 h) as ionic strength increased, but it remained nearly same over the whole filtration period (12 h). It indicates that ionic strength did not significantly influence BSA fouling on the PES-UF membrane surface at the final stage of filtration. It corresponds to the fouling potential as shown in Table 6.6. There was no noticeable change in $K_c$ as ionic strength increased. Both complete and intermediate pore blockings were simultaneously dominant at the initial stage (Table 6.5). However, the intermediate pore blocking was promoted as the ionic strength increased, corresponding to the slightly increasing $K_i$. It may be due to the reduced electrostatic repulsion via charge shielding effect as reported in the literature [21]. The result is in agreement with previous research presenting that increase in ionic strength can enhance fouling due to a decrease in electrostatic repulsion via hydration repulsion forces between BSA-BSA and membrane-BSA [10].
Fig 6.3 Comparison of permeability pattern with positively charged protein (Lys) and negatively charged protein (BSA) fouling under different ionic strength (concentration, monovalent/divalent ionic strength) (0.001, 0.01, 0.1 M NaCl).
6.3.4 Effect of solution chemistry on permeate flux with binary mixture

6.3.4.1 Permeate flux pattern as a function of pH

6.3.4.1.1 MWCNT membrane

Fig 6.4 shows the permeability MWCNT membrane in filtering mixture of two positively/negatively charged proteins (Lys + BSA). Overall, extremely low flux pattern was observed in the filtration with MWCNT membrane compared to that with a single protein. Interestingly, an opposite trend - the lowest flux in the vicinity of nearly IEP of each model protein was observed in permeate flux under protein mixture filtration test, compared to those in the single protein filtration. As seen in Fig 6.4(a), the permeate flux exhibited a considerable decrease in flux pattern (10 LMH/bar) at pH 4.7 and 10.4 compared to that (80 LMH/bar) at pH 7.0.

At pH 7.0, complete and intermediate pore blockings appeared to be simultaneously dominant at the initial stage while intermediate blocking played the main role in fouling at pH 4.7 and 10.4 (Table 6.3). As shown in Table 6.4, the fouling potential was low at pH 7.0 while severe intermediate pore blocking and cake formation at the initial stage occurred at IEP of both Lys (pH 10.4) and BSA (pH 4.7). It corresponds to the permeate flux pattern (Fig 6.4). It is suggested that IEP of both charged proteins may contribute to the permeate flux pattern, but it led to the opposite trend probably due to the intramolecular interactions (Lys-BSA) and that with the membrane surfaces. Apart from contributing to membrane transport via electrostatic interaction (repulsion) between single proteins and membrane surface, mixing of oppositely charged proteins seemed to generate more complicated intermolecular interactions between macro solutes (Lys-BSA, Lys-Lys, BSA-BSA) and charged membrane surface. Based on the fouling and permeate flux behavior at different pH, protein mixture fouling mechanism tends to be mainly governed by the intermolecular interaction (Lys-BSA). At pH 7.0, Lys-BSA mixture may agglomerate by intermolecular interaction in the feed solution. It decreased the deposition of the binary mixture on the membrane surface, leading to fouling alleviation, which is
comparable to the BSA filtration. However, at pH 4.7 and 10.4 where each of proteins is neutrally charged, the proteins deposited on the membrane, then induced the deposition of the counter charged proteins by bridge effect.

6.3.4.1.2 PES-UF membrane

In contrast, negatively charged PES-UF membrane showed the lowest permeate flux (20 LMH/bar) at pH 7.0 while the permeate flux was improved at pH 10.4 and 4.7 (to 24 and 43 LMH/bar, respectively) (Fig 6.4(b)). Complete and intermediate pore blockings were simultaneously dominant at the initial stage (Table 6.5). Like as severe flux decline at the initial stage at pH 7.0, high potential intermediate pore blocking appeared at the initial stage. It indicates that oppositely charged foulants were easily adsorbed on the membrane surface, leading to the severe pore blocking at the initial stage. The fouling at the initial stage was significantly alleviated at pH 4.7 and 10.4, at which each protein is neutralized. It means that the interaction between the neutralized protein, and charge membrane and counter protein may reduce pore blocking at the initial stage, but it promoted cake layer formation at the later stage via bridge effect, particularly at pH 4.7 where the membrane and model protein are oppositely charged.

6.3.4.2 Permeate flux pattern as a function of ionic strength

6.3.4.2.1 MWCNT membrane

Similar to the effect of pH, ionic strength also caused extremely low flux pattern in the filtering of protein mixture with MWCNT membrane. As seen in Fig 6.4(c), permeate flux of the MWCNT membrane remained at 80 LMH/bar for 12 h in the absence of NaCl. However, at the low concentration (0.001-0.01 M), flux decreased significantly to 20-27 LMH/bar, and then was recovered to that without NaCl. Such a trend in the presence of binary mixture is opposite to that of a single protein. It may be due to the charge shielding effect of NaCl ion, which probably had a negative impact on flux decline behavior. The intermolecular interaction (Lys-BSA, Lys-Lys and BSA-BSA) may contribute to protein
aggregation on the membrane surface, leading to an extremely low permeate flux behavior in the MWCNT membrane.

In mixed protein (binary) filtration at different ionic strength, complete and intermediate pore blockings appeared simultaneously dominant at the initial stage (Table 6.3). The addition of 0.001 M NaCl led to severe pore blocking and cake layer formation by reducing Lys-BSA interaction. However, the membrane fouling was reduced gradually when ionic strength increased to 0.1 M. It is probably due to the charge shielding effect of NaCl ion on the two oppositely charged proteins and the membrane surface, and it reduced the membrane-foulant interaction. Such effects may induce protein adsorption at a low concentration of NaCl and then tends to prevent deposition of binary protein particles on the membrane surface via charge shielding effect.

6.3.4.2.2 PES-UF membrane

An opposite trend was observed in the filtration of the PES-UF membrane with protein mixture solution compared with that of the MWCNT membrane. Fig 6.4(d) shows that there seemed to have a slight flux decline in the presence of 0.001 M NaCl at the initial filtration period. However, as ionic strength increased up to 0.1 M, the permeate flux increased nearly 1.5-fold (from 17 to 27 LMH/bar) as a function of ionic strength. The permeate flux with protein mixture seemed to decrease in the presence of 0.001 M NaCl, but it gradually increased as the ionic strength increased to 0.1 M. Further, severe flux decline at the initial stage was alleviated by the increase in ionic strength, corresponding to decrease in fouling potential (K_i) as a function of ionic strength. It indicates that combined effect of membrane-foulant and foulant-foulant interaction which resulting in a serious fouling at pH 7.0 was reduced by ionic strength via charge shielding effect on the foulant and the membranes. These results are in agreement with a previous study that increase in ionic strength can enhance the permeate flux by suppressing Lys-BSA interaction [11]. Further, complete and intermediate pore blockings were simultaneously dominant at the initial stage (Table 6.5).
Overall, a linear trend in permeate flux was observed as a function of ionic strength, compared to the irregularly increased flux pattern under single protein filtration test (Lys and BSA are individually added) (Fig 6.3(b) and 3(d)). With protein mixture, the charge-shielding effect seemed to contribute to the flux enhancement of the PES-UF membrane in the binary mixture filtration presumably due to the different mechanisms of negatively charged membrane.

Fig 6.4 Comparison of permeability pattern with binary mixture fouling under different pH (4.7, 7.0, 10.4) and ionic strength (NaCl 0.001, 0.01 and 0.1 M)
6.3.5 Fouling mechanisms under solution chemistry

Filtration models were used to explaining MWCNT filtration with two proteins (Lys and BSA) both at initial (~2h) and final (2-24h) stages of filtration. Overall, standard blocking and cake layer formation were found to be simultaneously dominant during MWCNTs filtration both with individual Lys and BSA solution, and protein mixture under different pHs and ionic strengths.

Based on the fouling potential estimated by these two fouling models and change of zeta potential at different pHs and ionic strengths in the MWCNT membrane and protein, fouling mechanisms can be explained by the electrostatic interaction between the proteins and the membrane surface and intermolecular interaction (Lys-Lys, BSA-BSA and Lys-BSA). The dominant organic matter removal mechanism was found to be increased electrostatic interaction between charged model compound and positively charged membrane surface [32]. Current research also reports that membrane fouling can be determined by the surface chemistry such as foulant-membrane interactions [39]. Thus, protein fouling can be explained by the pH and ionic strength influence on the electrostatic interaction between positively charged MWCNT membrane and both charged proteins (BSA and Lys).

The effects of charged proteins and solution chemistry such as pH and ionic strength on fouling mechanisms were examined by comparing coefficients from filtration model and flux decline behavior.

6.3.5.1 MWCNT membrane

a. For a same charged protein (Lys) filtration in the MWCNT membrane, the membrane fouling was found to be more influenced by intrafoulant interaction (Lys-Lys) based on the effect of increasing ionic strength on the flux decline and fouling mechanisms. For the effect of pH, at pH 4.7 the fouling alleviation was achieved due to the increased electrostatic interaction between the oppositely charged membrane surface and the foulants. At pH 10.4, Lys aggregation due to the neutralized particle reduced membrane fouling compared to at pH 7.0 thus higher flux was achieved at IEP of Lys (pH 10.4). Even
if electrostatic repulsion still exists at pH 7.0, highly hydrated Lys may decline permeate flux, resulting in severe membrane fouling.

b. For an oppositely charged protein (BSA) filtration in the MWCNT membrane, the membrane fouling was more governed by the electrostatic interaction between the membrane surface and the foulants according to the effects of pH and ionic strength. The membrane fouling was significantly alleviated at pH 4.7 and 10.4 at which the electrostatic interaction between the membrane and BSA weakened. Increasing ionic strength also reduced membrane fouling via charge shielding effect, but still higher than at different pH, demonstrating that the foulant-foulant attraction may have a less significant contribution to the membrane fouling than the membrane-fouling attraction.

c. For binary mixture filtration test in the MWCNT membrane, the foulant-foulant interaction was found to affect its fouling mechanisms dominantly. At pH 7.0 at which oppositely charged proteins are neutralized by agglomeration, fouling was alleviated. However, at pH 4.7 and 10.4, the neutralized protein deposited on the membrane surface, inducing deposition of counter charged proteins via bridging effect. Thus, severe fouling was observed. It demonstrates that foulant-foulant interaction played a major role under different pH condition. Meanwhile, NaCl addition seemed to promote binary proteins deposition on the membrane surface by reducing intermolecular reaction (Lys-BSA). However, as the ionic strength increased, the protein deposition was reduced by charge shielding effect on the foulant-foulant and membrane-foulant interactions. The fouling mechanisms of the MWCNTs membrane are illustrated in Fig 6.5.

Regarding the membrane performance recovery after fouling, it is assumed that the MWCNTs enhanced membrane after protein fouling is highly likely to get recovered by chemical cleaning that was introduced in Section 3.5, Chapter 3. The results of cleaning efficiency on HA fouling in Chapter 3 demonstrates that the 100 % of recovery on the permeate flux and rejection efficiency were achieved after proper cleaning procedure. It indicates that the membrane fouled by HA can be recovered by
chemical cleaning (0.1 M HCl and 0.1 M NaOH). Compared to MW of HA (350 Da), adsorbed Lys (14.3 kDa) and BSA (67 kDa) with much bigger MW on the membrane surface (12 kDa) could be more easily removed by chemical cleaning (0.1 M HCl and 0.1 M NaOH). It corresponds with the main fouling models in the MWCNTs membrane: protein deposition on the membrane surface by pore blocking and cake layer formation.
### Chapter 6. Protein fouling behaviour under different solution chemistry (pH and ionic strength)

<table>
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<tr>
<th>Foulant</th>
<th>Schematics</th>
<th>Fouling mechanisms</th>
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<td>- Foulant-foulant interaction</td>
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<td>(Lys-Lys)</td>
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<td><img src="image4.png" alt="Schematics" /></td>
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<td>Negatively charged protein</td>
<td><img src="image5.png" alt="Schematics" /></td>
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<td><img src="image6.png" alt="Schematics" /></td>
<td>Lys aggregation by charge shielding effect</td>
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<td><img src="image8.png" alt="Schematics" /></td>
<td>Decreased electrostatic interaction at near IEP of both membrane and foulant</td>
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### Chapter 6. Protein fouling behaviour under different solution chemistry (pH and ionic strength)

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<th>Mixed protein</th>
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<tr>
<td><img src="image1.png" alt="Diagram" /></td>
<td>Fouling mechanisms in the MWCNT membrane under different solution chemistry (a) Lys protein filtration, (b) BSA filtration and (c) Mixed protein filtration.</td>
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</table>
6.3.5.2 PES-UF membrane

a. For an oppositely charged protein (Lys) filtration in the PES-UF membrane, combined effect of membrane-foulant and foulant-foulant interactions was found to control the fouling mechanism at different pH. Particularly, at different ionic strength, membrane-foulant interaction played a major role in fouling via charge shielding effect on the protein and membrane surface. Different solution chemistry mainly affected building up the cake layer at the later stage of filtration.

b. For an oppositely charged protein (BSA) filtration in the PES-UF membrane, fouling was mainly governed by the membrane-fouling interaction at different solution chemistry. Severe pore blocking at the initial stage and cake layer formation at the later stage at pH 4.7 was alleviated at pH 7.0 and 10.4 due to the increased electrostatic repulsion. However, increase in ionic strength induced fouling due to the decreased electrostatic repulsion via charge shielding effect.

c. For binary mixture filtration test in the PES-UF membrane, combined effect of membrane-foulant and foulant-foulant interaction played an important role in fouling. Different pH affected oppositely charged foulants and membrane. It led to severe pore blocking at pH 7.0 via electrostatic interaction between the membrane and foulants. At pH 4.7, at which neutralized protein and oppositely charged protein promoted building up the cake layer at the later stage. Severe fouling was alleviated by an increase in ionic strength due to charge shielding effect. The fouling mechanisms of the PES-UF membrane are illustrated in Fig 6.6.
Chapter 6. Protein fouling behaviour under different solution chemistry (pH and ionic strength)

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<td>Positively charge protein</td>
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<td><strong>Foulant-foulant interaction</strong></td>
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<td>Increased electrostatic repulsion between BSA(-) and PES membrane (-)</td>
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<td><strong>pH 7</strong></td>
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Chapter 6. Protein fouling behaviour under different solution chemistry (pH and ionic strength)

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<td>Low fouling</td>
<td>Severe fouling</td>
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(c) Mixed protein

| Pressure | BSA | Lys | Na⁺ ion | Cl⁻ ion |
|-----------------|-----------------|-----------------|-----------------|
| 0 M | 0.001 M | 0.01 M | 0.1 M |
| Protein adsorption | Charge shielding effect | Less deposited proteins | Fouling alleviation |
| Severe fouling | | | |

Combined effect of membrane-foulant and foulant-foulant interaction

Electrostatic interaction between oppositely charged foulants and the membrane

Combined effect of membrane-foulant and foulant-foulant interaction

Decreased adsorption by the charge shielding effect on protein mixture

Fig 6.6 Fouling mechanisms in the PES membrane under different solution chemistry (a) Lys protein filtration, (b) BSA filtration and (c) Mixed protein filtration.
6.4. Conclusion

The fouling behavior of positively (Lys) and negatively charged (BSA) proteins was observed in the positively charged MWCNT membrane with high sensitivity to the pH and ionic strength of the feed solution. Overall, the MWCNT membrane with high sensitivity to the feed properties considerably affected the initial flux and fouling behaviour.

- The permeate flux of the MWCNT membrane was found to be strongly influenced by pH and ionic strength under single protein filtration test. In comparison, solution chemistry did not affect the permeate flux considerably in PES-UF membrane. Although severe flux decline behavior appeared on the MWCNT membrane at the initial stage of filtration, overall permeate flux outperformed the PES-UF membrane due to the extremely high flux of the MWCNT membrane. Further, ionic strength resulted in flux enhancement in single protein filtration with the MWCNT membrane. Meanwhile, protein mixture filtration had different permeate flux behavior in both membranes.

- For the MWCNT membrane filtration, fouling by Lys was controlled by combined effect of membrane-foulant and foulant-foulant interaction at different solution chemistry. Severe pore blocking was alleviated at pH 4.7 and increase in ionic strength, at which electrostatic interaction increased, and Lys became aggregated due to charge shielding effect. Severe pore blocking by BSA was alleviated at pH 4.7 and 10.4 where electrostatic interaction decreased, and an increase in ionic strength due to charge shielding effect. Intermolecular interaction (BSA-Lys) dominantly affected the MWCNT membrane fouling mechanism at different pHs. Meanwhile, in the presence of ionic strength, intermolecular interaction mainly controlled the membrane fouling, but as ionic strength increased, both the foulant-foulant and membrane-foulant interaction by charge shielding effect became a dominant factor in the fouling mechanism.
• For the PES-UF membrane filtration, severe pore blocking by singe proteins was dominantly controlled by the interaction with foulants. However, in a protein mixture filtration, severe cake layer formation was developed at pH, and it was alleviated by combined effect of membrane-foulant and foulant-foulant interaction.

• Severe flux decline and fouling, despite very high initial flux in the MWCNT membrane could be significantly alleviated by controlling solution pH and chemistry. It is suggested that the MWCNT membrane sensitive to pH and ionic strength can be widely applied in the wastewater reclamation.
References


Chapter 7 Conclusions

This research aimed to develop multi-walled carbon nanotube enhanced membrane with high permeability and effective natural organic matter which cannot be achieved by conventional low pressure driven membranes.

In the first part of the results (Chapter 4), optimization in membrane fabrication was conducted, and the membrane performance in natural organic matter removal was systematically examined. Further study built up finding critical factors in fast water flux and high NOM removal mechanism. Lastly, efficient cleaning method was thoroughly investigated for the purpose of overcoming flux decline due to the high removal efficiency.

- Multi-walled carbon nanotubes (MWCNTs)/polyaniline (PANI)/polyethersulfone (PES) membranes were fabricated by incorporation of in-situ polymerized MWCNTs/PANI complex for effective removal of natural organic matter (NOM) in water. The membranes exhibited up to 1400 LMH/bar of pure water permeability as MWCNTs increased to 2 wt%, which is 30 times greater than pure PES UF membrane. The NOM removal efficiency increased to 80 %, which is 4 times higher than the one of PES UF membrane.

- Based on analysis of the physical/chemical properties of the membranes, MWCNTs/PANI complex increased porosity (78→85 %) and hydrophilicity (73.5→52.9 °) as MWCNTs increased up to 2 %. Further, MWCNTs/PANI complex was revealed to tune the membrane structure to narrow pore size on the top surface and relatively large macrovoid below a well developed thinner skin layer, leading to the slippage effect. Such a superior performance in water flux is attributed to the synergetic effect of increased porosity, hydrophilicity and slippage effect.
- MWCNTs/PANI complex was found to alter the positively charged membranes. In addition, the complex formed the membrane with narrow pore size distribution. Thus, effective NOM removal was achieved mainly due to the synergetic effect of increased electrostatic interaction and enhanced size exclusion.

-The membrane demonstrated 100 % water flux recovery and 65 % total fouling ratio after cleaning with 0.1 M HCl/0.1 M NaOH solution for 1 hr, indicating that rapid flux decline can be easily overcome by the proper cleaning method.

Chapter 3 demonstrates that MWCNTs/PANI electron transfer complex successfully engineered chemical/physical properties of the membrane to have high NOM adsorption capacity and fast water flux.

In a second part of the results (Chapter 5), newly developed MWCNTs enhanced membrane was applied to SWRO pretreatment. The MWCNTs enhanced membrane outperformed conventional PES UF membrane when coupled with PAC adsorption system. Further, the impact of the ionic strength on the membrane performance was covered in depth by examining the applicability of MWCNTs membrane to alleviating RO membrane fouling in a desalination plant.

- MWCNTs membrane achieved superior permeate flux (300 LMH/bar) in seawater filtration, which was up to 4 times as PES-UF membrane. MWCNTs membranes itself reduced dissolved organic matter in seawater and required fewer amounts of adsorbent to achieve high permeate flux. The performance of MWCNTs membrane did not decline when PAC adsorbent decreased from 1.5 g/L to 0.5 g/L.
- Ionic strength such as NaCl was found to influence decreased organic removal efficiency (80 → 30 %) and nearly 2-fold enhanced permeate flux in seawater filtration by MWCNTs membrane. In the case of a divalent ion, greatly enhanced organic matter removal (90 %) was observed in the presence of 0.01 M CaCl₂, but the permeate flux rapidly declined.

In a third part of the results (chapter 6), protein fouling behavior was examined under different solution chemistry- pH, ionic strength and charge of proteins. This study would give a contribution to the extensive application of CNTs composite membrane for wastewater treatment and bioseparation for which solution chemistry such as pH, ionic strength and charge of model protein are critical factors of membrane fouling.

- PH and ionic strength affected permeate flux with positively and negatively charged proteins in the MWCNTs membrane. In contrast, permeate flux of the negatively charged PES membrane was not noticeably affected by different pH and ionic strength. MWCNTs membrane showed high permeate flux when the membrane had the same charge with the model protein.

- According to the results on the fouling mechanism, MWCNTs membrane filtration with proteins (Lys and BSA) dominated by standard blocking and cake layer formation. In comparison to previous studies on protein fouling, the MWCNTs membrane showed low protein fouling potential at IEP of the model compound due to the altering zeta potential of pH as a function of pH and ionic strength. Lys filtration resulted in more severe pore blocking and cake layer formation potential than BSA filtration due to its comparable size to the membrane pore diameter. Due to the electrostatic repulsion between the membrane surface and the model protein (Lys), the weakest fouling potential was observed at pH 4.7. The fouling potential was alleviated by increasing ionic strength most probably due to the shielding effect of the ion on the model
protein. For oppositely charged proteins filtration, membrane fouling was alleviated at IEP of proteins (pH 4.7) and pH 10.4 at which electrostatic interaction with the MWCNTs membrane lessens. Increasing ionic strength seemed to decrease fouling potential, but was found to be minor compared to the pH effect. Mixed protein filtration showed much more severe pore blocking and cake layer formation at the IEP of both BSA and Lys (4.7 and 10.4, respectively). It may be due to the bridging effect of neutralized proteins at their IEP with their counter proteins, corresponding to the high fouling potential.

Recommendation for future research:
- For the continuing research work in Chapter 3 and 4, more uniformed single wall carbon nanotube will contribute to improving the performance of mixed matrix membranes (MMMs).
- The synthesis of inorganic nanotubes is generally expensive, which will restrict their wide application in MMMS for water treatment. Thus, it is recommended that future work can be a synthesis of halloysite nanotubes (HNTs) which is naturally abundant and low cost as the filler for MMMS fabrication, and its performance evaluation.
- Tubular supported (porous polymeric and ceramic supports) carbon nanomaterials such as graphene is recommended to be a promising material for MMMS for water treatment.
ABBREVIATIONS

BSA: Bovine serum albumin
CA: Cellulose acetate
CNT: Carbon nanotube
CVD: Chemical vapor deposition
DBPs: Disinfection by-products
DCMD: Direct contact membrane distillation
DOC: Dissolved organic carbon
DOM: Dissolved organic matter
EPS: Extracellular polymeric substances
GO: Graphene oxide
HACNTs membrane: Horizontally aligned carbon nanotubes membrane
ICP: Internal concentration polarization
LC-OCD: Liquid chromatography–organic carbon detection
LMW: Low molecular weight
LMW-DOM: Low molecular weight dissolved organic matter
Chapter 7 Conclusions

Lys: Lysozyme

MD: Membrane distillation

MF: Microfiltration

MMMs: Mixed matrix membrane

MPD: m-phenylenediamine

MWCNTs: Multi-walled carbon nanotubes

NOM: Natural organic matter

NMP: N-methyl-2-pyrrolidone;

NF: Nanofiltration

NOM: Natural organic matter

PA: Polyamid

PAC: Powder activated carbon

PANI: Polyaniline

PECVD: Plasma-enhanced chemical vapor deposition

PES: Polyethersulfone

PPCPs: Pharmaceutical and personal care products

PSf: Polysulfone
Chapter 7 Conclusions

PTFE: Polytetrafluoroethylene

PVDF: Polyvinylidene fluoride

RO: Reverse osmosis

ROS: Reactive oxygen species

SA: Sodium alginate

SEC: Size exclusion chromatography

SWCNTs: Single-walled carbon nanotubes

SWOM: Seawater organic matter

SWRO: Seawater reverse osmosis

TFC: Thin film composite

UF: Ultrafiltration

UVD: Ultraviolet detector

VACNTs membrane: Vertically aligned carbon nanotube membrane