TITANIUM DIOXIDE COATED POLYETHERIMIDE PHOTOCATALYTIC NANOFIBER MEMBRANE FOR WATER TREATMENT

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy

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JANUARY 2020

ACKNOWLEDGEMENT

As I approach the completion of my MEng, it dawns on me that I could never have done this alone. I thank Allah for giving me the strength, knowledge, ability and opportunity to undertake my MEng research study and to continue and complete it satisfactorily. I also take this opportunity to thank Nanotechnology Research Center, Sultan Qaboos University that funded me and provided the most needed equipment and materials.

I would like to sincerely thank my main supervisor Assoc Prof Dr. Lau Woei Jye for his unlimited support, guidance, innovative and bright mind which have taught me valuable lessons. I'm privileged to have had the opportunity to work under his supervision. I would like to take the opportunity to express my sincere gratitude and thanks to my co-supervisor Assoc Prof Dr. Mohammed Al-Abri throughout my research work who had been great sources of encouragement, unlimited support, valuable criticism and great inspiration throughout my study. Sincere gratitude to Assoc Prof Dr. Goh Pei Sean for her co-supervision.

Special thanks to Mr. Ali Vakilinejad, Mr. Issa Al-Husaini, Dr. Mohammed Aly and Dr. Ibrahim Jumaan for their help in many of my academic issues. Sincere gratitude to Dr. Suliman Al-Obaidani for his help in mechanical tensile strength tests and to Dr. Sergey Dobrestov for his help in antibacterial activities tests. I would like to express my gratitude to Dr. Htet H Kyaw, Dr. Jamal Al-Sabahi, Dr. Maissa Souayeh and Dr. Myo Tay Zar for the valuable scientific discussion and interaction. My deep thanks to Azan Al-Khudori and Naser Al-Shukili from Nanotechnology Research Center and to all my friends, especially, Majda, Sara, Intisar, Zainab, Sumaya, Noor and many others, who put an excellent support to me during my MEng study.

Most importantly, infinite gratitude to my parents and siblings for their uncountable support and encouragement throughout my MEng study. Special thanks to my brother Ahmed and my sister Rehab for always being there when I needed them the most.

ABSTRACT

Access to clean water for human use is a growing concern across the world with the ever-increasing human population. Treatment of wastewater to produce usable water is essential to meet future clean water demand. Separation and decontamination processes using membrane technologies have been implemented worldwide. Photocatalytic membrane is an emerging technology that is capable of simultaneously separating and degrading organic pollutants (e.g., humic acid (HA) and dyes) present in aqueous solution under UV-irradiation besides microorganism disinfection. In view of this, the main objective of this work is to fabricate and characterize a new type of nanocomposite nanofiber membrane by incorporating photocatalytic nanomaterials – titanium dioxide (TiO_2) into a highly porous nanofiber made of UV-resistant polyetherimide (PEI). The nanofiber membrane was fabricated via an electrospinning method using a dope solution containing 15 wt% PEI dissolved in a mixed solvent of dimethylformamide (DMF)/n-methyl-2-pyrrolidone (NMP) with ratio of 2:8. The top surface of nanofiber membrane was further modified by coating it with different TiO_2 concentration (0.2 and 0.6 wt%) using electrospraying method. The properties of the TiO_2-modified PEI nanofiber membranes were then analysed using scanning electron microscope (SEM), water contact angle (WCA) goniometer and tensile strength machine. Results showed that 0.2 wt% TiO_2-modified PEI nanofiber displayed better behaviour by reducing WCA of unmodified nanofiber from 130.25° to 23.35° and improving water flux by 28%. Although the WCA of membrane was further reduced when a higher TiO_2 amount (0.6 wt%) was used, the resultant nanofiber suffered from decreased ultimate strength and significant nanoparticles leaching. Using the best performing 0.2 wt% TiO_2-modified PEI membrane, significant removal rate of *Escherichia coli* (99%) and humic acid (~80%) could be achieved along with 85% methylene blue degradation during photocatalytic process. The findings of this work provide an insight into the design of advanced nanocomposite nanofiber membrane for photocatalytic process.

ABSTRAK

Akses kepada bekalan air bersih menjadi isu global di seluruh dunia dengan jumlah populasi penduduk manusia yang semakin meningkat. Rawatan air kumbahan untuk menghasilkan air bersih adalah sangat penting untuk menjamin bekalan air bersih di masa akan datang. Proses pengasingan dan dekontaminasi menggunakan teknologi membran telah dilaksanakan di serata dunia. Membran fotokatalitik merupakan suatu teknologi yang sedang berkembang dan berupaya mengasingkan dan memecahkan bahan pencemar organik (contohnya, asid humik (HA) dan pewarna) yang wujud di dalam cecair selain dapat membasmi mikroorganisma yang wujud dalam cecair tersebut. Sehubungan dengan itu, objektif utama kajian ini adalah untuk menghasilkan sejenis nanokomposit nanofiber membran yang baru dengan menggabungkan bahan nano fotokatalitik – titanium dioksida (TiO_2), ke dalam nanofiber berongga, yang diperbuat daripada bahan tahan UV - polieterimida (PEI). Membran nanofiber dihasilkan daripada kaedah elektroputar dengan mencampurkan cecair yang mengandungi 15 wt% PEI bersama cecair campuran dimetilformamida (DMF)/n-metil-2-pirolidon (NMP) dengan nisbah 2:8. Permukaan membran nanofiber kemudiannya dilapiskan dengan kepekatan TiO_2 yang berbeza (0.2 dan 0.6 wt%) menggunakan kaedah elektrosemburan. Kandungan TiO_2 yang telah diubah suai ini kemudian dianalisis dengan menggunakan mikroskop pengimbas elektron (SEM), pengukur sudut sentuhan air (WCA) dan mesin pengukur tegangan. Kajian mendapati 0.2 wt% TiO_2 yang telah ditambah dengan PEI nanofiber adalah lebih baik dengan mengurangkan WCA nanofiber yang tidak diubah suai dari 130.25° ke 23.35° dan meningkatkan fluks air sehingga 28%. Walaupun WCA membran dapat dikurangkan apabila TiO_2 yang tinggi (0.6 wt%) digunakan, kekuatan dan tegangan nanofiber tersebut telah berkurang dan partikel nano telah larut. Justeru itu, dengan menggunakan 0.2% TiO_2, Escherichia coli (99%) dan asid humik (~80%) dapat disingkirkan dengan 85% degradasi metilin biru semasa proses fotokatalitik. Penemuan dan hasil daripada kajian ini dapat memberikan lebih pencerahan kepada rekabentuk membran nanokomposit nanofiber untuk proses fotokatalitik yang akan datang.

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LIST OF ABBREVIATIONS

AFM	-	Atomic force microscopy
ATR	-	Attenuated total reflectance
BSA	-	Bovine serum albumin
CA	-	Cellulose acetate
CFU	-	Colony forming units
DMAc	-	Dimethylacetamide
DMF	-	Dimethylformamide
DMSO	-	Dimethyl sulfoxide
E.coli	-	Escherichia coli
FTIR	-	Fourier transform infrared spectroscopy
MB	-	Methylene Blue
MF	-	Microfiltration
NF	-	Nanofiltration
NMP	-	N-methyl-2-pyrrolidone
NPs	-	Nanoparticles
PA	-	Polyamide
PEG	-	Polyethylene glycol
PEI	-	Polyetherimide
PES	-	Polyethersulfone
PWF	-	Pure water flux
SEM	-	Scanning electron microscope
TEM	-	Transmission electron microscope
TFC	-	Thin film composite membrane
TiO_2	-	Titanium dioxide
UF	-	Ultrafiltration
XRD	-	X-ray diffraction

LIST OF SYMBOLS

A_m	-	Effective area of the membrane
ε	-	Porosity
C_f	-	Concentration of feed
C_p	-	Concentration of permeate
C_t	-	Concentration at t time
C_0	-	Concentration at initial tie
J_v	-	Pure water flux
µL	-	Microliter
ρ_{H_2O}	-	Water density (1.00 g/cm^3)
ρ_{PEI}l	-	PEI density (1.27 g/cm^3)
θ	-	Contact angle
ΔV	-	Volume of permeate water flux
γ_{SI}	-	Liquid interfacial free energy
γ_{IV}	-	Liquid surface free energy
γ_{SV}	-	Solid surface free energy

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Fresh water scarcity is a strong issue already in an area of land affecting over one third of the world's population. This problem is expected to double by 2050, and the overuse of natural freshwater resources in many countries is already showing signs of reaching unsustainable levels. This issue has been further complicated by rapid population growth and industrialization that demand large volumes of clean water resources. According to the World Health Organization (WHO) and the United Nations International Children's Emergency Fund (UNICEF), 2.1 billion population lack access to safe, readily available water at home (Program, 2014).

The presence of some organic contaminants in water like humic substances can easily react with some types of disinfectants products like chlorine to form disinfection by-products (DBP) such as trihalomethanes (THMs) and haloacetic acid (HAAs) which are the most prevalent DBP. The concentration and formation of those DBPs is strongly dependant on raw water characterization, residual chlorine available in the water distribution system and an operational parameter (Zhou *et al.*, 2014). Moreover, organic dyes like Methylene blue (MB), Methylene orange (MO) and Rhodamine B (RHB) (Zangeneh *et al.*, 2015) are commonly found in wastewater, and they are considered to have significant environmental impacts owing to their toxicity to living aquatic organisms (Akpan and Hameed, 2009).

In addition to organic contaminants, waterborne pathogenic microorganisms like *Escherichia coli (E.coli)* bacteria are widely spread in wastewater which causes many diseases to humans (Alrousan *et al.*, 2009). However, the conventional wastewater treatment plants are not designed to remove emerging and related contaminants as there is no single technology that is suitable for removing all contaminants. Additionally, Many of these compounds occur at different concentrations in natural water bodies (Arrubla *et al.*, 2016; Gupta *et al.*, 2016).

Membrane technologies are a reliable technology and have been used for more than 50 years for water filtration. Membrane separation process is used for both pre and post water treatments. It also has a wide range of industrial (Cartwright, 2010), medical (Baker and Staff, 2000) and environmental applications (Khin *et al.*, 2012). The separation process-based membrane technology is mainly dependent on the pore size of the fabricated membranes. According to the pore size, membranes can be classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes as shown in Figure 1.1 (Khin *et al.*, 2012; Baker and Staff, 2000). MF and UF membrane processes are based on size exclusion of the molecules. MF is used for the removal of submicron suspended materials which have molecular size in the range 0.01-1 μm including bacteria, algae and sediments in water pre-treatment applications. UF membranes have pore size ranges of 10-100 nm for the removal of dissolved organic matter, pathogens like viruses and proteins (Baker and Staff, 2000).

Generally, the commercial membranes are classified as polymeric membranes and inorganic membranes. However, the polymeric membranes like polysulfone (PSF), polyvinylidene fluoride (PVDF) (Lee *et al.*, 2016), polyvinylpyrrolidone (PVP) (Horikoshi *et al.*, 2001), polyvinyl chloride (PVC) (Gesenhues, 2000), polybenzimidazole (PBI) (Kushwaha *et al.*, 2014c) and polycarbonate (PC) (Geretovszky *et al.*, 2002) are esteemed in water treatment plants. The key advantage of polymeric membranes is their high selectivity for water components at different sizes during the separation process, which depends on the method of fabrication (Lalia *et al.*, 2013; Ray *et al.*, 2016). Polymeric membranes are widely used as pre-treatment in water filtration as they have unique characteristics like thermal stability, heat resistant and high pH resistance compared to other commonly used membranes in filtration application (Frenot and Chronakis, 2003; Ray *et al.*, 2016). They have the advantages of low cost fabrication and salt rejection properties compared to inorganic membranes (Buonomenna and Golemme, 2012). Polyetherimide (PEI) polymer is possesses unique properties such as excellent thermal stability, chemical resistance to a wide range of pH and excellent mechanical strength (Wang *et al.*, 2016). It is mainly related to the strong chemical bonds and surface chemistry of PEI structure as it has bonds with high dissociation energy.

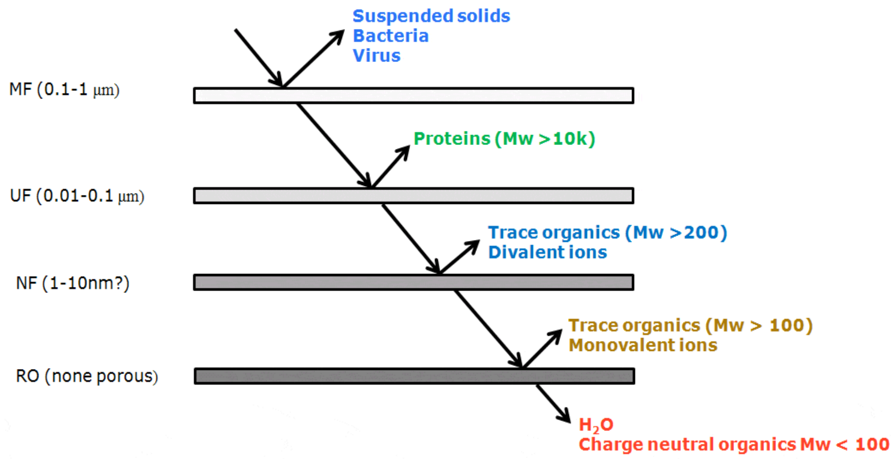

Figure 1.1 The particles rejected by membrane as a function of pore size (Yoon 2006)

Different membrane fabrication methods have been reported in the literature including phase inversion, powder sintering, interfacial polymerization, film etching and stretching and electrospinning. These methods depend mainly on the polymer, structure or configuration of the membrane and application (Barth *et al.*, 2000). However, there is an emerging interest towards using nanofibers membrane largely due to its high surface area, high porosity and tunable surface chemistry.

Electrospinner overperformed other fabrication methods, as it a simple technique that applies electrostatic force to form nanofibers in nanometer size as several studies have mentioned that the average diameter of electrospun nanonanofibers ranges from 100 nm to 500 nm (Ray *et al.*, 2016) and so nanofibers are consider to be microfiltration membranes. This technique has been extensively explored as the best and most simple method to prepare nanofibers from polymer solutions or melts with advanced applications in filtration, barrier membranes for energy storage and engineered tissue scaffold (Ma *et al.*, 2009). Nanofiber membranes outclass other membranes because of the ease of production and cost-effectiveness, besides its simple setup.

Biofouling is the attachment and growth of microbial organisms, such as bacteria (Mohammad and Amin, 2013; Nguyen *et al.*, 2012). This process may result in pore blocking, adsorption of hydrophobic particles and nonpolar solutes, gel layer formation and cake layer formation. In addition, scaling occurs when dissolved metal salts in the feed water precipitate on the membrane due to the increase of salt concentration exceeding the solubility limit. These obstacles lead to decline in rejection and net water flux. Therefore, the consequence of these problems is the short lifetime of the membrane and eventual replacement (Nguyen *et al.*, 2012).

Introduction of photocatalysis process can overcome this obstacle as it is based on the use of semiconductor metal oxides with a large band gap. These include zinc oxide (ZnO), titanium dioxide (TiO_2), iron (III) oxide (α-Fe_2O_3) and zinc sulfide (ZnS). They were incorporated to enhance physical and chemical properties of the membranes. The nanomaterials can be defined as materials with at least one dimension in the nano-scale (1-100 nm) with defined structure. Compared to the chlorination and ozonation process, photocatalysis is a promising method for the removal of organic pollutants in water, and it is cost effective because its sustainable source is sunlight (Zhang *et al.*, 2014a; Herrmann, 2005). Generally, there is an emerging interest toward the modification of the surface of membranes to ensure a good rejection of low weight solutes by pore size control and surface charge.

The special characteristic of nanomaterials is that they exhibit a high surface area-to-volume ratio compared to bulk materials, which enhances the catalytic activity at nanoscale levels (Binns, 2010). In general, metal oxides is consist of either binary, ternary or quaternary compounds. Binary oxides are often wide band gap semiconductors that generate electron-hole pairs upon exposure to light irradiation (UV or visible light). The photo-generated e^- - h^+ pair then produces highly reactive oxidizing species (ROS) such as superoxide anions ($O_2^{-\cdot}$)and hydroxyl radicals ($OH^{\cdot}$) in water.

1.2 Problem Statement

Photocatalytic membrane is an emerging technology that is capable of simultaneously separating and degrading organic pollutants present in the aqueous solution under UV irradiation (Ong *et al.*, 2015). The presence of organic contaminants in water sources such as humic substances can easily react with disinfectant products like chlorine to form harmful DBPs, e.g., HAAs and THMs (Aseri *et al.*, 2019). Moreover, waterborne pathogenic microorganisms like *E.coli* bacteria are widely spread and cannot be fully removed by filtration process using MF membranes only (Al-Ghafri *et al.*, 2018).

For the conventional membrane technology (e.g., NF and UF), its performance is negatively affected by fouling due to pore blockage, adsorption, cake layer formation and scaling. Moreover, biofouling caused by microorganisms is another main concern of conventional membrane applications (Mohammad and Amin, 2013). The consequences of these problems are a decline in net water flux and reduced membrane life span, leading to higher operating and maintenance costs (Singh, 2014).

Although polymeric membranes are widely used in water/wastewater treatment plants to separate unwanted solutes/pollutants, these kinds of membranes are not suitable to be used as photocatalytic membrane process. This is mainly because there exist no catalysts within the membrane matrix. Furthermore, the polymeric materials used to manufacture commercial polymeric membranes are not UV-resistant and are very likely to suffer from severe degradation under UV light illumination, owing to the breakage of chemical bonds of polymeric materials such as methine, C-S and C-O groups (Kushwaha *et al.*, 2014b; Rupiasih *et al.*, 2013).

In addition to the surface chemistry changes, alternation on the membrane microstructure and morphology upon UV light illumination could also take place which reduces membrane separation efficiency. Many studies have reported that the membranes made of polysulfone (PSF), polyvinylidene fluoride (PVDF) (Lee *et al.*, 2016), polyvinylpyrrolidone (PVP) (Horikoshi *et al.*, 2001), polyvinyl chloride (PVC) (Gesenhues, 2000), polybenzimidazole (PBI) (Kushwaha *et al.*, 2014c) and polycarbonate (PC) (Geretovszky *et al.*, 2002) suffered from severe degradation upon UV light exposure. Therefore, there is a need to consider using UV-resistant polymers like PEI for the fabrication of photocatalytic membranes. Besides being UV-resistant, PEI also shows unique properties such as good thermal stability, excellent chemical resistance to a wide range of pH, and excellent mechanical strength (Wang *et al.*, 2016).

Modification processes of the polymeric membrane has emerging interest toward reducing fouling affinity of the membranes and controlling the pore sizes. Nanoparticles-blended membrane is famous way in membrane modifications, however, Rahimpour et al. studied the effect this way on photo-sensitisation efficiency and found that blending reduced efficiency due to the entrapment of NPs in random positions in the membrane shielded UV light penetration (Rahimpour *et al.*, 2008). Therefore, coated method used in this work to overcome the drawback of the blended way.

A literature search revealed that titanium dioxide (TiO_2) is perhaps the most commonly reported photocatalyst, owing to its low price and commercial availability (Thiruvenkatachari *et al.*, 2008). It acts as a semiconductor in water purification due to its high stability, nontoxic nature and high oxidizing potential (Nakamura *et al.*, 2004). It requires energy from UV light to excite electrons to produce hydroxyl radicals, which are the key to the photodegradation of organic pollutants (Noothongkaew *et al.*, 2017a).

Based on a thorough survey of literature, the photocatalytic behaviour of TiO_2/PEI nanofibers has not been reported yet. This work addresses this issue and probes the formation of TiO_2/PEI nanocomposite nanofibers. TiO_2/PEI nanofibers are prepared by using Nanospinner, and their performance will be evaluated with respect to photocatalytic activity against HA and MB dye, in addition to *E. coli* disinfection.

1.3 Research Objectives

In order to address the aforementioned problems, the main objectives of this work are:

1. To investigate the establishment of nanocomposite nanofiber membranes by incorporating PEI membranes with mixed solvents at different concentration of TiO_2 nanoparticles (NPs).
2. To study the effect of TiO_2 nanoparticles on PEI membranes surface, morphology, and chemical properties, aiming to enhance the membrane properties as well as performance.
3. To investigate the performances of TiO_2/PEI nanocomposite nanofiber membranes in degrading organic pollutant removal (MB and HA) and bacterial disinfection under UV irradiation.

1.4 Scope of Work

The performances of the resulting PEI ENMs incorporated with TiO_2 are characterized with respect to water flux, contaminants rejection, bacteria removal and water flux recovery, in addition to the instrumental characterizations using an optical contact angle measuring instrument (WCA), Scanning Electron Microscopy (SEM), Energy-dispersive spectroscopy (EDS) and Fourier Transform Infrared (FTIR).

1. Fabricating PEI nanocomposite nanofiber membrane
   (a) Dissolving 10-20 wt% PEI polymer in a mixture of DMF/NMP solvents with different ratio (3:7, 2:8 and 1:9).
   (b) Optimizing the electrospinner parameters during fabrication process of nanocomposite ENMs by varying applied voltage (19.7-23.5 kV kV),

flow rate (0.8-1.2 mL/h), spinning distance (130-145 cm) and rotation speed of the drum (220 rpm) at fixed humidity (60 RH%).

2. Fabricating TiO_2/PEI nanocomposite nanofiber membrane

a) Dissolving TiO_2 NPs in a mixture of NMP:DMF at 8:2 weight ratio.

b) Coating the PEI nanonanofibers with different percentages of TiO_2 NPs (0.2 and 0.6 wt%) via electrospinner instrument under optimal spraying parameters. Spraying process was lasted for 6 h with a flow rate set at 0.4 mL/h. Other electrospinning conditions remained the same as for PEI nanofiber fabrication, with a fixed voltage at 18.2 kV.

3. Characterizing PEI and TiO_2/PEI nanocomposite nanofiber membrane.

(a) Characterizing TiO_2/PEI ENMs by SEM, EDS, FTIR and WCA

(b) Measuring the pure water flux (MF), HA flux and bacteria media flux using dead-end cell.

4. Investigating the performance of TiO_2/PEI nanofibers

(a) Evaluating the performance of TiO_2/PEI using dead-end cell mode at operated pressure < 0.5 bar in terms of water flux and flux recovery.

(b) Studying the decontamination of organic pollution for 3 h using 10 µM MB as model of contaminant and applying UVA (365 nm) as a source of light illumination.

(c) Studying the decontamination and rejection of HA (50 ppm).

(d) Analysing the permeate samples of the fabricated membrane using UV-vis spectrophotometer.

(e) Investigating the inhabitation growth of *E.coli* bacteria by calculating the colony forming unit (CFU) and antifouling properties.

(f) Studying the surface chemistry and degradation of the used membranes using FTIR

1.5 Significance of Research

In this study, a new approach of photocatalysis-based membrane was established using newly developed TiO_2/PEI nanofiber membrane. No work has been done on photocatalysis-based membrane using PEI electrospun nanofibers and UV as a source for photons. Although membrane fouling tendency remains a major problem in polymeric membranes, photocatalysis process is potentially viable for solving critical environmental problems and it is often used for water treatment.

There is a need to consider using UV-resistant polymers for the fabrication of photocatalytic membranes. One of the UV-resistant polymers that could be considered is PEI. The PEI polymeric electrospun nanofibers have attracted a great deal of attention by their special features and characteristics such as thermal stability, chemical and physical inertia, good mechanical strength and UV-resistance behaviour which has been used in a variety of applications

Besides separating pollutants based on sieving mechanism, the nanofiber membrane developed in this work also act as host for the TiO_2 photocatalysts to distribute. TiO_2 overperform other nanoparticles such as ZnO in photocatalysis performance under UV light illumination because the photocatalytic activity of ZnO is lower due to photocorrosion which frequently occurs with the illumination of UV light (Zaghlool, 2011). A literature search revealed that TiO_2 is perhaps the most commonly reported photocatalyst owing to its low price and commercial availability (Awazu *et al.*, 2008; Thiruvenkatachari *et al.*, 2008).

Another new approach in this research is coating the PEI nanofiber surface with TiO_2 via electrospinner to solve the conventional blending problems that affect the efficiency of photocatalysis process. This approach could offer higher porosity and provide better water flux stability due to better hydrophilicity (Qiu *et al.*, 2005). Moreover, the recent problems of the conventical methods of disinfection of bacteria can also be solved using the photocatalytic-based membrane technology. Hence, the membrane developed in this study not only remove the bacteria but also kill it by attacking cellular DNA of bacteria and make then disable (Sosnin *et al.*, 2004). This

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