

**IMPREGNATION OF MWCNT/ZnO DUAL NANOFILLER  
MIXED MATRIX MEMBRANE**

**PANG WEN YU**

**UNIVERSITI SAINS MALAYSIA**

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**IMPREGNATION OF MWCNT/ZnO DUAL NANOFILLER  
MIXED MATRIX MEMBRANE**

**by**

**PANG WEN YU**

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## LIST OF ABBREVIATIONS

|               |   |
|---------------|---|
| AA            | Acrylic acid                            |
| AFM           | Atomic force microscopy                 |
| BSA           | Bovine serum albumin                    |
| CA            | Cellulose acetate                       |
| CAP           | Cellulose phthalate                     |
| CFU           | Colony forming unit                     |
| CNT           | Carbon nanotube                         |
| DBP           | Disinfectant by products                |
| DI            | Deionized                               |
| DMAc          | Dimethylacetamide                       |
| <i>E.coli</i> | <i>Escherichia coli</i>                 |
| EDS           | Energy dispersive X-ray spectroscopy    |
| EPA           | Environment Protection Agency           |
| EPS           | Extracellular polymeric substances      |
| FA            | Fulvic acid                             |
| FCNT          | Functionalized carbon nanotube          |
| FRR           | Flux recovery ratio                     |
| FS            | Flat sheet                              |
| FTIR          | Fourier transform infrared spectroscopy |
| GO            | Graphene oxide                          |
| HA            | Humic acid                              |
| HF            | Hollow fiber                            |
| HMO           | Hydrous manganese oxide                 |

|             |   |
|-------------|---|
| HS          | Humic substance   |
| ID          | Inner diameter  |
| MBR         | Membrane bioreactor   |
| MCL         | Minimum contaminant limit   |
| MEA         | Malt extract agar   |
| MF          | Microfiltration   |
| MM          | Mixed matrix  |
| MMA-AA-VP   | Poly (methyl methacrylate–acrylic acid–vinyl pyrrolidone)         |
| MMM         | Mixed matrix membrane   |
| MW          | Molecular weight  |
| MWCNT       | Multiwalled carbon nanotube                                       |
| NF          | Nanofiltration  |
| NIPS        | Non-solvent induced phase separation                              |
| NOM         | Natural organic matter  |
| NP          | nanoparticles   |
| OD          | Outer diameter  |
| PAN         | Polyacrylonitrile   |
| PANI        | Polyaniline   |
| PDMAEMA     | Poly(N,N–dimethylamino-2-ethyl methacrylate)                      |
| PEG         | Polyethylene glycol   |
| PEO         | Poly(ethylene oxide)  |
| PES         | Polyethersulfone  |
| PES-b-PHEMA | Polyethersulfone- <i>block</i> -poly(2-hydroxyethyl methacrylate) |
| PP          | Polypropylene   |
| PPO         | Poly(propylene oxide)   |

|               |  |
|---------------|--|
| PS-b-PAA      | Polystyrene-block poly(acrylic acid)                             |
| PS-b-PEG      | Amphiphilic copolymer comb of PEG and polystyrene                |
| PSf           | Polysulfone  |
| PVC           | Polyvinyl chloride   |
| PVDF          | Polyninylvinylidene fluoride                                     |
| PVP-b-PMMA-b- | Poly(vinyl pyrrolidone)-b-poly(methyl methacrylate)-b-poly(vinyl |
| PVP           | pyrrolidone)   |
| PWF           | Pure water flux  |
| RAFT          | Reversible addition-fragmentation chain transfer                 |
| RFR           | Relative flux reduction  |
| rGO           | Reduced graphene oxide   |
| RO            | Reverse osmosis  |
| SA            | Sodium alginate  |
| SEM           | Scanning electron microscope                                     |
| SPC           | Soybean phosphatidylcholine                                      |
| SPES          | Sulfonated polyethersulfone                                      |
| TEM           | Transmission electron microscope                                 |
| TGA           | Thermagravimetric analysis                                       |
| THM           | Trihalomethanes  |
| TMP           | Transmembrane pressure   |
| UF            | Ultrafiltration  |
| UV            | Ultraviolet  |
| VIPS          | Vapor induced phase separation                                   |

## LIST OF SYMBOLS

|           |   |                         |
|-----------|---|-------------------------|
| $A_m$     | Membrane effective area   | $\text{cm}^2$           |
| $C_f$     | Feed HA concentration   | $\text{mg/L}$           |
| $C_p$     | Permeate HA concentration   | $\text{mg/L}$           |
| $d_p$     | Polymer density   | $\text{g/cm}^3$         |
| $I_D$     | Intensity of D band   | -                       |
| $I_R$     | Intensity of G band   | -                       |
| $J_{HA}$  | Humic acid permeate flux  | $\text{L/m}^2.\text{h}$ |
| $J_{WF}$  | Pure water flux   | $\text{L/m}^2.\text{h}$ |
| $J_{WF2}$ | Final water flux  | $\text{L/m}^2.\text{h}$ |
| $R$       | Ratio of intensities for D and G band                                     | -                       |
| $R_a$     | Mean roughness  | $\text{nm}$             |
| $R_f$     | Total fouling resistance  | $\text{m}^{-1}$         |
| $R_{ir}$  | Irreversible fouling resistance   | $\text{m}^{-1}$         |
| $R_m$     | Membrane resistance   | $\text{m}^{-1}$         |
| $R_q$     | Root mean square roughness  | $\text{nm}$             |
| $R_r$     | Reversible fouling resistance   | $\text{m}^{-1}$         |
| $R_t$     | Total fouling resistance  | $\text{m}^{-1}$         |
| $R_z$     | Average difference in the height between the highest and the lowest point | $\text{nm}$             |
| $t$       | Filtration time   | $\text{h}$              |
| $T_d$     | Decomposition temperature   | -                       |
| $V$       | Collected permeated volume  | $\text{L}$              |
| $W_d$     | Dry membrane weight   | $\text{g}$              |

|            |                        |    |
|------------|------------------------|----|
| $W_w$      | Wet membrane weight    | g  |
| $\Delta P$ | Transmembrane pressure | Pa |

#### GREEK LETTERS

|               |           |      |
|---------------|-----------|------|
| $\mu$         | Viscosity | Pa.s |
| $\varepsilon$ | Porosity  | %    |

#### SUBSCRIPT

|      |               |
|------|---------------|
| $d$  | Decomposition |
| $f$  | Fouling       |
| $ir$ | Irreversible  |
| $m$  | Membrane      |
| $r$  | Reversible    |
| $t$  | Total         |

# **IMPREGNASI DWI PENGISI NANO MWCNT/ZnO MEMBRAN MATRIKS BERCAMPUR**

## **ABSTRAK**

Penapisan membran untuk penyingkiran asid humik merupakan cabaran dari segi penyumbatan membran yang berlaku melalui penyumbatan zarah asid humik dan bakteria yang terdapat dalam aliran suapan pada membran. Membran berpengisi tunggal mengalami masalah untuk mencapai sifat antisumbat dan antibakteria pada masa yang sama. Oleh itu, membran polietersulfona (PES) dwi pengisi dihasilkan melalui proses pemisahan fasa dengan mencampurkan zarah nano zink oksida (ZnO) dan tiub karbon nano dinding berlapis (MWCNT) pada pelbagai nisbah ke dalam larutan dop PES. Sebelum dicampurkan, MWCNT difungsikan (FCNT) dengan menggunakan asid nitric bagi menghasilkan kumpulan berfungsi hidrofilik hidroksil dan karboksilik pada permukaan tiub. Oleh itu, kedua-dua pengisi nano tersebut digunakan untuk menghasilkan membran bersifat antisumbat dan antibakteria yang baik. Kesan sinergi kedua-dua pengisi nano akan dicirikan dari segi kelikatan larutan dop, morfologi, kekasaran permukaan, size liang membran dan keliangan membran, kehidrofilikan, kestabilan haba serta prestasi penapisan. Dapatan penyelidikan menunjukkan bahawa membran yang mengandungi dwi pengisi adalah lebih berliang berbanding dengan membran berpengisi tunggal dan membran PES yang tidak berpengisi. Di samping itu, peningkatan nisbah FCNT telah menyebabkan peningkatan kehidrofilikan membran. Penambahan kedua-dua pengisi nano didapati meningkatkan kelikatan larutan dop dan mengurangkan kekasaran permukaan membran. Fluks resapan meningkat dengan peningkatan nisbah FCNT. Apabila pengisi nano pada membran didominasi oleh FCNT (nisbah melebihi 0.5), penolakan asid humik (HA)



tidak terjejas walaupun keluasan liang membran meningkat. Dapatan juga menunjukkan bahawa tanpa tindakbalas fotobermangkin, fungsi antibakteria disumbangkan oleh ZnO adalah dengan fungsi antirekatan dan bukannya perencetan bakteria. Dari semua membran yang dihasilkan, FZ3 dengan nisbah FCNT dan ZnO yang sama dapat mencapai prestasi optima dengan fluks air tulen sebanyak 89.66 L/m<sup>2</sup>.h dan penolakan HA sebanyak 93.21%. Berpandukan pada perintang kotoran dan kurang pelekatan bakteria pada permukaan membran, FZ3 merupakan membran dwi pengisi bersifat antisumbat dan antibakteria yang terbaik.

# **IMPREGNATION OF MWCNT/ZnO DUAL NANOFILLER MIXED MATRIX MEMBRANE**

## **ABSTRACT**

Membrane filtration for humic acid removal faced challenges in term of fouling caused by solute itself and the bacteria found in the feed stream. There were a lot of studies showed great antifouling and antibacterial properties at the same time. Hence, dual nanofiller polyethersulfone (PES) membrane was synthesized via phase inversion method by blending different ratio zinc oxide (ZnO) and multiwalled carbon nanotube (MWCNT) into PES dope solution. Prior blending, MWCNT was functionalized using nitric acid to form hydrophilic hydroxyl and carboxylic group on the tube surface for dispersion. The combination of both MWCNT and ZnO was able to produce combined effect improved antifouling and antibacterial synergistic effect that does not require additional reaction or interaction between them. The synergistic effect of both nanofiller on the membrane properties was characterized in term of dope solution viscosity, morphology, surface roughness, membrane pore size and porosity, hydrophilicity, thermal stability and filtration performance. The results reveal that the membrane containing dual nanofiller was porous compared to single filler membrane and neat PES membrane. Furthermore, the increase of FCNT ratio caused the membrane hydrophilicity increased. The addition of both nanofiller was found to increase the dope solution viscosity and reduced the surface roughness of the membrane. As FCNT ratio in the membrane increased, higher permeate flux was recorded. When the nanofiller of the membrane was dominated by FCNT (i.e., ratio

more than 0.5), the humic acid (HA) rejection was not affected much even though pore size of the membrane was increased. It was also been found that without photocatalytic reaction, the antibacterial properties contributed by ZnO was antiadhesion effect rather than inhibition of the bacteria. Out of all the fabricated membranes, FZ3 (dual nanofiller membrane produced with 1wt% of equal ratio functionalized MWCNT and ZnO mixture) was able to achieve optimum performance with pure water flux of 89.66 L/m<sup>2</sup>.h and HA rejection of 93.21%. Judging from its lower fouling resistance and less bacterial adhesion onto the membrane surface, FZ3 was the most antifouling and antibacterial dual nanofiller membrane.

## **CHAPTER ONE**

### **INTRODUCTION**

This chapter begins with some brief introduction on membrane technology in water treatment. Then, it was followed with surface discussion about mixed matrix membrane (MMM) and their role in improving the antifouling and antibacterial properties of the membrane. Finally, the chapter is wrapped up with the problem statement, objectives and thesis organization of this research project.

#### **1.1. Removal of humic acid from water source**

Humic acid (HA) is an ancient soil-derived substance aged 50-100,000 years old that originated from vegetation in freshwater lakes or edge of marine environments as well as other water source (Laub, 2012). It been proven to be beneficial for plant growth and only caused colour problem. However, the present of it in conventional treatment processes especially chlorination can induce the formation of carcinogenic disinfectant by-product (Cowman and Singer, 1996). Therefore, humic substances were limited to value of 2.5 mg/L in drinking water according to standard STN 757111 (Barlokova and Ilavsky, 2012). Various method such as coagulation (Sudoh et al., 2015), electromagnetic treatment (Ghernaout et al., 2010), flotation (Zouboulis et al., 2003) and oxidation processes (Matilainen and Sillanpää, 2010) been employed to remove humic acid prior chlorination process. However, these methods are prone to electrode fouling, required higher operating cost and energy input (Teow et al., 2017b). This situation has led researchers to select membrane technology as the more

favourable separation method for humic acid due to its relatively simple operation with lower cost and high efficiency. However, the major concern surrounding the usage of UF membrane for HA removal was the fouling of the membrane due to HA deposition and adsorption. Since, the HA removal is done prior to chlorination or the disinfection step, biofouling can also be another source of membrane fouling. Looking into this situation, extensive researches have been carried out by researchers to improve the membrane resistance both toward HA and bacteria to make the application of UF membrane for HA feasible in future.

To improve the membrane properties, filler integration into membrane has been the preference and various researches. In this perspective, the selection of filler could be a key point to decide the membrane behaviour based on the intended separation performance. This was because different nanofiller inherited different properties and can interact differently with membrane base material. As stated Mari et al. (2017), the selection of fillers was the main challenges that decide the performance and separation characteristic of the membrane. Furthermore, integration of these filler into membrane often limited by their agglomeration due to their large surface area/particle size ratio. Agglomeration of filler could potentially degrade the membrane performance and separation efficiency (Ursino et al., 2018). Therefore, in recent researches, researches start to pay more attention on filler dispersion rather than filler selection since most filler has been well studied.

## **1.2. Problem statement**

With increasing demand toward portable water, membrane technology emerges as versatile method to recover water from various sources. Polymeric UF

membrane is commonly made of polymer such as polyethersulfone (PES), polyvinylidene fluoride (PVDF) and polysulfone (PSf). Out of these, PES is one of the most popular polymers used for UF water treatment membrane researches. The reason being is due to their excellent thermal and mechanical properties and lower swelling tendency compared to other hydrophilic polymers. However, this anti-swelling property that come with the hydrophobicity of PES can be a major cause that made PES prone for the fouling by hydrophobic solute such as humic acid (HA). Besides solute fouling, biofouling due to attachment of bacterial onto the membrane surface can also be another major concern for membrane separation especially in case of separation of HA, since UF is done prior disinfection/chlorination step which bacterial can potentially found in the feed water. Such fouling can greatly reduce the membrane performance and reduce the membrane flux along time. Thus, reduce the lifespan of the membrane and its reusability. Moreover, as fouling occur along the time, pumping cost can also increase too. Both of this indirectly increase the membrane unit operating cost. To mitigate the problem, extensive researches been done to reduce the fouling tendency of the membrane as well as improve the antibacterial properties of the membrane. One of the most used method is the blending of nanoparticles into polymeric membrane to form composite or mixed matrix membrane (MMM).

Out of the all polymeric material, PES is one of the most popular polymers for ultrafiltration membrane study. This is due to their low commercial prize, outstanding oxidative, thermal, hydrolytic stability and good mechanical property (Zhao et al., 2013a). These properties are granted due to the present of aromatic compound which able to restrain the chain mobility (Bowen et al., 2001, Mockel et al., 1999). Despite all these advantages, the major problem of the PES membrane is due to its high hydrophobicity (Rahimpour and Madaeni, 2010)

As far as the author aware, most of the mixed matrix PES membrane produced only focused on the study of antifouling properties by model solute such as HA and bovine serum albumin (BSA) (Saraswathi et al., 2018, Teow et al., 2017a, Lavanya et al., 2019). Yet, there are fewer study of UF membrane that focus on the antibacterial properties of the membrane. One of the method was utilize silver as the nanofiller in the MMM as Ag was a bactericide nanoparticles which also able to improve the membrane surface hydrophilicity (Sawada et al., 2012). However, concern raise on its toxicity when leaching occur (Fewtrell, 2014). Hence, researchers move on to utilization of ZnO nanoparticles for antibacterial study (Chung et al., 2017). Yet, ZnO mixed matrix membrane could suffer from flux reduction if used at higher ZnO loading due to pore plugging (Ahmad et al., 2015). MWCNT also another particle that able to inhibit bacterial growth (Lohan et al., 2016), but blending MWCNT into membrane required it to be functionalized first for better dispersion (Daramola et al., 2017). Unfortunately, MWCNT will lost it bactericide activity once being functionalized (Arias and Yang, 2009). MWCNT blending into the membrane could be challenging method as raw MWCNT tend to agglomerate and hence, blending of functionalized MWCNT was done to improve it dispersion. To date, there are various methods used to functionalize MWCNT. Depending on the reaction involved, the properties functionalized carbon nanotube can be different Great oxidized surface always involves aggressive reaction condition and this always associated with serious damage toward the tube structure or rupture of carbon nanotube wall. Thus, affecting the performance of functionalize MWCNT in the membrane. Hence, functionalized MWCNT should be carefully characterized prior blending into membrane.

Currently, most of the research being done to produce mixed matrix membrane was through blending only one type of nanoparticles into the membrane

matrix. Only few papers focused to study the synergism and the membrane properties of mixed matrix membrane produced by blending two types of nanofillers. Looking into this situation, in this work, mixed matrix membrane was prepared by blending well dispersed oxidized MWCNT that can improve/maintain the membrane flux and hydrophilicity with the hydrophilic ZnO with antibacterial properties into PES membrane, producing PES membrane with both antifouling and antibacterial properties for separation of HA in long run. The combined properties contributed by both ZnO and functionalized MWCNT grant synergistic effect toward the membrane. The synergistic effect contribute by the intrinsic properties of both nanofiller membrane can be varies based on their mixture ratio as studied by Esfahani et al. (2015). The variation of this properties in turn can effectively affected the separation performance as well as the antifouling properties and antibacterial properties of the membrane. Therefore, in this study dual nanofiller membrane was done by blending different ratio of nanofiller into the membrane at the same time maintaining the overall nanofiller content in the membrane.

### **1.3. Research objectives**

The objectives of this research are:-

1. To study the characteristics of functionalized carbon nanotubes for membrane fabrication.
2. To fabricate and characterize dual nanofiller mixed matrix membrane with different ratio of MWCNT and ZnO.
3. To investigate the performance, antifouling and antibacterial behaviour of the fabricated dual nanofiller mixed matrix membrane toward HA separation.