

# Fabrication of Dual Layer Hollow Fibre Membranes for Photocatalytic Degradation of Organic Pollutants

Hazlini Dzinun, Mohd Hafiz Dzarfan Othman, A. F. Ismail, Mohd Hafiz Puteh, Mukhlis A. Rahman, and Juhana Jaafar

**Abstract**—In recent years, the membrane photocatalytic reactor (MPR) systems have attracted much attention due to their promising function in treating organic pollutant and filtering clean water. Suspended photocatalyst titanium dioxide (TiO<sub>2</sub>) particle always become a problematic in hybrid MPR system due to membrane fouling and TiO<sub>2</sub> loss. In the past few years, considerable attention has been paid to immobilize TiO<sub>2</sub> nanoparticles on various materials. Since ultraviolet (UV) source and TiO<sub>2</sub> are required for the photocatalytic reaction, thus, it is crucial to immobilize high concentration of TiO<sub>2</sub> on the outer surface of the polymeric membrane support. By using co-extrusion approach, a dual layer hollow fibre (DLHF) membrane was fabricated. The effect of additives on the dope polymer solutions and membrane morphologies of DLHF were investigated using of scanning electron microscopy (SEM). The SEM results showed that DLHF membranes have a good adhesion between layers with no delamination.

**Index Terms**—Dual-layer hollow fibre membrane, co-extrusion, photocatalytic degradation, Titanium dioxide.

## I. INTRODUCTION

Several studies have showed difficulties in degrading some organic pollutants in wastewater using conventional biodegradation technique [1]. Fortunately, the degradation and mineralization of the pollutant are possible to be achieved by the application of advanced technologies such as photocatalytic oxidation [2], [3]. Photocatalysis, based on the generation of hydroxyl radicals (OH) is considered as a promising approach for removal of organic pollutants. Organic pollutants can be degraded up to 90% under operation by using suspended catalyst which commonly is titanium dioxide (TiO<sub>2</sub>) nanoparticles due to its remarkable charge transport property and superior oxidation ability [4]. Unfortunately, the suspended catalyst reactor needs the additional process in order to separate catalyst from the treated water after the degradation. A number of researchers have suggested photocatalyst immobilization onto a suitable solid support. Even though this approach would eliminate the

need of post-treatment process, but it would reduce the surface area available for photocatalytic reaction [5], [6]. Most of studies reported the same results which was the suspended catalyst give better degradation than catalyst deposited on the membrane [7]–[9]. Some other inherent problems create by immobilization of the photocatalyst are potential loss of TiO<sub>2</sub> and decreased adsorption of organic substances on the TiO<sub>2</sub> surface during long-time use [10].

However, the photocatalyst immobilization within polymeric membrane still has some specific practical advantages: (i) the catalyst is embedded into the membrane without any covalent bond formation, thus avoiding its chemical modification. (ii) polymeric membranes show different affinities for different chemicals, therefore, the adsorption and the diffusion of the reactants can be modulated, (iii) the photocatalytic degradation process may be performed in a system in which reaction and separation processes occur simultaneous. (iv) finally, all advantages of true membrane processes, such as modularity, design, and easy scale-up, may be attained [11].

Early development of photocatalytic membranes has been focused on flat sheet membranes made from polyacrylonitrile (PAN) and quite stable to UV light over a 24 h period of irradiation [12]. In contrary, Chin et al., in 2006 found out that PAN membrane is not suitable to be exposed to 10 days of 200mM H<sub>2</sub>O<sub>2</sub>/UV condition and revealed that polytetrafluoroethylene (PTFE) and hydrophobic polyvinylidene fluoride (PVDF) are the better choice for photocatalytic applications [13].

To date, many researchers attracted to fabricate dual layer hollow fibre membranes via a single-step co-extrusion technique due to its advantages such as low material cost, less complex post treatment process and better membrane performance. However, it is very challenging to produce high performance dual layer hollow fiber membranes because it involves a sophisticated spinning process where two different phase inversion pathways occur simultaneously. The major problem in dual layer hollow fibre membranes is low integrity and delamination problem. A good adhesion between inner and outer polymers dope can only be achieved by properly control the spinning parameters such as bore fluid composition, spinning process temperature, air gap height [14] and ratio of outer layer dope flow rate to inner dope flow rate [15].

To our best knowledge, the degradation of organic pollutants by using photocatalytic dual layer hollow fibre membranes has not been reported. Therefore, the development of a novel dual layer hollow fibre membrane, as shown in Fig. 1, for photocatalytic system was carried out in this study. The effect of additives such as polyethylene glycol

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(PEG), titanium dioxide ( $\text{TiO}_2$ ), ethanol and methanol on the dope viscosity and membrane morphology was examined.

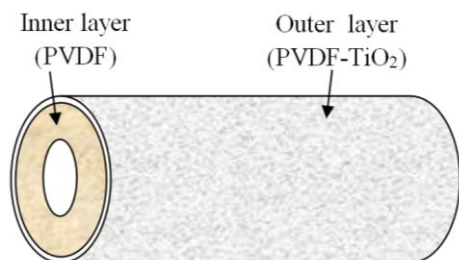


Fig. 1. PVDF- $\text{TiO}_2$ /PVDF dual layer hollow fiber membrane.

## II. PROCEDURE

### A. Materials

PVDF (Polyvinylidene fluoride, Solef 6000 Series - powder, Solvay Specialty Polymers France) was used as polymer based without purification.  $\text{TiO}_2$  nanoparticles was supply by Johnson Matthey, UK. PEG, methanol and ethanol (analytical grade) were purchased from Fluka. DMAC (Dimethylacetamide, Sigma Aldrich) was used as solvent to dissolve polymer without further purification.

### B. Preparation of Dope Solution

The PVDF and  $\text{TiO}_2$  nanoparticles were dried in a  $50^\circ\text{C}$  vacuum oven for 24 hour before they were used for dope preparation. Spinning solutions were prepared by addition of the  $\text{TiO}_2$  nanoparticles to the DMAC solvent in Scott bottle with an overhead stirrer. Table I lists the composition of both inner and outer layers of the membrane.

TABLE I: DIFFERENT DOPE COMPOSITION OF POLYMER MEMBRANES

Parameters	Values
Outer dope flow rate (ml/min)	1
Inner dope flow rate (ml/min)	8
Bore fluid	Distilled water
Bore fluid flow rate (ml/min)	8
Air gap (cm)	10
Take up speed (m/s)	0.18
Aging time	1 day in water
Post treatment	<ol style="list-style-type: none"> <li>1. Immersion of hollow fibre in (ethanol: water, 50:50wt.% ) for 1 hours, then 100% of ethanol for 1 hours in order to improve the membrane wettability and pore collapse [16].</li> <li>2. Drying of hollow fibre at room temperature for 3 days before module fabrication.</li> </ol>

For preparing the blend dope solutions, the  $\text{TiO}_2$  nanoparticles were fully dispersed in the solvent by stirring for a period of 12 hour before the polymers were added to the mixture. The prepared solutions were degassed overnight by using ultrasonic bath system at ambient temperature before they were used for spinning.

### C. Spinning of Dual Layer Hollow Fibre

The prepared spinning dope mixture was extruded using a triple orifice spinneret to form dual layer hollow fibre membranes as stated detail elsewhere [17]. The dimension of

the spinneret is shown in Fig. 2.

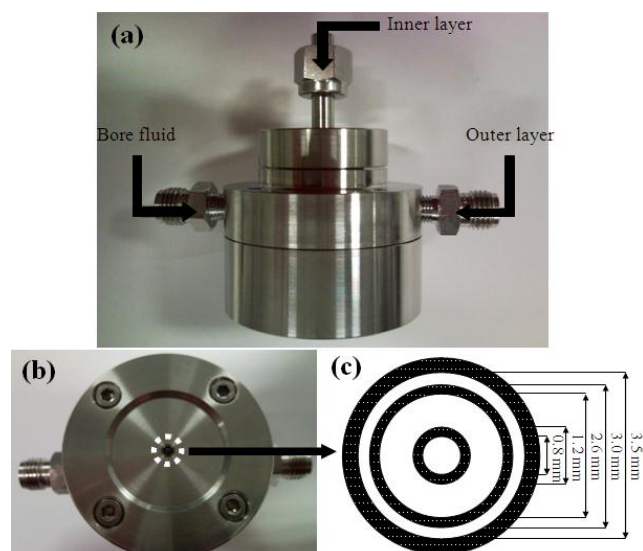


Fig. 2. Photographic images of (a) triple orifice spinneret from side, (b) triple orifice spinneret from bottom, and (c) dimension of the triple orifice spinneret [17].

The spinning conditions that were applied to fabricate the hollow fibre membranes are summarized in Table II.

TABLE II: SPINNING CONDITIONS FOR THE DUAL LAYER HOLLOW FIBRE MEMBRANES

Layer type	Polymer/Additives/Solvent	Composition (wt%)
Inner	PVDF/DMAc	18/82
	PVDF/PEG/DMAc	18/5/77
	PVDF/Ethanol/DMAc	18/5/77
Outer	PVDF/PEG/ $\text{TiO}_2$ /DMAc	18/5/2/75
	PVDF/Methanol/ $\text{TiO}_2$ /DMAc	18/5/2/75
	PVDF/ $\text{TiO}_2$ /DMAc	18/2/80

### D. Characterization of Dual Layer Hollow Fibre

Before spinning, the viscosity of prepared solutions was measured using viscometer 20-2 million centPoise (Cole Parmer, Model: EM-98965-40).

The structural morphology of the membrane inner and outer layers was examined qualitatively by scanning electron microscopy (SEM, Model: TM 3000, Hitachi). To prepare the samples, the membranes were immersed in liquid nitrogen for 10 min and then fractured to reveal their cross sectional morphology. The samples were then positioned on a metal holder and sputter-coated with gold under vacuum for 3 min. Micrographs of their cross sectional and surface morphologies were taken and inspected at various magnifications.

## III. RESULT AND DISCUSSION

Fig. 3 shows the effect of additives on viscosity of the dope solution, where the viscosity increased with the addition of additives. The high viscosity of dope solution would slow down the mass transfer rate during the membrane formation process and prevent the formation of macroporous structure, consequently improving the membrane mechanical strength.

However, too high viscosity would result to inconsistent flow and thus affect the production of membrane with desired structure. Based on the viscosity values shown in Fig. 3, two dopes for the inner layer (i.e. PVDF/DMAc and PVDF/ethanol/DMAc) and the outer layer (i.e. PVDF/TiO<sub>2</sub>/DMAc and PVDF/PEG/TiO<sub>2</sub>/DMAc) were subjected to the co-spinning of dual layer hollow fibre membranes.

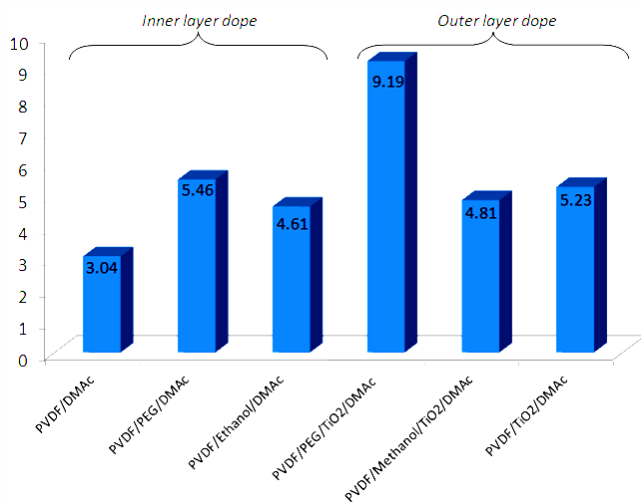


Fig. 3. Effect of additives on viscosity of dope solution.

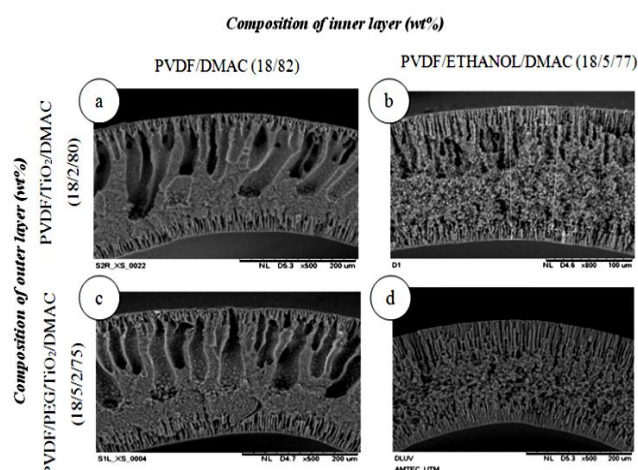


Fig. 4. SEM images of dual layer hollow fibre PVDF membranes with different inner and outer dope composition.

Fig. 4 shows the cross-sectional morphologies of four membranes were spun from different compositions of the outer and inner dope solutions. It can be seen that the finger like void structure formed in the outer layer. When the pore former PEG was added in the outer layer dope, the morphology of finger like structure was adjusted as clearly shown in Fig. 4 (c) compared with Fig. 4 (a).

Ethanol was added in the inner layer dope in order to achieve desired morphology of clear thickness of sponge like structure that could act as separation layer. Based on the Fig. 4 (b), it can be seen that the morphology on the cross section of dual layer hollow fiber spun is sandwich-like structure where finger-like voids formed from the bottom and the top surface of membrane and separated by sponge-like structure at the middle of the membrane cross-section. Ethanol has high mass exchange rate with water at the precipitation front. The water intrusion during coagulation bath was retarded when ethanol was introduced into the inner layer dope [18].

When PEG was introduced in the outer dope solution, the

morphology of dual layer hollow fiber membranes remained sandwich structure but the length of finger-like structure increased as shown in Fig. 4 (d). This result is in agreement with the finding reported by [19], where they observed the enlargement of pore size and porosity of membrane. Such structure is expected could enhance pure water flux and reduce solute rejection of membranes [20]. It is also worth to note that all hollow fibre possessed a good adhesion between layers as no delamination could be observed.

#### IV. CONCLUSION

Dual layer hollow fibre membranes have successfully fabricated by single step co-extrusion techniques. The obtained dual layer hollow fibre membranes consists of sandwich-like structure where finger-like voids formed from the inner and the outer surface of membrane and separated by sponge-like structure at the middle of the membrane cross-section. The results obtained from the analysis conducted indicate that viscosity of the dope solution have significant effect on phase inversion process and thus, affect the final structure of the hollow fibre membrane.

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