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Antifouling Enhancement of Dual Layer Hollow Fiber Membrane By Adding TiO_2 Nanoparticles

Mohd Hafiz Dzarfan Othman, Hanif Mossadeq, Hazlini Dzinun, Ahmad Fauzi Ismail, Mohd Hafiz Puteh, Mukhlis A. Rahman, Juhana Jaafar

Advanced Membrane Technology Research Centre (AMTEC)
FUniversitiTeknologi Malaysia, 81310 UTM Johor Bahru, MALAYSIA
Faculty of Civil Engineering, UniversitiTeknologi Malaysia, 81310 UTM Johor Bahru, MALAYSIA
e-mail: hafiz@petroleum.utm, myhan.if91@yahoo.com, hazlini4@live.utm.my, afauzi@utm.my, mukhlis@petroleum.utm.my, juhana@petroleum.utm.my, mhafizputeh@utm.my

Abstract

Recently, titanium dioxide (TiO_2) has been widely studied as a good antifouling material, low cost, good stability, environmental benefit, and its potential in commercial applications. Many of the pure and modified TiO2 powders, films, nanorods and nanosheets have been prepared previously for the improvement of filtration in water purification process. Polyvinylidene fluoride (PVDF) as a ferroelectric material of high ionic conductivity, good mechanical and membrane-forming properties, was known to have high chemical stability in acidic, basic, rigorous thermal and hydrolytic environment. PVDF has been combined with many different antifouling material to improve its antifouling properties. This paper reports the characterization and performance of dual layer hollow fiber with immobilized TiO2 in the outer layer membranes. In comparison, neat membrane and single hollow fiber membrane were also analyzed. The hollow fiber membranes were characterized using scanning electron microscopy (SEM), contact angle goniometer and filtration experiments. The experimental results demonstrated that dual layer hollow fiber membranes able to enhance the pure water flux and antifouling properties.

Keywords : *Antifouling, PVDF, Titanium dioxide, Nanocomposite membrane*

1 INTRODUCTION

Membrane filtration is playing a more prominent role in the treatment of wastewater due to its advantages: no chemical additives are needed to break the pollutant, high chemical oxygen demand (COD) removal efficiencies are achieved, and treatment facilities are quite compact and fully automated.Membrane filtration does not only facilitate the separation of suspended catalysts but also improves the effluent quality by selective separation at molecular level(Ho, Vigneswaran, & Ngo, 2009). Many studies have been done on the wastewater treatment with different membranes(Alhakimi, Studnicki, & Al-ghazali, 2003; R. A. Damodar, You, & Ou, 2010; Masuelli, Marchese, & Ochoa, 2009; Nghiem, Manis, Soldenhoff, & Schfer, 2004; Wintgens, Gallenkemper, & Melin, 2002). The selection of polymers in membrane fabrication are most important because the success of any separation system involving membrane depends on the quality and suitability of membrane incorporated in the system.

Several high performance membrane materials are found within last two decades accordingly to the advancement of membrane technology. Polyvinylidene fluoride (PVDF) has been selected as one of the most attractive polymer in membrane fabrication due to its unique properties such as excellent chemical resistance and thermal stability, high mechanical strength, its outstanding antioxidation activity, highly organic selectivity, as well as good mechanical and membrane forming properties(Ngang, Ooi, Ahmad, & Lai, 2012; Yuliwati & Ismail, 2011)In the previous study, they stated that PVDF membranes is one of membranes that possess highest stability and resistivity in comparison to other membrane types.2Due to hydrophobic nature of PVDF, a number of novel strategies have been carried out on improving the PVDF membrane hydrophilicity and performance (Cruz, Semblante, Senoro, You, & Lu, 2013; Dong et al., 2012; Li, Shao, Zhou, Li, & Zhang, 2013; Madaeni, Zinadini, & Vatanpour, 2011; Rahimpour, Jahanshahi, Rajaeian, & Rahimnejad, 2011; Yan, Hong, Li, & Li, 2009)

A variety of nanoparticles have been introduced to modify organic membranes, such as SiO_2, Al_2O_3(Yan et al., 2009), $Mg(OH)_2$ (Dong et al., 2012)and TiO_2(Rahimpour et al., 2011; Vatanpour et al., 2012)have been extensively studied. Between them, TiO_2has acquired popularity in the hydrophilic modification of membranes because of it is superb stability, inexpensiveness, and accessibility(Razmjou et al., 2011).Moreover, it displays photocatalytic, antibacterial, self-cleaning, and ultra-hydrophilic properties upon UV irradiation(R. a Damodar, You, & Chou, 2009; Rahimpour, Jahanshahi, Mollahosseini, & Rajaeian, 2012).

Recently, many researchers have attracted to fabricate dual layer hollow fibre membrane due to its advantages such as (1) low material cost; (2) elimination of complex post treatment process; (3) optimized membrane performance by using a functional material of high performance as the selective layer. Various studies clearly reveal the applicability of dual layer fibre spinning technology for various gas (Ahmad & Ramli, 2013; Fei, Chung, Wang, & Liu, 2002; Husain, 2006; Jiang, Chung, Fei, Cao, & Kulprathipanja, 2004; Widjojo, Chung, & Kulprathipanja, 2008) and liquid separations applications (Bonyadi & Chung, 2007; Ong & Chung, 2012; Sun, Hatton, Chan, & Chung, 2012; Wang, Teoh, & Chung, 2011). Most of the researchers have focused on morphological studies and application of dual layer hollow fibre membranes as a separation medium. There is a very limited publication reported on the dual layer hollow fibre membrane structure for antifouling properties. As mentioned by Bhandari (Bhandari, Olanrewaju, Bessho, Breedveld, & Koros, 2013), the morphology of inner and outer layer of hollow fibre membrane are formed based on the required properties in each layer by manipulating of spinning parameters.

Therefore, the objective of this study is to investigate the effectiveness of TiO_2 as an antifouling property in the outer layer of dual layer nanocomposite PVDF/TiO2 hollow fiber. For comparison, single layer nanocomposite PVDF/TiO_2 hollow fiber that comprised the same formulation as the outer dope of dual layer hollow fibre membranes was also fabricated and characterized. Dual layer pristine PVDF hollow fiber membranes also fabricated as a control membrane.It is expected that the dual layer hollow fiber as illustrated in Figure 1 would reduce the amount of TiO_2 used and also enhance the TiO_2 dispersion in the membrane.

2 RESEARCH METHODOLOGY

2.1 Preparation of Membrane

PVDF and TiO_2 were dried in a 50° vacuum oven for 24 hour to remove moisture prior to dope preparation. Two dopes was prepared where the outer layer comprised of 15wt% of PVDF/ 3wt% of titanium dioxide while the inner layer was 18wt% of PVDF and the rest was dimethylacetamide (DMAc) solution. Firstly, the TiO_2 and DMAc were added in Scott bottle with an overhead stirrer. After the TiO_2 mixture became a homogeneous solution, the desired amounts of polymer was added to the solution. Then, the solution was degassed by using ultrasonic bath system at ambient temperature over night prior to spinning.The spinning dope mixture was extruded using a triple orifice spinneret to form dual layer hollow fiber membranes as stated detail elsewhere (Dzinun et al., 2015). Three types of hollow fibers were fabricated which are (i) dual layer nanocomposite PVDF/TiO_2 hollow fiber (DL-T3), (ii) single layer nanocomposite PVDF/TiO2 hollow fiber (SL-T3) and (iii) dual layer pristine PVDF hollow fiber (DL-T0). For the nanocomposite membrane, 3wt.% of TiO_2 was used together with 15wt.% of PVDF in dimethylacetemide (DMAc) solvent.

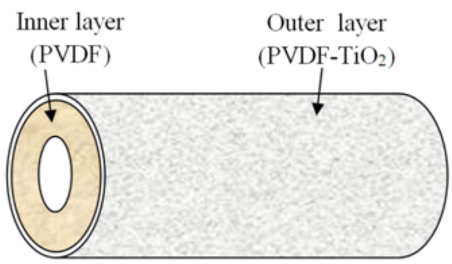

Figure 1: Illustration of dual layer nanocomposite hollow fiber

2.2 Characterization Methods

The morphology of the cross section membranes were inspected by SEM (Model: TM 3000, Hitachi). The hollow fibres were immersed in liquid nitrogen for 10 min and then fractured into short samples, for the purpose of maintaining the original cross sectional of the membranes. The samples were then positioned on a metal holder and sputter coated with gold under vacuum for 3 min. The micrographs of the cross section and surface of the hollow fibre membranes were taken at various magnifications. The images of membranes before and after UV irradiation were also captured for comparison purposes.

Contact angle measurements on the hollow fibre membranes were conducted using the contact angle goniometer (Model: OCA 15EC, Dataphysics) with deionized water as contact liquid. The water droplets of 2 L were dropped on the fibre surfaces. An average and standard deviation of at least 10 independent measurements was obtained at different points of one sample.

Pure water flux experiments were conducted in a U-like membrane module filtration apparatus. For each module, twenty fibres with 30 cm length were assembled into the filtration module and pure water flux measurements were performed in a cross flow mode through outside-in configuration. The compressed distilled water will be used as permeate for pure water flux measurements. Membranes will initially pressurized with distilled water at 0.15MPa for 0.5h to compact membranes for getting a constant flux. The steady water fluxes will be measured at 0.1MPa and the flux will be calculated according to equation 1 and 2:

$$F = \frac{V}{Axt} \tag{1}$$

$$A = \Pi d_{\circ} L \tag{2}$$

where F is the membrane flux (L/m^2h), V is the volume of permeate at time t (L), A is the effective filtration area of the membrane (m2), $d\circ$ is the outer diameter of hollow fibers (cm) and L is the effective length of hollow fibers (cm).

2.3 Nonylphenol Rejection

Nonylphenol(NP) rejection test is the same as water permeability test. A 1 ppm of feed solution was prepared by dissolving 1 g nonylphenol (NP) in 1L of volume.Permeate was collected after 30 minutes and examined using a HACH DR5000 UV-Vis spectrophotometer. The scanning determination of absorbance at a fixed wavelength at 282nm.NP rejection was calculated from the NP solution at initial feed 1ppm using the equation 3:

$$NP_{rejection} = \left(\frac{Abspermeate}{Abs_{feed}}\right) \tag{3}$$

3 RESULTS AND DISCUSSION

Figure 2 shows SEM images of the PVDF/TiO2 hollow fiber membranes with different configurations. As can be seen in the Figure 2 (a & b), both layers are compatible with each other and there are no delamination and interfacial resistance when PVDF was used for both inner and outer layer dopes.All hollow fiber membrane exhibits sandwich like structure that consists of finger like structure in the inner and outer layer, separated by sponge like structure. As stated in Table 1, single layer hollow fiber membrane was slightly thicker compared to dual layer PVDF/TiO_2 hollow fiber membranes and neat membranes. This thickness wouldaffectthe pure water flux and also NP rejection as can be discussed in the next section.

Surface hydrophilicity is a membrane property that influences flux and antifouling ability. It is evaluated by measuring thecontact angle between water and membrane surface, wherein a decrease in angle indicates an increase in hydrophilicity. The contact angle data as stated in Table 1 shows that in addition of TiO_2 resulted to an improvement in the hydrophilicity due to the hydroxyl groups of TiO_2 nanoparticles on the membrane surface.

Even though the single layer hollow fiber is more hydrophilicity than the dual layer, the pure water flux results were not in good agreement with the hydrophilicity as shown in Figure 3.It may due to the particle aggregation causing decrease in affective hyrophilic area

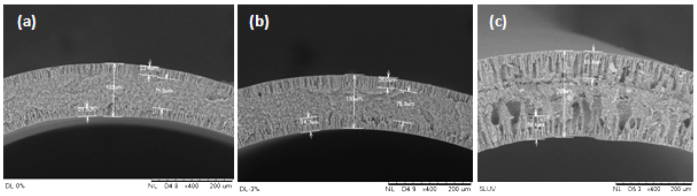

Figure 2: Partial cross sectional SEM images of the hollow fiber membranes with different configurations; (a) DL neat membrane, (b) DL TiO2 3wt%, (c) SL TiO2 3wt%

Table 1: Examples of writing table

Configuration	Membrane identification code	Thickness (m)	Contact angle (degree)
Dual Layer Hollow Fibre TiO2 3wt%	DL-T3	130	76.3
Dual Layer Hollow Fibre TiO2 0wt%	DL-T0	130	80.4
Single Layer Hollow Fibre TiO2 3wt%	SL-T3	209	71.7

and hydroxyl group number (Cruz et al., 2013). Besides, the pore size and macrostructure difference between these two membranes could be the main reason for such trend.

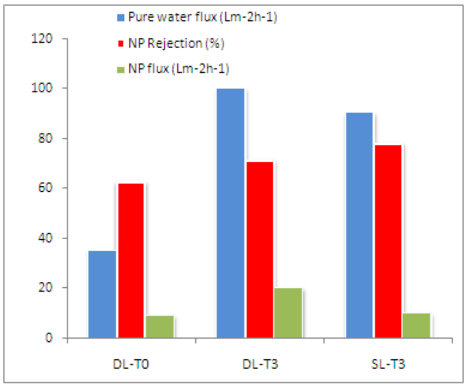

Figure 3: Pure water flux, NP flux and rejection by using different membrane configuration

The NP flux of nanocomposite dual layer hollow fibe (DL-T3) possesses the highest value compared to single layer and neat membrane. The obtained results clearly reveal that the antifouling property of TiO_2 in the dual layer hollow fiber membranes was significantly improved.

From Figure 4, the fouling behavior of the membrane can also be observed. In comparison to dual layer pure PVDF hollow fiber, it can be seen that the nanocomposite PVDF/TiO_2 membranes (both single and dual layer hollow fiber) have better anti-fouling property since the flux drops from minute 30 to minute 240 of the membranes with TiO_2 are much lower than the pure PVDF one. The result indicates that membrane fouling will increase drastically with absence of TiO_2. In addition, the obtained results also shows that the dual layer hollow fiber that utilized much smaller amount of TiO_2 (since TiO_2 only dispersed on the thin outer layer) has a comparable anti-fouling property compared to single layer one, which used more amount of TiO_2 due to its thicker nanocomposite thickness.

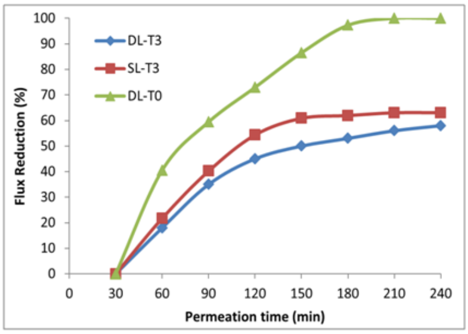

Figure 4: Flux behaviors during NP filtration

4 CONCLUSION

This work has focused on the effectiveness of TiO_2 nanoparticles as an antifoulant in different membrane configuration. The experimental results showed that by addition of TiO_2 in the membrane could enhanced the membrane hydrophilicity and resulted increase the flux. It revealed that TiO_2 nanoparticlesare more effective in the dual layer configuration. It will reduce the material cost due to the amount of TiO_2 used in outer layer of dual layer hollow fibre membranes will be less than single layer.

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References

Ahmad, a. L., & Ramli, W. K. W. (2013). Hydrophobic PVDF membrane via two-stage soft coagulation bath system for Membrane Gas Absorption of CO2. *Separation and Purification Technology*, *103*, 230240.

Alhakimi, G., Studnicki, L. H., & Al-ghazali, M. (2003). *Photocatalytic destruction of potassium hydrogen phthalate using TiO 2 and sunlight: application for the treatment of industrial wastewater*, *154*, 219228.

Bhandari, D., Olanrewaju, K. O., Bessho, N., Breedveld, V., & Koros, W. J. (2013). Dual layer hollow fiber sorbents: Concept, fabrication and characterization. *Separation and Purification Technology*, *104*, 6880.

Bonyadi, S., & Chung, T. S. (2007). *Flux enhancement in membrane distillation by fabrication of dual layer hydrophilic hydrophobic hollow fiber membranes*, *306*, 134146.

Cruz, N. K. O., Semblante, G. U., Senoro, D. B., You, S. J., & Lu, S. C. (2013). Dye degradation and antifouling properties of polyvinylidene fluoride/titanium oxide membrane prepared by solgel method. *Journal of the Taiwan Institute of Chemical Engineers.*

Damodar, R. a, You, S.-J., & Chou, H.-H. (2009). Study the self cleaning, antibacterial and photocatalytic properties of TiO2 entrapped PVDF membranes. *Journal of hazardous materials*, *172*(2-3), 13218.

Damodar, R. A., You, S., & Ou, S. (2010). Coupling of membrane separation with photocatalytic slurry reactor for advanced dye wastewater treatment. *Separation and Purification Technology*, *76*(1), 6471.

Dong, C., He, G., Li, H., Zhao, R., Han, Y., & Deng, Y. (2012). Antifouling enhancement of poly(vinylidene fluoride) microfiltration membrane by adding Mg(OH)2 nanoparticles. *Journal of Membrane Science*, *387-388*, 4047.

Dzinun, H., Othman, M. H. D., Ismail, a. F., Hafiz Puteh, M., Rahman, M. a., & Jaafar, J. (2015). Morphological study of co-extruded dual-layer hollow fibre membranes incorporated with different TiO2 loadings. *Journal of Membrane Science.*

Fei, D., Chung, T., Wang, R., & Liu, Y. (2002). *Fabrication of fluoropolyimide / polyethersulfone (PES) dual-layer asymmetric hollow fiber membranes for gas separation*, *198*, 211223.

Ho, D. P., Vigneswaran, S., & Ngo, H. H. (2009). Photocatalysis-membrane hybrid system for organic removal from biologically treated sewage effluent. *Separation and Purification Technology*, *68*(2), 145152.

Husain, S. (2006). *MIXED MATRIX DUAL LAYER HOLLOW FIBER MEMBRANES FOR NATURAL GAS SEPARATION.*

Jiang, L., Chung, T., Fei, D., Cao, C., & Kulprathipanja, S. (2004). *Fabrication of Matrimid / polyethersulfone dual-layer hollow fiber membranes for gas separation*, *240*, 91103.

Li, J.-H., Shao, X.-S., Zhou, Q., Li, M.-Z., & Zhang, Q.-Q. (2013). The double effects of silver nanoparticles on the PVDF membrane: Surface hydrophilicity and antifouling performance. *Applied Surface Science*, *265*, 663670.

Madaeni, S. S., Zinadini, S., & Vatanpour, V. (2011). A new approach to improve antifouling property of PVDF membrane using in situ polymerization of PAA functionalized TiO2 nanoparticles. *Journal of Membrane Science*, *380*(1-2), 155162.

Masuelli, M., Marchese, J., & Ochoa, N. a. (2009). SPC/PVDF membranes for emulsified oily wastewater treatment. *Journal of Membrane Science*, *326*(2), 688693.

Ngang, H. P., Ooi, B. S., Ahmad, A. L., & Lai, S. O. (2012). *Preparation of PVDF TiO 2 mixed-matrix membrane and its evaluation on dye adsorption and UV-cleaning properties*, *197*, 359367.

Nghiem, L. D., Manis, a., Soldenhoff, K., & Schfer, a. I. (2004). Estrogenic hormone removal from wastewater using NF/RO membranes. *Journal of Membrane Science, 242*(1-2), 3745.

Ong, Y. K., & Chung, T. (2012). High performance dual-layer hollow fiber fabricated via novel immiscibility induced phase separation (I2PS) process for dehydration of ethanol. *Journal of Membrane Science*, 421-422, 271282.

Rahimpour, A., Jahanshahi, M., Mollahosseini, A., & Rajaeian, B. (2012). Structural and performance properties of UV-assisted TiO2 deposited nano-composite PVDF/SPES membranes. *Desalination, 285*, 3138.

Rahimpour, A., Jahanshahi, M., Rajaeian, B., & Rahimnejad, M. (2011). TiO2 entrapped nano-composite PVDF / SPES membranes: Preparation , characterization , antifouling and antibacterial properties. *Desalination, 278*(1-3), 343353.

Razmjou, A., Mansouri, J., & Chen, V. (2011). The effects of mechanical and chemical modification of TiO2 nanoparticles on the surface chemistry, structure and fouling performance of PES ultrafiltration membranes. *Journal of Membrane Science, 378*(1-2), 7384.

Sun, S. P., Hatton, T. A., Chan, S. Y., & Chung, T.-S. (2012). Novel thin-film composite nanofiltration hollow fiber membranes with double repulsion for effective removal of emerging organic matters from water. *Journal of Membrane Science, 401-402*, 152162.

Vatanpour, V., Siavash, S., Reza, A., Salehi, E., Zinadini, S., & Ahmadi, H. (2012). TiO 2 embedded mixed matrix PES nanocomposite membranes: Influence of different sizes and types of nanoparticles on antifouling and performance. *Desalination, 292*, 1929.

Wang, P., Teoh, M. M., & Chung, T. (2011). Morphological architecture of dual-layer hollow fiber for membrane distillation with higher desalination performance. *Water Research, 45*(17), 54895500.

Widjojo, N., Chung, T., & Kulprathipanja, S. (2008). *The fabrication of hollow fiber membranes with double-layer mixed-matrix materials for gas separation*, 325, 326335.

Wintgens, T., Gallenkemper, M., & Melin, T. (2002). *Endocrine disrupter removal from wastewater using membrane bioreactor and nanofiltration technology, 146*, 387391.

Yan, L., Hong, S., Li, M. L., & Li, Y. S. (2009). Application of the Al2O3PVDF nanocomposite tubular ultrafiltration (UF) membrane for oily wastewater treatment and its antifouling research. *Separation and Purification Technology, 66*(2), 347352.

Yuliwati, E., & Ismail, a. F. (2011). Effect of additives concentration on the surface properties and performance of PVDF ultrafiltration membranes for refinery produced wastewater treatment. *Desalination, 273*(1), 226234.