J. Applied Membrane Science & Technology, Vol. 19, December 2016, 33-42

Study of the Effectiveness of Titanium Dioxide (TiO_2) nanoparticle in Polyethersulfone (PES) Composite Membrane for Removal of Oil in Oily Wastewater

Munawar Zaman Shahruddin, Nuratikah Zakaria, Nurul Fattin Diana Junaidi, Nur Hashimah Alias, Nur Hidayati Othman*

Fakulti Kejuruteraan Kimia, Universiti Teknnologi MARA (UiTM) Shah Alam, 40450 Shah Alam, Selangor, Malaysia

ABSTRACT

Polyethersulfone/Titanium oxide (PES/TiO_2) composite membranes at various compositions of TiO_2 nanoparticle (0, 0.1 and 0.5 wt. %) were prepared via phase inversion method. The prepared composite membranes were then tested for degradation process and separation process for oily wastewater. It was found that the addition of TiO_2 that possess visible-light response activity led to an improvement of the membrane performances especially in photocatalytic activities. The membrane performances were also investigated by using liquid separation system in order to obtain the flux/permeation rate and also the percentage of oil removal by the membranes. The results indicate that the increment the amount of TiO_2 nanoparticle in the composite membrane reduced the permeation flux. Further study has been made by characterizing the membranes in terms of contact angle, Field Emission Scanning Electron Microscope (FESEM), Fourier Transform Infrared Spectrometer (FTIR) and X-Ray Diffraction (XRD) analysis. The characterization results indicate that the TiO_2 nanoparticles were uniformly mixed in the membrane. The increased of membrane hydrophilicity was demonstrated by the contact angle measurement. By adding TiO_2, the membrane hydrophilicity was observed to be better than the neat PES composite membrane. Cross sectional images from FESEM also indicate that the addition of TiO_2 nanoparticles help in increasing the macro-void of the membranes. Finally, a comparison between neat PES membrane and PES/TiO_2 nanoparticle membrane proved that addition of TiO_2 nanoparticle can be one of the ways to maximize the removal of oil.

Keywords: TiO_2 nanoparticles, cross sectional, oil degradation, PES membrane, phase inversion

1.0 INTRODUCTION

Huge amount of industrial wastewater was discharged into rivers, lakes and coastal areas caused serious pollution problems in water environment and negative effects to the human's life and eco-system. Industrial wastewater can be divided into two types, which are inorganic industrial wastewater and organic industrial wastewater. Inorganic industrial wastewater usually produced in the coal and steel industry, surface processing of metals industry and non-metallic mineral industry [1]. This wastewater contains large amount of suspended solids which usually can be removed by sedimentation, chemical flocculation and addition of iron and aluminium salts. Organic industrial wastewater contains organic industrial waste from chemical industries that mainly used organic substance for chemical reaction. This type of wastewater can be treated by special pre-treatment, followed by biological treatment [1].

* Corresponding to: Nur Hidayati Othman (email: nurhidayati0955@salam.uitm.edu.my)

Oily wastewater from industry has been reported as one of the main causes of water pollution [2]. This type of oily wastewater was usually produced by petrochemical, pharmaceutical, metallurgical, food industries, and especially by oil field. Generally, there are three categories of oily wastewater from industry which are free-floating oil, unstable oil/water emulsion, and stable oil/water emulsion [3]. Free-floating oil and unstable oil/water emulsions can be removed easily by conventional separation processes, such as ultrasonic separation, coagulation/ flocculation, electric field, and air flotation [4]. Unfortunately, these techniques are not proficient enough to remove stable oil/water emulsion.

Membrane types and materials are very important in order to determine the final performance of the membrane processess. Most microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO) and nanofiltration (NF) membranes are made from synthetic organic polymers [5]. Polymer-based membranes are usually cheaper in compared to inorganic membranes. But, it may contain natural variations in pore size and are prone to fouling and degradation [6].

Recently, titanium dioxide (TiO_2) nanoparticles blended within polymeric membranes have shown significant improvements in controlling fouling. Sotto *et al.* [7] reported the fabrication and characterization of PES–TiO_2 nanoparticle composite membranes made from synthesis casting solution consisting of various compositions of solvents and TiO_2 additives. The results revealed that the membrane permeation and rejection rates, pore size, and porosity were dependent on the TiO_2 and solvent concentrations. The modified membranes showed a structural change from a sponge-like to a finger-like structure. Fouling resistance of modified membranes was significantly improved, while the rejection potential of the membranes was hardly affected by the nanoparticles and solvent incorporation into the polymeric solution.

Razmjou *et al*. [8] studied the effects of mechanical and chemical modification of TiO_2 nanoparticles on the surface chemistry, structure, and fouling performance of PES ultrafiltration membranes. In the study, mechanical and chemical modification approaches were adapted using Degussa P25 TiO_2 nanoparticles to improve their dispersion. Afterward, the modified TiO_2 nanoparticles were incorporated into PES based in-house membranes and their effect on microstructure, surface chemistry, and fouling performance were investigated. The results showed that good dispersion of nanoparticles in the membrane was achieved after both chemical and mechanical modifications of particles, as a result of less agglomeration.

Reddy *et al*. [9] modified PES UF membranes by pre-adsorption of poly (sodium 4-styrenesulfonate) (PSSS) upon the permeation of aqueous solution of the polymer for about 100 min. The antifouling nature of the unmodified and surface modified membranes was compared by ultrafiltration of aqueous solutions. The surface modified membranes showed better antifouling property compared to unmodified

2.0 METHODS

PES and TiO_2 nanoparticles were used as polymer and additives and were supplied by Sigma Aldrich. N-Dimethylacetamide (DMAc) was used as a solvent for the dope solution preparation and was supplied by Merck Chemicals.

2.2 Membrane Preparation

Firstly, PES pellet was dried in oven at 60˚C in order to remove the moisture content. PES pellet was added into the DMAc solution and mixed thoroughly at the room temperature for 24 hours until a homogeneous solution was formed. The PES composite with TiO_2 nanoparticle membrane was prepared by adding the different compositions of the TiO_2 nanoparticle in the solution. The solution was then stirred until homogeneous. The ratio of PES and TiO_2 nanoparticle used for synthesis membrane are shown in Table 1. The solution was casted onto a glass plate using casting knife and immediately immersed into the coagulation bath of distilled water. The membrane was slowly detached from the glass plate and was soaked in the distilled water overnight for solvent exchange process to occur.

Table 1 PES/TiO_2 nanoparticle casting composition

Membrane	PES (wt%)	DMAc (wt%)	TiO_2 (wt%)
M1	15	85.0	0.0
M2	15	84.9	0.1
M3	15	84.5	0.5

2.3 Oily Wastewater Preparation

The oily wastewater was prepared by using crude oil and deionized water. The mixture was vigorously stirred at 2000 rpm until homogeneous solution was obtained. The stability of the emulsion was observed over 24 hours period and the mixture maintain cloudy and turbid, which indicate that the emulsion oil is stable.

2.4 Degradation Activity

The degradation of oil is one of the methods used to evaluate the visible-light response activity of PES/TiO_2 membrane. The visible light was provided from 18 W fluorescent lamp. The membrane samples were kept 10 cm distance off the visible light resources in this study. The typical photo degradation process was carried out as following: 50 ml of oily wastewater was put in a 100 ml conical flask and then a membrane was placed into the solution. The solution was placed in the dark and then the visible light was turned on. At a designated time interval of 1 hour, 3 ml solution was collected to measure the oil concentration.

2.5 Permeation Test

The membrane sample was cut into a circle shape to fit into the membrane liquid separation system. The sample was placed in the permeation cells at lower chamber of the still support. Next, the upper chamber was attached together with lower chamber. Afterwards, the pressure was adjusted until 3 bar. Finally, the sample was collected at 120 minutes to determine the percentage of oil removal by the membrane..

2.6 Concentration Measurement

The concentration of oil in feed and permeate solutions were measured using UV-Vis Spectrometer (Perkin Elmer Lambda 650).

2.7 Membrane Characterization

Field Emitting Scanning Electronic Microscope (FESEM) (JEOL, JSM-6700F) was used to examine the cross section structure of membrane at 500x magnification.

The crystalline structures of TiO_2 in the PES/TiO_2 membrane was recorded via XRD Diffractometer (Rigaku, Ultima III) operated at 40 mAand 40 kV from 10˚ to 80˚.

The hydrophilicity of the membrane was characterized by a Contact Angle Goniometer (VCA 3000). To minimize the experimental error, the recorded data were measured at least three times and then averaged.

FTIR spectra (Perkin Elmer FTIR Spectrometer 100) were employed to functional identification of the modified TiO_2 nanoparticles. This technique was used to study the chemical structure of PES/TiO_2 nanoparticle membranes with different dosage of TiO_2 nanoparticle.

3.0 RESULTS & DISCUSSION

3.1 The Membrane Performance in Degradation and Separation of Oil from Oily Wastewater

The concentrations of oil in the wastewater that have undergone the photo degradation and separation process were determined by UV-Vis Spectrometer with absorbance measured at 377 nm which the maximum absorption occurs.

Figure 1 shows the calibration graph for oil concentration used as a point of reference to determine the concentration of oil in wastewater after undergo the treatment process. Four readings of difference concentration of oily wastewater were taken to get the absorbance (A) reading of the UV-Vis Spectrometer.

Tables 2 and 3 show the percent removal of oil from wastewater after undergone the degradation for PES/TiO2 nanoparticles (0.1 wt. % and 0.5 wt. %) membrane for 6 hours. The results from Table 2 and Table 3 indicate that the percentage of oil removal for both PES/TiO_2 (0.1 wt. % and 0.5 wt. %) membrane are increasing. According to Lia [11], this is because of the visible light provided from the fluorescent lamp (18W) which photon-electron can be absorbed and applied for membrane's photocatalytic activity.

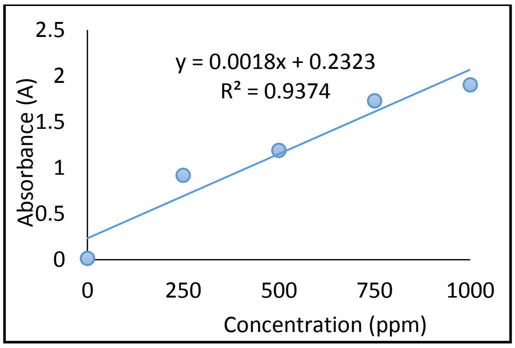

Figure 1 Calibration graph for oil concentration

Table 2 Absorbance (A) reading of oily wastewater using PES/TiO_2 (0.1 wt. %) membrane

Time (hour)	Absorbance (A)	Percent Removal (%)
1	1.688	18.6
2	1.613	22.8
3	1.505	28.8
4	1.456	31.5
5	1.285	41.0
6	1.279	41.4

Table 3 Absorbance (A) reading of oily wastewater using PES/TiO_2 (0.5 wt. %) membrane

Time (hour)	Absorbance (A)	Percent Removal (%)
1	1.273	49.0
2	1.301	47.0
3	1.244	51.1
4	1.216	53.1
5	1.206	53.8
6	1.095	61.7

The electrons can be captured by the oxygen molecule (O_2) on the TiO_2 surface to produce O_2^-, HO_2^-, H_2O_2 and •OH as well as the holes can interact with water molecule and hydroxyl group (-OH) to produce hydroxyl radical (•OH) [12]. The hydroxyl radical (•OH) can occur oxidizing reaction with most inorganic and part organic materials. The hydroxyl radical (•OH) can cause the degradation of oil under visible light illumination [13, 14]. From the observation, the colour of oily wastewater showed the slight changes from cloudy to more clear which indicate the process is able to degrade the oil (Figure 2).

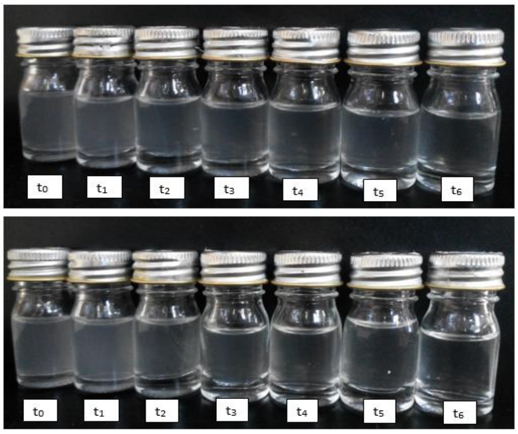

Figure 2 The colour changes of wastewater after degradation process:
(a) PES/TiO_2 (0.1 wt. %) membrane
(b) PES/TiO_2 (0.5 wt. %) membrane

Afterward, the membrane samples were tested by using membrane liquid separation system. The membrane samples were cut into area with diameter of 4.5 cm to fit into the membrane rig. Table 4 shows the average value of the percentage oil removal by three different types of membrane.

Table 4 Average reading of percentage oil removal by different types of membranes

Types of membrane (wt. % TiO_2)	Percent Removal (%)
0	65.1
0.1	68.6
0.5	92.2

Figure 3 shows flux reading for different dosage of concentration of TiO_2 nanoparticles (0, 0.1, and 0.5 wt. %). Two measurements were made for each sample and then the average value was reported together with its standard deviation. To determine the membrane water flux, equation (1) was used as the value of V (mL) were depends on the permeate flow from the liquid separation system. Based on Figure 3, the trend showed the flux decreasing with time. This may be due to the depositing of TiO_2 nanoparticles on the surface of PES membrane and consequently the plugging of the membrane pores [15]. The data indicated that the flux reading of neat PES (0 wt. % TiO_2) membrane was high compared to the TiO_2 composited membranes during time. Further increment of TiO_2 concentration declined the flux strongly. This may be attributed to the blockage of membrane surface pores by TiO_2 nanoparticles [15].

Figure 4 displays the colour of the wastewater before and after undergoes the separation process. From the observation, the colour of wastewater changed completely from cloudy to clear which indicated that the membrane are effective to use for separation process since the percentage of oil removal are quite high.

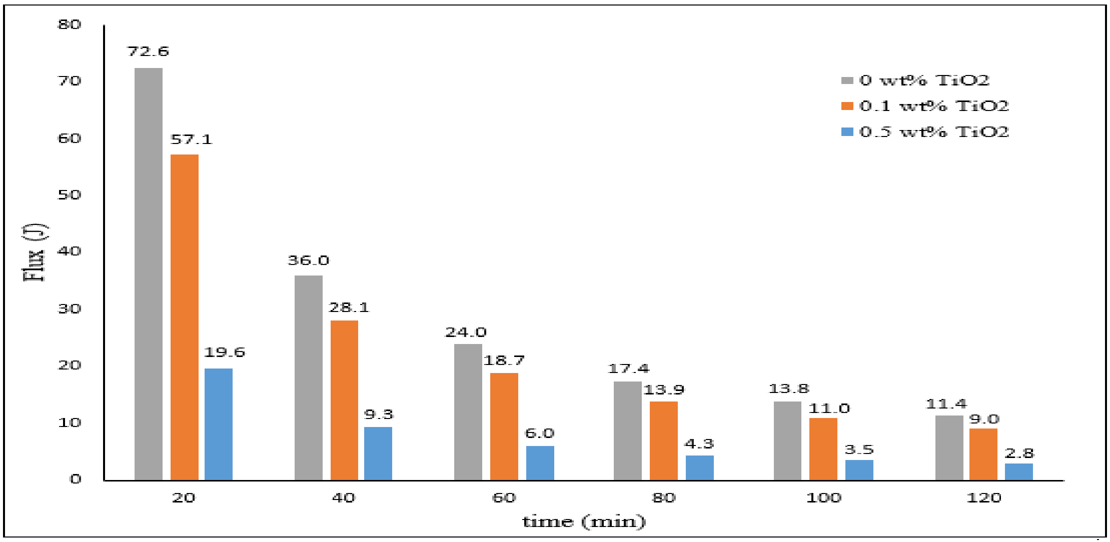

Figure 3 Flux reading for different types of membrane for every 20 minutes time interval

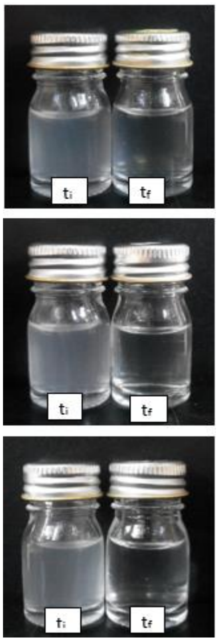

Figure 4 The colour changes of wastewater after degradation process: (a) PES/TiO_2 (0 wt.%) membrane b) PES (b PES/TiO_2 (0.1 wt.%) membrane (c) PES/TiO_2 (0.5 wt. %) membrane

3.2 XRD Analysis

The presence of TiO_2 nanoparticles in the membrane structure was confirmed by XRD analysis. The XRD patterns for PES composite membrane with different dosage of TiO_2 nanoparticle (0, 0.1, and 0.5 wt. %) content is shown in Figure 5. The results revealed the change in dominant crystal phases due to composite of TiO_2 nanoparticles in the PES membrane. The pattern of PES/TiO_2 nanoparticles (0.1 wt. %) showed the crystalline characteristic peak at $2\Theta = 27.78^{\circ}$. For PES/TiO_2 nanoparticles (0.5 wt. %), a peak at $2\Theta = 25.1^{\circ}$ showed a little shift, which was almost similar with previous study [16]. It revealed that the TiO_2 nanoparticles have been distributed to the membrane and there also existed a slight interaction between TiO_2 nanoparticles and PES.

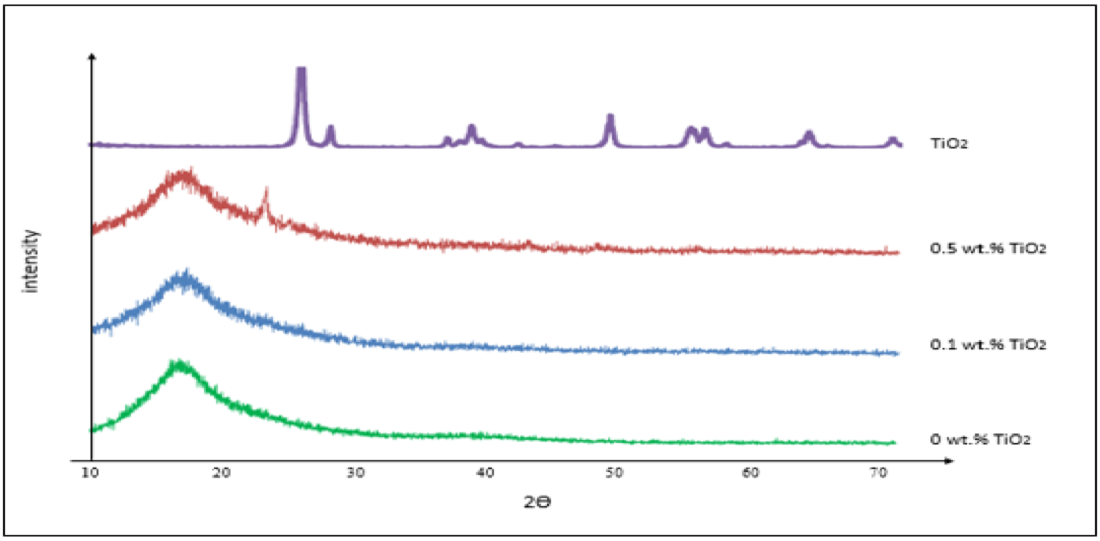

Figure 5 XRD patterns for TiO2 nanoparticles and PES composite membrane with different TiO2 nanoparticles (0, 0.1 and 0.5 wt. %)

3.3 Observation of Membrane Morphology

Cross sectional images of membranes was prepared from PES composite membrane with different compositions of TiO_2 (0 wt. %, 0.1wt. % and 0.15 wt. %) are shown in Figure 6. The FESEM image showed that all prepared membrane are highly porous membrane and sponge-like cross section could be obviously observed. As the sequence of the increase of the nanoparticles compositions from 0 to 0.15 wt %, three different effects can be observed such as the structure with more macro-voids are obtained and the macro-void length increases. It also can be assumed for the composition at 0.5wt. % TiO_2 nanoparticles which the structure and the length of micro-voids will be increased.

In terms of the aggregation of TiO_2 nanoparticles on the membrane, FESEM images (Figure 7) of 0.15 wt. % TiO_2 nanoparticles shows the higher aggregation tendency of TiO_2 nanoparticles rather than membrane of 0.1 wt. % TiO_2 nanoparticles. According to Vahid [16], by increment of TiO_2 nanoparticles, the sizes of aggregated nanoparticles were increased. Based from the images, it reveals that 0.1 wt. % TiO_2 nanoparticles have low tendency for aggregation and do not clog membrane pores leading to high pure water flux for membrane 0.1 wt. % TiO_2 nanoparticles. In other words, the addition of the TiO_2 nanoparticles to the polymeric solution, results in the increase of macro-void dimensions and lengths with contrast of the membrane porosity and flux.

3.4 FTIR Analysis And Membrane Surface Hydrophilicity

In this study, FTIR measurement was conducted to investigate the changes in functional groups on the membrane surface. Figure 8 shows the FTIR spectra for PES/TiO_2 composite membrane with three different compositions of TiO_2 nanoparticle (0, 0.1, and 0.5wt %). The peaks at wave numbers ~ 1239.37 cm^{-1}, ~ 1321.51 cm^{-1} are due to C-O-C, asymmetric and symmetric stretches of S=O and aromatic C=C asymmetric stretching vibration in the PES molecule.

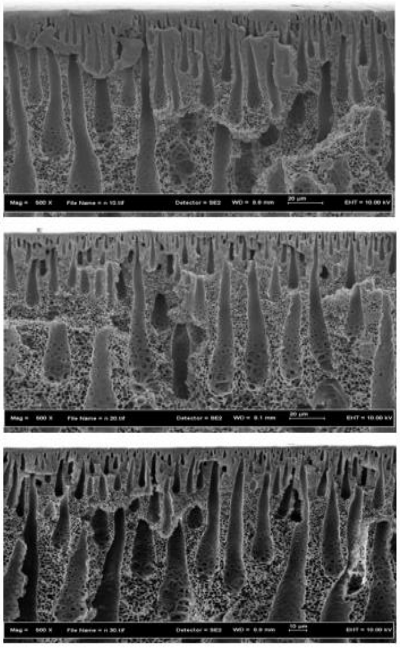

Figure 6 FESEM images of the cross-sectional morphology of (a) PES / TiO_2 (0 wt. %),(b) PES / TiO_2 (0.1wt %) and (c) PES / TiO_2 (0.15wt %)

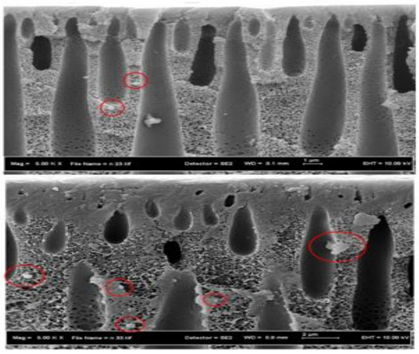

Figure 7 FESEM images of different TiO_2 nanoparticles' composition: (a) 0.1 wt. % TiO_2 (b) 0.15 wt. % TiO_2

A peak was appeared in TiO_2 (0.1 wt. % and 0.5 wt. %) mixed PES membrane in 1578.18cm^{-1} and 1578.02 cm^{-1}, respectively which related to the interactions of TiO_2 nanoparticles with the sulfone group and ether bond in PES structure [17].

The presence of OH bonds in the membrane structure is the main factor for settlement of TiO_2 nanoparticles on the membrane surface. The membrane compositing was accomplished by self-assembly of TiO_2 nanoparticles and the polymer with OH bonds. The self-assembly was carried out by co-ordinance bonding between Ti_4^+ (from TiO_2) and oxygen (from OH bonds). The self-assembly of TiO2 and establishment of a strong bond with membrane polymer, prevents washing and removing of nanoparticles from membrane surface [18].

Contact angle measurement was employed to characterise the hydrophilicity and wetting ability of membrane surface. The results obtained are shown in Figure 9. The results show that membrane hydrophilicity decreases with increment of TiO_2 compositions. This is due to higher affinity of TiO_2 to water. The contact angle has reverse proportion with hydrophilicity. The lower contact angle indicates the higher hydrophilicity [12].

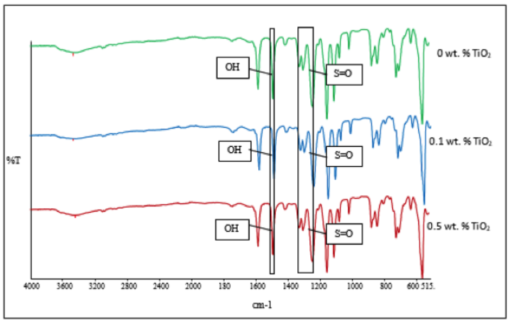

Figure 8 FTIR spectra of PES composite membrane with PES/TiO_2 (0, 0.1, 0.5 wt%)

4.0 CONCLUSIONS

Three types of PES modified membrane were prepared via compositing the TiO_2 nanoparticles with different compositions (0, 0.1 and 0.5 wt. %) in the casting solution. The PES/TiO_2 composite membrane was successfully prepared by phase inversion method. For degradation and separation process, the permeation flux from the membrane with higher TiO_2 nanoparticle content was lower compared with the membrane that has low content of TiO_2 nanoparticles. In other words, TiO_2 made the performance of PES membrane superior to that of neat PES membrane, especially in terms of hydrophilicity and surface morphology. After the composition TiO_2 on the PES membrane, the peak of PES/TiO_2 nanoparticle membrane in XRD result appeared at the same peak of the TiO_2 nanoparticle which indicate that the TiO_2 nanoparticle successfully composite into the PES membrane. The surface morphology from FESEM result also showed that the number of micro void and its length of the membrane increasing with the TiO_2 nanoparticle but decreasing the pure water flux as well as porosity. And the hydrophilicity of the membrane is increasing since the water contact angle decreasing with the addition of TiO_2 nanoparticle on membrane.

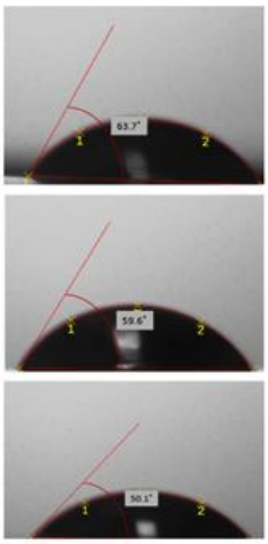

Figure 9 The contact angle of membrane: (a) PES / TiO_2 (0 wt. %), (b) PES / TiO_2 (0.1wt %) and (c) PES / TiO_2 (0.5wt %)

ACKNOWLEDGEMENT

The authors fully acknowledged Ministry of Higher Education and Universiti Teknologi MARA for the approved FRGS fund (600-RMI/FRGS 5/3 (75/2015)) which makes this important research viable and effective

REFERENCES

[1] S. H. I. Hanchang. 2015. Point Sources Of Polution: Local Effects And It's Control. *Industrial wastewater-Types, Amounts and Effects*. 1: 1–6.

[2] H. W. Xin, Y. Wang, H. Liu, Z. Wang, Zhang. 2015. Treatment Of Oily Waste Water By PVP Grafted PVDF Ultrafiltration. *Journal of Chemical Engineering*. 273: 421–429.

[3] M. J. Um, S. H. Yoon, C. H. Lee, K. Y. Chung, K.Y. Kim. 2001. Flux Enhancement With Gas Injection In Crossflow Ultrafiltration Of Oily Wastewater. *Journal of Water Resistance*. 35: 4095–4101.

[4] P. Canizares, F. Martinez, C. Jimenez, C. Saez, M. A. Rodrigo. 2008. Coagulation And Electrocoagulation Of Oil-In-Water Emulsions. *Journal of Hazardous Materials*. 151: 44–51.

[5] I. Freeman, & Pinnau. 2004. Gas And Liquid Separations Using Membranes: An Overview. *ACS Symposium Series*. 876: 1–23.

[6] S. P. Nunes, K. V. Peinemann. 2001. *Membrane Technology in the Chemical Industry*. Wenham: John Wiley & Sons, Ltd.

[7] A. Sotto, A. Boromand, R. X. Zhang, P. Luis, J. M. Arsuaga, J. Kim, *et al.* 2011. Effect Of Nanoparticle Aggregation At Low Concentrations Of TiO_2 On The Hydrophilicity, Morphology, And Fouling Resistance Of PES– TiO2 membranes. *Journal of Colloid*

Interference Science. 363: 540–50.

[8] A. Razmjou, J. Mansouri, V. Chen. 2011. The Effects Of Mechanical And Chemical Modification Of TiO_2 Nanoparticles On The Surface Chemistry, Structure And Fouling Performance Of PES Ultrafiltration Membranes. *Journal of Membrane Science*. 378: 73–84.

[9] A. V. R .Reddy, D. J. Mohan, A. Bhattacharya, V. J. Shah, P. K. Ghosh. 2003. Surface Modification Of Ultrafiltration Membranes By Preadoption Of A Negatively Charged Polymer. *Journal of Membrane Science*. 214: 211–221.

[10] K. Prashantha, S. G. Park. 2005. Nanosized TiO_2-filled Sulfonated Polyethersulfone Proton Conducting Membranes For Direct Methanol Fuel Cells. *Journal of Application Polymer Science*. 98: 1875–1878.

[11] B. F. Lia, X. S. S. Yana, W. Shuang, T. Yan, Z. Qing. 2015. Influence Of A g/TiO2 Nanoparticle On The Surface Hydrophilicity And Visible-Light Response Activity Of Polyvinylidene Fluoride Membrane. *Applied Surface Science*. 324: 82–89.

[12] Y. Yang, H. Zhang, P. Wang, Q. Zheng, J. Li. 2007. The Influence Of Nano-Sized TiO2 Fillers On The Morphologies And Properties Of PSF UF Membrane. *Journal of Membrane Science*. 288: 231–238.

[13] Y. Zhao & W. Chen. 2011. Ag/TiO_2 Sol Prepared By A Sol–Gel Method And Its Photocatalytic Activity. *Journal of Physic Chemical Solid*. 72: 1312–1318.

[14] S. T. Hoffmann, W. Martin, D. W. Choi. 1995. Environmental Applications Of Semiconductor Photo Catalysis. *Chemical Revision*. 95(1): 69–96.

[15] A. Rahimpour, J. Mohsen, M. Arash, R. Babak. 2012. Structural And Performance Properties Of UV-Assisted Tio_2 Deposited Nano-Composite PVDF/SPES Membranes. *Desalination*. 285: 31–38.

[16] V. Vahid, S. M. Sayed, R. K. Ali, S. Ehsan, Z. Sirus, A. M. Hossein. (2012. TiO_2 Embedded Mixed Matrix PES Nanocomposite Membranes: Influence Of Different Sizes And Types Of Nanoparticles On Antifouling And Performance. *Desalination*. 292: 19–29.

[17] Y. Mansourpanah, S. S. Madaeni, A .Rahimpour, Z. Kheirollahi, M. Adeli. 2010. Changing The Performance And Morphology Of Polyethersulfone/Polyimide Blend Nanofiltration Membranes Using Trimethylamine. *Desalination*. 256: 101–107.

[18] A. Rahimpour, S. S Madaeni, A. H. Taheri, Y. Mansourpanah. 2008. Coupling TiO_2 Nanoparticles With UV Irradiation For Modification Of Polyether Sulfone Ultrafiltration Membranes. *Journal of Membrane Science*. 313: 158–169.

[19] P. Sarah, A. Rahimpour, J. Mohsen. 2012. Synthesis And Characterization Of PVA/PES Thin Film Composite Nano Filtration Membrane Modified With Tio_2 Nanoparticles For Better Performance And Surface Properties. *Journal of Industrial and Engineering Chemistry*. 18: 1398–1405.