

Preparation of PVDF/SiO₂ composite membrane for salty oil emulsion separation: Physicochemical properties changes and its impact on fouling propensity

H P Ngang*, A L Ahmad, S C Low and B S Ooi*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia,
Seri Ampangan 14300, Nibong Tebal, Pulau Pinang, Malaysia

Email: hueyping0404@gmail.com (H P Ngang), chobs@usm.my (B S Ooi)

Abstract. In this study, polyvinylidene fluoride (PVDF)/silica (SiO₂) composite membranes were prepared by diffusion induced phase separation through direct blending method. The roles of SiO₂ particles concentration on membrane physicochemical properties were evaluated through oil emulsion separation under high ionic strength environment whereby hydrophobic interaction is prevalent. Membranes were characterized using field emission scanning electron microscope (FESEM), atomic force microscopy (AFM), contact angle measurement, membrane porosity and pore size distribution. It was expected that by adding the monodispersed SiO₂, it will render the membrane with hydrophilic characteristic. However, it is concomitantly changing the physical properties of the membrane. Addition of SiO₂ caused the changes to the physicochemical properties of the composite membrane and its effects on the fouling propensity were evaluated. It was found that the mean pore size of the membranes increased with the increase of SiO₂ concentration. The addition of hydrophilic SiO₂ had accelerated the precipitation of the membrane dope solution resulting in changes of membrane cross section morphology. FESEM images showed the membrane cross-section morphology of PVDF/SiO₂ composite membrane had gradually changed from finger-like to macrovoid-like structure with the increased of SiO₂ concentration. The hydrophilicity of the PVDF/SiO₂ composite membrane was enhanced which is a desired property for water purification. However, the changes in physical properties (pore size, porosity, and surface roughness) had played more dominant role in the oil emulsion fouling behaviour rather than hydrophilicity enhancement. Due to the salting out effect under high ionic strength environment, hydrophobic interaction played an important role in the oil adsorption. The increment in membrane pore size, porosity, and surface roughness after incorporation of SiO₂ particles had encountered more serious relative flux reduction and lower flux recovery ratio.

1. Introduction

Produced-water is the largest waste stream generated in oil and gas industry [1]. The global produced-water production was estimated to be ~ 250 million barrels per day in year 2007 [2]. It contains mixture of organic and inorganic compounds including dissolved minerals, dispersed oil compound, suspended particles, chemical compound such as corrosion inhibitor, dissolved gases, and surfactant [2]. Discharging produced-water without treating it can pollute surface and underground water soil, which leads to serious environmental problems. The maximum total oil and grease concentration in discharge waste was set by environmental regulation to be 10-15 mg/L. However, major oil fields industries



generate produced water with concentration range between 100 and 1000 mg/L or higher depending on the nature of the crude oil [3, 4].

Many researchers have focused on treating oily saline produced-water in order to meet environmental regulations as well as reuse and recycling of produced-water. Produced-water is conventionally treated through various physical, chemical, and biological methods which include gravity separation and skimming, air flotation, centrifugation, fibrous/packed bed coalescence, de-emulsification and flocculation, which have the intrinsic disadvantages such as low efficiency, high operating cost as well as corrosion problems [5-7]. Most of the conventional treating method cannot effectively treat stable oil emulsion (size < 20 μm) [3, 8]. Therefore, it is appropriate to incorporate membrane technology to refine the final effluent. The use of membrane technology offers a potential solution to the problems of micro or submicron sized of oily wastewater. Ultrafiltration membrane was considered a promising method for treating oily wastewater due to its suitable pore size (0.002-0.05 μm), as compared to common oil droplet size in oily wastewater (0.1-10 μm), which has the capability to remove emulsified oil droplet without any de-emulsification processes [9].

Polyvinylidene fluoride (PVDF) has been widely used for ultrafiltration membrane due to its outstanding thermal stability, chemical resistant, as well as high mechanical strength. However, its low surface energy and hydrophobicity often leads to severe fouling problem and decline in permeability which had limited their application in water treatment process [10, 11]. Therefore, it is necessary to modify the PVDF membrane to improve its membrane hydrophilicity. Membrane surfaces modification by altering their hydrophilicity, surface charge and morphology, are some of the practical ways to reduce membrane fouling propensity [12]. It is well known that nanoparticles can be used to improve the capabilities of polymers in certain extent due to their small size and large surface to volume ratio. Thus, organic-inorganic composite membranes have become an emerging technology for improving their membrane performances, at the same time it can acquire benefit from both organic and inorganic materials such as superior hydrophilicity, permeability and selectivity [13].

Nanoparticles that have been used to modify organic membranes include titanium dioxide (TiO_2), alumina (Al_2O_3), silica (SiO_2), etc [14-18]. Among different inorganic materials used, silica (SiO_2) has received most attention owing to its convenient operation, mild reactivity, good thermal and mechanical stability, and well known chemical properties [19]. These studies showed that the blending of the hydrophilic inorganic materials into membrane matrix increased the surface hydrophilicity and reduce potential adsorption of foulant. However, it is known that the addition of inorganic components as additive to a polymer dope solution did play an important role in affect the formation of membrane structure. The final membrane morphology varies greatly in term of membrane pore size, porosity, hydrophilicity as well as membrane surface roughness which are the controlling factors for membrane fouling.

The aim of this paper is to study the role of SiO_2 particles towards membrane physicochemical properties changes and its fouling evaluation using high salinity oil emulsion as the foulant. The physicochemical properties of prepared membranes were expected to change during high salinity oil emulsion separation due to exclusion of charge repulsion and salting out effect, which could indirectly affect the fouling propensity.

2. Experimental

2.1. Materials

Tetraethylorthosilicate (TEOS, 99.999 %), sea salts, and Triton X-100 were purchased from Sigma Aldrich. Ethanol, ammonium solution 25 %, and Dimethylformamide (DMF) were purchased from Merck, Germany. Polyvinylidene fluoride (Solef® PVDF) was supplied by Solvay Solexis, France. Crude oil was supplied by Petronas Malaysia. PVDF was dried in oven at 70 °C overnight prior to use, while other organic chemicals were obtained in reagent grade and used as received.

2.2. Preparation of silica particles

Monodispersed silica particles were synthesized using Stöber method [20]. Firstly, 200 mL of ethanol, 22 mL of deionized water and 12 mL of ammonium solution 25 % were added together into 500 mL three neck flask and stirred using magnetic stirrer at 350 rpm. Next, 12 mL of TEOS was added to the mixture at 30 °C. The reaction was continued for 24 h. The produced silica particles were purified by three cycles of centrifugation and re-suspension in deionized water. The SiO₂ particles were then re-dispersed in DMF solvent and the particle concentration was determined using gravimetric method prior to use.

2.3. Membrane Preparation

The predetermined amount of SiO₂ particles suspension was dispersed in DMF solvent under sonication for 15 min. 18 wt.% of PVDF powder was dissolved into the SiO₂ particles suspension and stirred at 65 °C for 4 h. The solution was left to be stirred overnight at 40 °C to form a homogenous solution. The final solution was then subjected to degassing for 10 min to remove all the trapped bubbles and let it stand for 30 min prior to membrane casting. The solution was cast on the tightly woven polyester sheet using an automatic film applicator (Elcometer 4340, E.U.). The membrane casting nominal thickness was fixed at 200 µm and cast at constant speed of 0.06 cm/s. It was then immediately immersed into the water bath of distilled water (25 °C) and leave it overnight in order to remove the DMF solvent residual. The detail of membrane synthesis parameter used was summarized in Table 1.

Table 1. Detail of the membrane synthesis parameter.

Membrane	PVDF (wt.%)	DMF (wt.%)	SiO ₂ (wt.%)
M18-0	18	82.0	0.0
M18-0.1	18	81.9	0.1
M18-0.5	18	81.5	0.5
M18-1.0	18	81.0	1.0
M18-2.0	18	80.0	2.0

2.4. Preparation of oil emulsion

Oil emulsion was freshly prepared before every filtration test. Firstly, saline solution was prepared by dissolving 32 g of sea salts in 1 L of distilled water under stirred condition. Subsequently, 50 mg of crude oil was added into the prepared salty solution to obtain 50 mg/L high salinity oil emulsion. Surfactant (Triton X-100) was then added into the solutions to stabilize the oil emulsion. The prepared oil emulsion was then dispersed using a blender (Khind BL-1515, power = 300 W) for 2 min. Finally, the dispersed solution was sonicated for 5 min to remove any air bubble which might exist during the dispersing process.

2.5. Characterizations

2.5.1. Field emission scanning electron microscope. The membrane surface and cross sectional morphology were observed using Field Emission Scanning Electron Microscope (FESEM, Quanta Feg 450, FEI, USA) at an accelerating voltage of 5 kV. The membranes were immersed into liquid nitrogen and cryogenically cracked for membrane cross-sectional observation to prevent membrane structure rupture.

2.5.2. Pore size distribution. Capillary Flow Porometer, Porolux 1000 (Benelux Scientific, Belgium) was used to determine the pore size distributions of the prepared membranes. Perfluoroethers was used as a pore wetting agent. Three membrane samples (diameter of 20 mm) were characterized and analysed using the LabView software to minimize the experimental error.

2.5.3. Contact angle measurement. Water contact angle instrument (Rame-Hart Model 300 Advanced Goniometer) based on sessile drop methods was employed to measure the membrane surface wettability. The acquired images were analysed using DROPimage software to obtain the contact angles.

2.5.4. Atomic force microscopy. The surface topography and roughness of the membranes in the dry state were analysed by using atomic force microscope, AFM (Park Scientific, Korea, XE-100). The membrane areas of $20\ \mu\text{m} \times 20\ \mu\text{m}$ were scanned by non-contact mode.

2.5.5. Dynamic light scattering analysis. A dynamic light scattering apparatus (Malvern Zetasizer Nano ZS90) was used to measure the size of the oil droplets in oil emulsion with refractive index of 1.47 and 1.335 for the crude oil and dispersant (sea salt solution), respectively. The refractive index of 1.46 (SiO_2) and 1.428 (DMF) were applied to measure the hydrodynamic diameter (D_h) of SiO_2 particles in DMF solvent.

2.5.6. Membrane porosity. The membrane porosity (ε_p) represents the total volume of the pores divided by the total volume of the porous membrane. Five pieces of square-sized membranes with an area of $6.25\ \text{cm}^2$ each were dried in an oven at $60\ ^\circ\text{C}$ until a constant weight was observed. Then, the membrane dry weight was measured. The dried membranes were then immersed into 2-butanol and degassed for 30 s at room temperature to prevent air trapped in the membrane internal pores and let in room temperature for 2 h. After that, the membrane surface was dried using filter paper and weighed immediately to avoid evaporation of 2-butanol from membranes internal pores. The membrane porosity was calculated using equation (1),

$$\varepsilon_p = \left(\frac{w_1 - w_2}{\rho_b} \right) / \left(\frac{w_1 - w_2}{\rho_b} + \frac{w_2}{\rho_p} \right) \quad (1)$$

where ε_p is the membrane porosity (%), w_1 is the weight of the wet membrane (g), w_2 is the weight of the dry membrane (g), ρ_p is the specific gravity of the PVDF polymer ($1.78\ \text{g/cm}^3$) and ρ_b is the specific gravity of 2-butanol ($0.81\ \text{g/cm}^3$). 2-butanol was chosen as a wetting liquid because it did not swell the PVDF membrane and could wet the hydrophobic PVDF membrane well to ensure complete pores filling.

2.6. Membrane permeation test

The membrane performance in high salinity oil emulsion separation was evaluated using cross-flow ultrafiltration (UF) unit (Figure 1). The membrane chamber (Sterlitech, CF042) has an effective area of $0.0042\ \text{m}^2$. The pure water and oil emulsion were re-circulated at a constant flow rate of $0.4\ \text{L/min}$ using a peristaltic pump (Flex-Pro A4 Series). The membranes were subjected to $30\ \text{min}$ compression at transmembrane pressure (TMP) of $1.5 \pm 0.1\ \text{bar}$ prior to each filtration process. After the membrane compression process, the pure water permeation was carried out to measure the membrane pure water flux (J_1) by using equation (2). The permeate was collected at a time interval of $1\ \text{min}$ and the readings were directly recorded using an electronic balance which was connected to a data acquisition system (AND Super Hybrid Sensor, Model: Fx-3000i, A&D Company, Limited). One litre of $50\ \text{mg/L}$ oil emulsion was first prepared in the feed tank. The feed solution was then continuously pumped and recirculated through the cross-flow filtration cell. Feed pressure was monitored continually throughout the experiments. After $1\ \text{h}$ of oil emulsion filtration, the membranes were rinsed by circulating pure water ($25 \pm 1\ ^\circ\text{C}$) for $10\ \text{min}$ to remove loosely bound oil droplet. The pure water flux (J_2) ($\text{L/m}^2 \cdot \text{h}$) at $25 \pm 1\ ^\circ\text{C}$ was recorded and the flux recovery ratios (FRR) was calculated based on equation (2) and equation (3). The relative flux reduction (RFR) was applied to examine the antifouling properties by using equation (4).

$$J = \frac{V}{A \cdot t} \quad (2)$$

$$FRR = \frac{J_2}{J_1} \times 100\% \quad (3)$$

$$RFR = \left(1 - \frac{J_p}{J_1}\right) \times 100\% \quad (4)$$

where V (L) is the volume of water permeate, A (m^2) is the membrane area, t (h) is time taken for permeate collected, J_1 is the initial pure water flux, J_2 is the pure water flux after 10 min crossflushing, and J_p is oil emulsion permeate flux. All the presented results are average data obtained from three measurements. Membranes with higher value of FRR with lower value of RFR indicate better antifouling properties.

The oil concentration in the permeate samples were determined using UV-visible spectrophotometer (UV mini-1240, Shimadzu) at maximum absorbance of wavelength 220 nm. The rejection of the solute, R (%) was calculated based on equation (5):

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \quad (5)$$

where c_p is the oil concentration in the permeate (mg/L) and c_f is the initial concentration of the oil in the feed (mg/L).

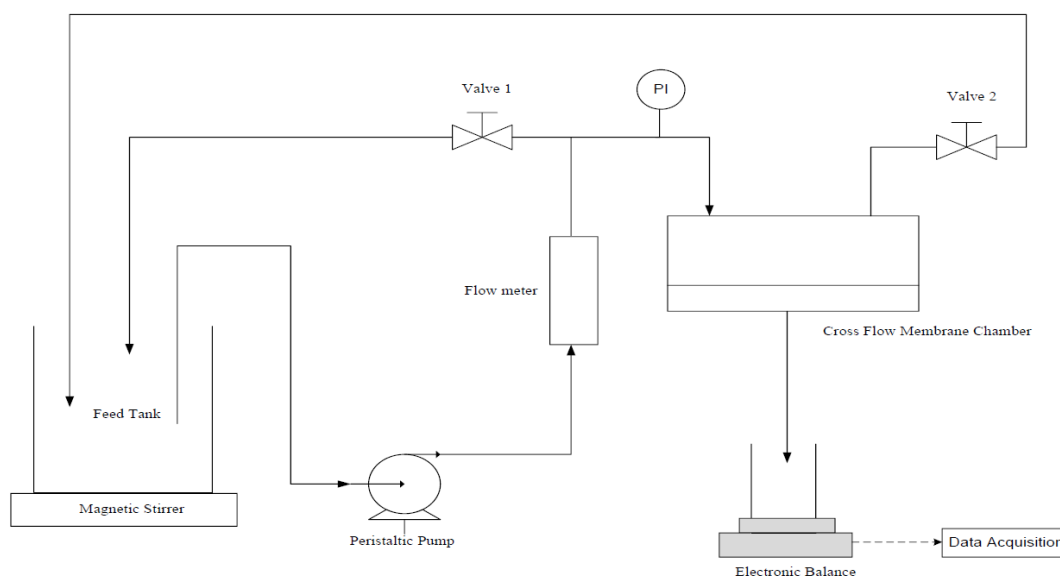


Figure 1. Schematic diagram of cross flow ultrafiltration unit.

3. Results and discussion

3.1. Characterization of oil emulsion and SiO_2 particles

The hydrodynamic diameter (D_h) of the oil emulsion was calculated based on Brownian motion of the oil droplet. Figure 2 shows the measurement of intensity based oil droplet hydrodynamic diameter distribution. The oil droplet size distribution for 50 mg/L oil emulsion was found in the range of 38 – 900 nm with an average oil droplet diameter of 153 ± 4.83 nm. The bigger oil droplet size compared to membrane mean pore size (40 – 50 nm) was used as foulant to minimize direct pore blocking effect.

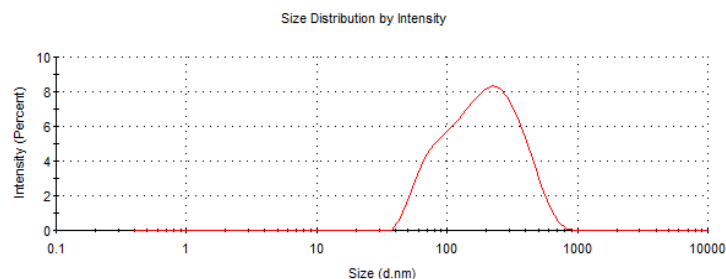


Figure 2. Size distributions of oil droplets in oil emulsion (oil concentration = 50 mg/L).

The hydrodynamic size distribution of SiO₂ particles in DMF solvent was characterized using dynamic light scattering prior to use. Figure 3 shows the SiO₂ particle size distribution in DMF solvent. The result shows average SiO₂ particle size with narrow distribution at 248.6 nm with 0.018 polydispersity index.

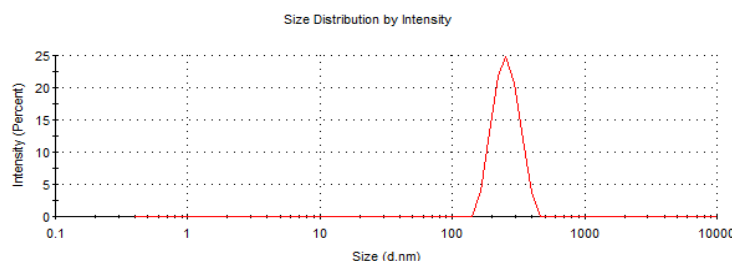


Figure 3. Size distributions of SiO₂ particles in DMF solvent.

3.2. Physicochemical properties of the PVDF/SiO₂ composite membrane

Surface and cross-sectional images of membrane prepared from PVDF/SiO₂/DMF systems with different contents of SiO₂ additive are shown in Figure 4. The SEM images show that all prepared membranes were typical highly porous surface and combination of finger-like and sponge-like cross-section. It can be seen that the membrane surface pore sizes as well as surface porosity had increased with the increase of SiO₂ concentration as shown in Figure 4 (left). The SiO₂ particles dispersed well on the membrane surface and the support structure without observable particle aggregation. The phenomenon of pore widening was observed due to two fold reasons. Addition of hydrophilic SiO₂ particles increased the non-solvent influx and cause instantaneous demixing and pore enlargement. In addition, the different in shrinkage rate between polymer and SiO₂ during membrane drying process had further enhanced the pore rupture and enlargement.

Figure 4 (right) shows the SEM cross-sectional images of membranes prepared with different SiO₂ concentration added. Generally, non-solvent (water) inflow and solvent outflow (DMF) will be changed accordingly with the addition of additives into polymer dopes solution. The addition of SiO₂ particles increases the instability and viscosity of the polymer dope solution, caused instantaneous demixing during phase inversion process, resulting in macrovoid-like structure at higher SiO₂ concentration. The hydrophilic nature of SiO₂ particle (high affinity of SiO₂ towards water) enhances the kinetic of water influx during the phase inversion process. The diameter of finger-like structure became larger and irregular in shape after addition of 2 wt.% of SiO₂ particles. Apart from thermodynamics aspects, the membrane formation process is also influenced by the kinetic aspects during phase inversion process. In term of kinetic aspects, increasing SiO₂ concentration will enhance the viscosity of the polymer dopes solution. Higher viscosity will cause a slower diffusion rate of solvent and non-solvent exchanges, resulting macrovoid formation in the membrane structure [21, 22].

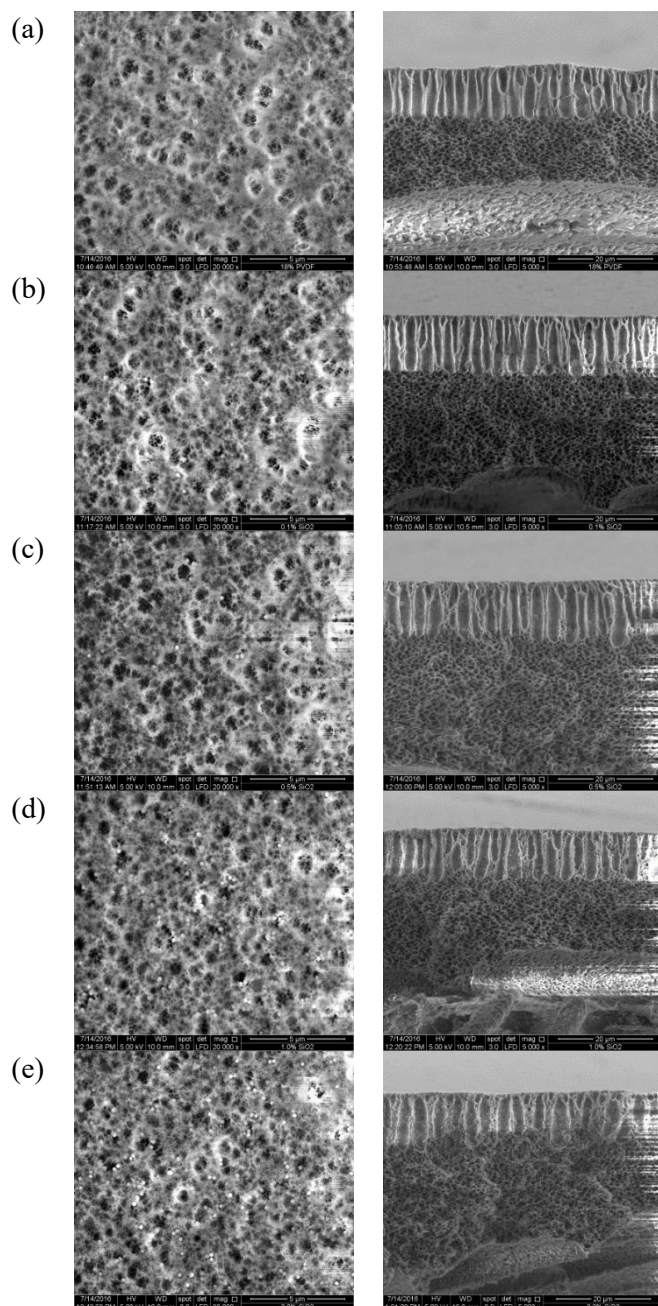


Figure 4. FESEM images of membrane surface structure (left) and cross sectional structure (right) for (a) M18-0, (b) M18-0.1, (c) M18-0.5, (d) M18-1.0, and (e) M18-2.0.

The surface morphology of the prepared membranes was further analysed using AFM as shown in Figure 5. The surface roughness values (R_q) was tabulated in Table 2. The pure PVDF membrane exhibits the R_q value of 63.128 nm, which is lowest among all prepared membranes. These images indicated that the membranes surface micro-roughness increased structurally with the increased of SiO₂ contents which might relate to the higher surface porosity as seen in previous FESEM surface morphology (Figure 4 (left)). Results in Table 2 show that the R_q had increased from 63.128 nm to 87.430 nm with the increase of SiO₂ concentration from 0 wt.% to 2 wt.%. The surface roughness increment was governed by the SiO₂ particles itself rather than the polymer nodular structure.

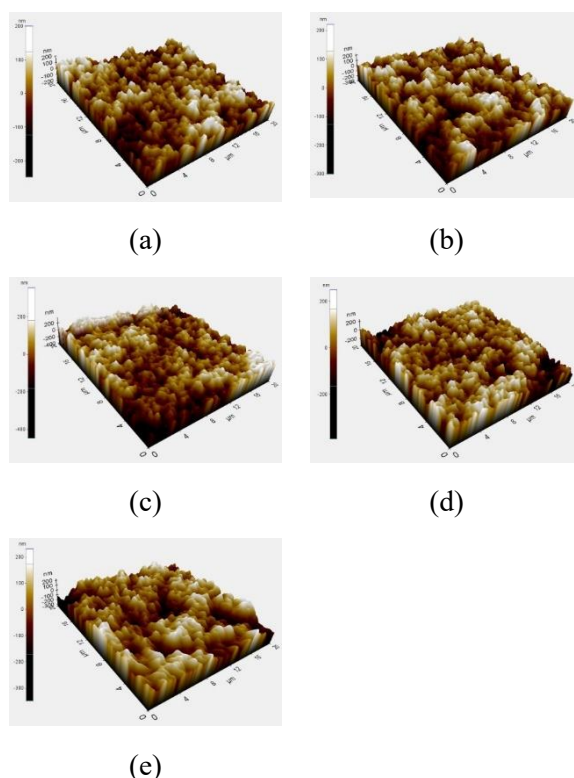


Figure 5. AFM images of PVDF membrane surface for (a) M18-0, (b) M18-0.1, (c) M18-0.5, (d) M18-1.0, and (e) M18-2.0.

Table 2. The effect of SiO₂ concentration on membrane physical properties.

Membrane	R_q (nm)	Porosity (%)	Pore Size (nm)
M18-0	63.128	64.17 ± 0.06	39.81 ± 6.80
M18-0.1	65.162	64.73 ± 0.13	40.06 ± 8.44
M18-0.5	74.874	65.39 ± 0.33	44.87 ± 7.29
M18-1.0	85.132	65.90 ± 0.28	47.97 ± 5.75
M18-2.0	87.430	66.28 ± 0.19	50.78 ± 8.08

The PVDF/SiO₂ composite membranes were then characterized in term of surface wettability. Theoretically, surface wettability (contact angle) is affected by membrane surface porosity, roughness, and its hydrophilicity. It was expected that the membrane prepared at higher concentration of hydrophilic additives will possess lower contact angle. Figure 6 shows that at low SiO₂ content, the hydrophilic nature of the particles slightly reduced the surface contact angle. However, at higher particle concentration (2 wt.%), concomitant increased of porosity induced lower surface energy and gave higher contact angles.

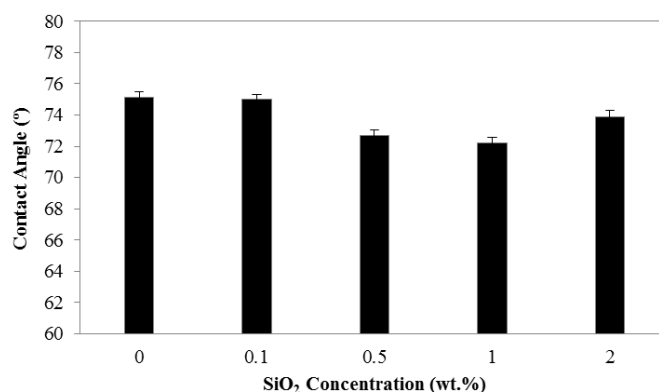


Figure 6. Effect of SiO₂ concentration on membrane contact angle.

3.3. Permeability and antifouling properties of PVDF/SiO₂ composite membranes for salty oil emulsion separation

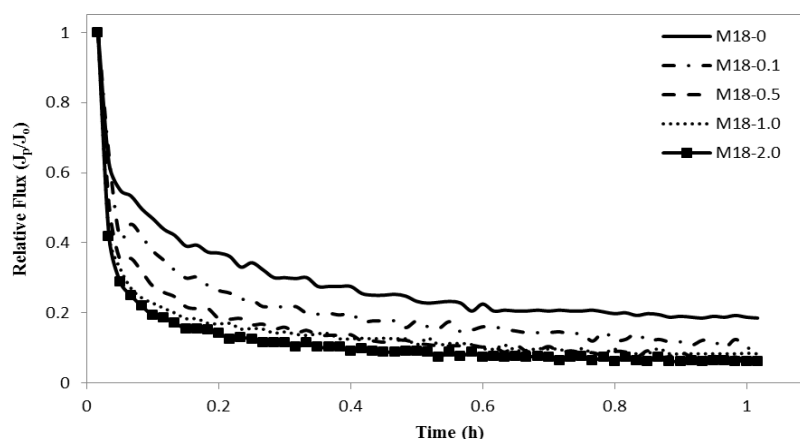
The prepared membranes were evaluated in terms of membrane permeability, oil emulsion rejection, relative flux reduction (RFR) and flux recovery ratio (FRR) using cross-flow ultrafiltration experiments. Table 3 shows the effect of SiO₂ concentration on membrane performance. The membrane pure water fluxes increased with the increase of SiO₂ concentration from 57 to 93.86 L/m²·h for M18-0 to M18-2.0, with the mean pore size from 39.81 to 50.78 nm, respectively. Theoretically, pore enlargement and hydrophilicity improvement are considered as main reason for membrane flux enhancement. However, in this study, the role of pore size enlargement seems to be more dominant than membrane hydrophilicity as can be seen from the highest contact angle of M18-2.0 which still having high flux. The addition of SiO₂ particles gave a positive effect on membrane pure water flux due to the pore size enlargement which allow higher passage of water permeate through the membrane. This result was also in accordance to the results of porous FESEM surface morphology for PVDF/SiO₂ composite membrane (Figure 4 (left)) as discussed earlier.

The oil rejection performance data was demonstrated in Table 3. It was found that all prepared membranes showed very promising oil rejection with 99 % of oil removal achieved. It is due to the bigger mean oil droplet size (153 nm) as compared to prepared membranes mean pore size (39.81 - 50.78 nm). The prepared membrane pores were relatively smaller which enable it to retain bigger oil droplet in high salinity oil emulsion from passing through.

The relative flux reduction (RFR) of oil emulsion was calculated and compared to evaluate the membrane fouling behaviour. Membrane with lower RFR value possesses high antifouling properties. Table 3 shows the RFR values for PVDF membrane with different SiO₂ concentration added. It is interesting to know that the RFR value of the prepared membrane is increased with the increased of SiO₂ concentration, which indicated that the oil droplet fouling behaviour was getting serious after introducing SiO₂ particles into the polymer matrix. The oil droplets start to deposit or adsorb onto the membrane surface by hydrophobic interaction. Figure 7 shows drastic reduction of relative flux for membrane M18-2.0 (0.42) compared to M18-0 (0.65) once the oil emulsion was introduced into the system. More serious oil permeate flux reduction was observed in PVDF/SiO₂ composite membrane as compared to pure PVDF membrane especially at high SiO₂ concentration (M18-2.0), which is due to the higher membrane porosity, pore size, and surface roughness as tabulated in Table 2. The chemical property of hydrophilic PVDF/SiO₂ membranes deteriorate due to the exclusion of charge repulsion under high salinity oil emulsion separation. The presence of salt ions in oil emulsion could disrupt the SiO₂ hydration layer, thus losing its hydrophilicity (Hofmeister effect) [23-25]. In this case, the membrane physical properties (surface roughness, porosity and pore size) are playing more dominating role in oil emulsion fouling.

Table 3. The effect of SiO₂ concentration on membrane performance

Membrane	PWF (L/m ² ·h)	Rejection (%)	RFR (%)	FRR (%)
M18-0	57.00 ± 2.53	99.35 ± 0.13	81.45 ± 1.07	57.89 ± 1.20
M18-0.1	59.57 ± 1.27	99.19 ± 0.17	89.92 ± 1.17	48.92 ± 1.21
M18-0.5	80.71 ± 3.15	99.08 ± 0.20	93.27 ± 1.26	41.24 ± 1.39
M18-1.0	87.14 ± 2.90	99.09 ± 0.21	93.30 ± 1.20	40.31 ± 1.20
M18-2.0	93.86 ± 4.36	98.99 ± 0.24	93.76 ± 1.40	33.64 ± 1.47

**Figure 7.** Effect of SiO₂ concentration on relative flux profile during oil emulsion separation.

The regeneration or reusability of the membrane is always a critical concern in membrane technology. The membrane (after oil emulsion separation) were washed thoroughly by circulating the fresh distilled water for 10 min, and the cleaned membrane's water flux was measured again in order to calculate the flux recovery ratio (FRR). The membrane FRR has direct relation with membrane physical properties including membrane pore size, porosity and surface roughness, as discussed earlier. Membrane with bigger pore size and porosity was expected to have difficulties in membranes cleaning, resulting in lower values of flux recovery ratio. Table 3 reveals that the FRR values were decreased with the increased of SiO₂ concentration. This phenomenon was due to the higher pore size and surface roughness at higher SiO₂ concentration which can easily trap the foulant in the valley as well as inside the pore, thus resulting in difficulty to wash away via crossflushing.

4. Conclusion

PVDF/SiO₂ composite membranes were synthesized by using diffusion induced phase separation technique for oil emulsion separation. The influence of SiO₂ concentration on membrane properties and fouling evaluation were studied. FESEM results show that addition of hydrophilic SiO₂ particles had increased the non-solvent (water) inflow thus caused instantaneous demixing to occur during phase inversion process, resulting in gradual change of membrane cross-sectional structure from finger-like to macrovoid-like structure. The results showed that the pore size, porosity and surface roughness of the PVDF membranes were increased with the addition of SiO₂ particles. Although the addition of SiO₂ particles increases the surface wettability, however the effect of microstructure roughness, pore size, and porosity increment has compensated the hydrophilic characteristic of SiO₂ particles during high salinity oil emulsion separation. The RFR value of the prepared membrane increased with the increase of SiO₂ concentration, indicated the oil droplet fouling behaviour getting serious after introducing of

SiO₂ particles into the polymer matrix. The membrane physical properties play an important role in the oil emulsion fouling behaviour rather than its hydrophilicity enhancement. It is because the high salinity oil emulsion resulted in exclusion of charge repulsion and at the same time disrupts the hydration layer of SiO₂ particles, thus losing its hydrophilicity properties. Furthermore, the results show low flux recovery ratio for PVDF/SiO₂ composite membranes compared to pure PVDF membrane. It is due to the higher pore size and surface roughness which can easily trap the foulant within the valley and pores thus exert higher difficulty in cleaning the membrane via crossflushing.

Acknowledgements

The authors are grateful for the financial supports from Universiti Sains Malaysia (RU Grant) (1001/PJKIMIA/814210) and Membrane Science and Technology Cluster (1001/PSF/8610011). In addition, the first author also thanks the Ministry of Higher Education (MyPhD) for financial support.

References

- [1] Munirasu S, Haija M A and Banat F 2016 *Process Saf. Environ.* **100** 183-202.
- [2] Fakhru'l-Razi A, Pendashteh A, Abdullah L C, Biak D R A, Madaeni S S and Abidin Z Z 2009 *J. Hazard. Mater.* **170** 530-51.
- [3] Chakrabarty B, Ghoshal A K and Purkait M K 2010 *Chem. Eng. J.* **165** 447-56.
- [4] Tummons E N, Tarabara V V, Chew Jia W and Fane A G 2016 *J. Membr. Sci.* **500** 211-24.
- [5] da Silva S S, Chiavone-Filho O, de Barros Neto E L and Foletto E L 2015 *Desalin. Water Treat.* **56** 1802-08.
- [6] Krebs T, Schroën C G P H and Boom R M 2012 *Chem. Eng. Sci.* **71** 118-25.
- [7] Chen X, Lu H, Jiang W, Chu L-Y and Liang B 2010 *Ind. Eng. Chem. Res.* **49** 9279-88.
- [8] Chen W, Peng J, Su Y, Zheng L, Wang L and Jiang Z 2009 *Sep. Purif. Technol.* **66** 591-97.
- [9] Chen W, Su Y, Zheng L, Wang L and Jiang Z 2009 *J. Membr. Sci.* **337** 98-105.
- [10] Kang G-d and Cao Y-m 2014 *J. Membr. Sci.* **463** 145-65.
- [11] Zuo D-y, Xu Y-y, Xu W-l and Zou H-t 2008 *Chinese J. Polym. Sci.* **26** 405.
- [12] Rana D and Matsuura T 2010 *Chem. Rev.* **110** 2448-71.
- [13] Cong H, Radosz M, Towler B F and Shen Y 2007 *Sep. Purif. Technol.* **55** 281-91.
- [14] Ngang H P, Ooi B S, Ahmad A L and Lai S O 2012 *Chem. Eng. J.* **197** 359-67.
- [15] Razmjou A, Mansouri J and Chen V 2011 *J. Membr. Sci.* **378** 73-84.
- [16] Yan L, Li Y S and Xiang C B 2005 *Polymer* **46** 7701-06.
- [17] Huang X, Zhang J, Wang W, Liu Y, Zhang Z, Li L and Fan W 2015 *RSC Adv.* **5** 18258-66.
- [18] Ahmad A L, Majid M A and Ooi B S 2011 *Desalination* **268** 266-69.
- [19] Ogoshi T and Chujo Y 2005 *J. Polym. Sci. Poly. Chem.* **43** 3543-50.
- [20] Stöber W, Fink A and Bohn E 1968 *J. Colloid Interf. Sci.* **26** 62-69.
- [21] Zheng Q-Z, Wang P, Yang Y-N and Cui D-J 2006 *J. Membr. Sci.* **286** 7-11.
- [22] Pagidi A, Saranya R, Arthanareeswaran G, Ismail A F and Matsuura T 2014 *Desalination* **344** 280-88.
- [23] Jhon Y K, Bhat R R, Jeong C, Rojas O J, Szleifer I and Genzer J 2006 *Macromol. Rapid Comm.* **27** 697-701.
- [24] Schild H G and Tirrell D A 1990 *J. Phys. Chem.* **94** 4352-56.
- [25] Von Hippel P H and Schleich T 1969 *Accounts Chem. Res.* **2** 257-65.