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Effect of poly(ethylene glycol) on the properties of mixed matrix membranes for improved filtration of highly concentrated oily solution

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Abstract. Mixed matrix membrane (MMM) composed of organic and inorganic materials has been widely studied for its potential use in water and wastewater treatment, owing to its improved properties compared to the pristine membrane. In this work, the filtration performance of MMM composed of polyethersulfone (PES) and hydrous manganese oxide (HMO) nanoparticles was further improved by adding pore forming agent - poly(ethylene glycol) (PEG) into dope solution to improve membrane hydrophilicity and structural morphology so as the developed membranes are suitable for handling highly concentrated oily solution (30,000 ppm oil concentration). Compared to the structure of control PES membrane that was composed of irregular microvoids, the presence of PEG and hydrophilic nanomaterial in the MMM was able to form extended finger-like structure from top to the bottom section of membrane and enhance its surface hydrophilicity, significantly improving water permeability. The improved water flux of MMM did not compromise the rejection rates of oil and chemical oxygen demand (COD) as the MMMs achieved comparable separation efficiency like the control membrane. The findings of this work revealed the potential use of MMM for the treatment of highly concentrated oily wastewater.

Keywords: mixed matrix membranes; PEG; HMO; oil rejection; flux

1. Introduction

Mixed matrix membrane (MMM) composed of organic and inorganic materials has been widely researched for water purification (Jamshidi Gohari *et al.* 2013) and wastewater treatment (Jamshidi Gohari *et al.* 2014a). The advancement in the nanomaterial synthesis over the last decade had opened up the opportunity to further improve the MMM performance with respect to surface hydrophilicity, water permeability, antifouling resistance and solute removal rate.

Some of the nanomaterials that have been used for MMM fabrication are titanium dioxide (TiO2) (Ong *et al.* 2015), hydrous aluminum oxide (HAO) (Jamshidi Gohari *et al.* 2015), halloysite nanotube-hydrous ferric dioxide (HNT-HFO) (Wan Ikhsan *et al.* 2018) and iron oxide (Al-Husaini *et al.* 2019). In addition to these nanomaterials, our group had worked on hydrous manganese oxide (HMO) nanoparticles for MMM synthesis and used the membrane particularly for oily solution

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treatment (Jamshidi Gohari *et al.* 2014a, Lai *et al.* 2017). Compared to the commercially available TiO2 nanoparticle, HMO is found to be more hydrophilic owing to the presence of large quantity of -OH functional groups (Jamshidi Gohari *et al.* 2014b). Besides, it also offers several advantages such as large surface area and microporous structure. The results from our previous work indicated that the HMO-modified MMMs showed better water flux and antifouling resistance compared to the pristine membrane without experiencing negative effect on the separation rate. However, these membranes were developed for handling low concentrated oily solution (100-2000 ppm).

In order to examine the potential of the MMM for the treatment of highly concentrated oily solution (up to 30,000 ppm), the properties of the membrane are required further modification. To ensure the MMM is still able to produce reasonably good water flux under harsh conditions, the membrane with low tortuosity and greater porosity without affecting surface chemistry is desirable. A literature research revealed that hydrophilic poly(ethylene glycol) (PEG) is potential for this purpose. PEG is widely used as pore forming agent as another material - polyvinylpyrrolidone (PVP) for ultrafiltration (UF) membrane to improve structural porosity, leading to enhanced water permeability (Lau *et al.* 2015). In addition, the highly soluble characteristic of PEG tends to leach out easily during membrane fabrication process that uses water as coagulation medium. This phenomenon will ensure small amount of PEG remaining in the membrane matrix and would not create issue of incompatibility with main forming membrane material and inorganic nanoparticles.

The objective of this work is to investigate the impact of pore forming agents-PEG on the properties of MMMs composed of PES and HMO for enhanced filtration of highly concentrated oily solution. The quantity of the PEG in the MMM was varied in the range of zero and 10 wt% and the resultant membranes were evaluated with respect to the permeability, oil rejection and COD rejection. Instrumental analyses carried out using Fourier transform Infrared (FTIR) spectroscope, scanning electron microscope (SEM) and contact angle goniometer were also included in this work to provide additional supporting evidence on the improved filtration performance of MMMs.

2. Methodology

2.1 Materials

HMO nanoparticles were self-synthesized via precipitation between potassium permanganate (KMnO4, purity >99%, Fisher Chemical) and manganese(II) sulfate monohydrate (MnSO4•H2O, purity >98%, Acros Organics). Polyethersulfone (PES) with molecular weight of 15,000 g/mol (Solvay RadelR A-300), N-methyl-2-pyrrolidone (NMP, purity 99%, RCl Labscan), polyvinylpyrrolidone (PVP) with molecular weight of 24,000 g/mol (Sigma-Aldrich) and poly(ethylene glycol) (PEG) with molecular weight of 600 g/mol (Thermo Fisher Scientific) were used as the raw materials in fabricating polymeric membranes. Synthetic oily solution was prepared by mixing crude oil sample obtained from Terengganu Crude Oil Terminal, East Coast of Peninsular Malaysia with sodium dodecyl sulfate (SDS, Sigma-Aldrich). Reverse osmosis (RO) water (ASTM Type III) produced from Millipore® water system was used as water source in all experimental works in this study.

2.2 Dope solution preparation

Six different dope solutions with various compositions as shown in Table 1 were prepared in this

Table 1 Dope formulation of PES membrane and MMMs

Dope solution (wt%)	PES	M0	M1	M3	M5	M10
PES	15.00	12.79	12.79	12.79	12.79	12.79
PVP	1.50	1.28	1.28	1.28	1.28	1.28
NMP	83.50	71.22	71.22	71.22	71.22	71.22
HMO	-	14.71	14.71	14.71	14.71	14.71
PEG[a]	-	-	1.00	3.00	5.00	10.00
PES:HMO ratio	1: 0	1:1.15	1:1.15	1:1.15	1:1.15	1:1.15

[a] The weight percentage of PEG was calculated as weight percentage of the M0 solution without PEG.

work. MMMs with different PEG loading (M0-M10) were fabricated and compared with control PES membrane to investigate the effect of PEG on the membrane properties for oily wastewater treatment. The dope formulation of control membrane was exactly same as our previously published work (Doraisammy *et al.* 2018). In brief, dehydrated PES pellets, PVP and PEG were completely dissolved in NMP to form homogenous PES solution by vigorous stirring for overnight. To prepare dope solution for MMM fabrication, HMO was first dispersed in NMP under ultrasonication effect prior to addition of polymer and additives. The dope solution was then degassed for 1 h followed by storage at room temperature for overnight before being used for casting.

2.3 Flat sheet membrane casting

Flat sheet membrane was fabricated by pouring slowly as prepared dope solution onto a smooth glass plate followed by casting using a glass rod. The casted film (with thickness of 100±10 μm) was then immersed into water coagulation bath at room temperature for solvent/non-solvent exchange to occur to form asymmetric membrane structure. The formed membrane film was then transferred to another clean water bath after peeling off from the glass plate. This is to ensure residual solvent and pore-forming agents could be removed from the membrane. At last, the membrane was dried at room temperature and stored in dry condition prior to use. MMMs were denoted as M0, M1, M3, M5 and M10 according on the weight percentage of PEG in the dope solution (Table 1).

2.4 Characterization

Membrane surface wetting properties were examined by contact angle goniometer (DataPhysics OCA 15Pro) using RO water as probe water. PerkinElmer Frontier™ Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometer was utilized to characterize the presence of functional groups on membrane surface. The spectra were recorded at wavelength of 650-4000 cm^{-1} at resolution of 4 cm^{-1} and a total of 32 scans were made for each sample. The membrane surface and cross-sectional morphologies were visualized via scanning electron microscope (SEM, TM3000, Hitachi). The membrane sample was freeze-fractured in liquid nitrogen in preparing sample for cross-sectional imaging. All membrane samples were sputter-coated with platinum to avoid charging during SEM analysis.

2.5 Filtration experiments

2.5.1 Synthetic oily wastewater preparation

Highly concentrated oily wastewater sample (30,000 ppm) was synthesizing by blending pre-determined weight of crude oil and SDS (in 9:1 ratio) with RO water using a mechanical blender. The blending process was performed for 15 min to obtain stabilized oil-in-water emulsion. The oily wastewater was freshly prepared for each set of experimental works.

2.5.2 Membrane performance evaluation

Sterlitech™ CF042P crossflow permeation cell with 42-cm^2 effective membrane surface area was utilized to study the separation performance of fabricated membranes in treating oily wastewater. Prior to any sample collection, each membrane was compacted at 2 bar for 30 min followed by 1 bar for 15 min to achieve steady state of permeate flux. The membrane separation performance was then evaluated with respect to pure water permeability (PWP), oily solution permeability and oil/ chemical oxygen demand (COD) rejection at 1 bar. The permeability of the membranes, A (L/m^2.hr.bar) was calculated using Eq. (1).

$$A = \frac{\Delta V}{A_m \cdot \Delta t \cdot P} \tag{1}$$

where ΔV, A_m, Δt and P are the collected permeate volume, effective membrane area, time used to collect permeate, operating pressure, respectively. The rejection, R(%) of the membranes was calculated using Eq. (2).

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where C_p and C_f are the solute concentration in permeate and feed solution, respectively. The oil concentration and COD level of water samples was determined by Hach DR5000 UV-vis spectrophotometer at wavelength of 305 nm (for oil concentration) and with 435 HR COD reagents, respectively.

3. Results and discussion

Fig. 1 compares the FTIR spectra of control PES membrane with the MMMs modified by different PEG quantity. As PES is the main membrane forming material used for both control membrane and MMMs fabrication, the peaks corresponding to the PES polymer are able to be detected for all the membranes fabricated in this work. These include asymmetric *O=S=O* stretching at 1290 cm^{-1}, symmetric *O=S=O* stretching at 1150 cm^{-1}, asymmetric C-O-C stretching at 1250 cm^{-1} and CH_3-C-CH_3 stretching at 1500 cm^{-1}. However, by comparing between the control PES membrane and MMMs, it is found that the MMMs exhibit higher band intensity at the region of 3250-3500 cm^{-1} and this can be attributed to the presence of hydrophilic HMO that is associated with abundant amount of -OH functional group in the membrane matrix (Jamshidi Gohari *et al.* 2014b). No significant difference is able to be seen among the MMMs although different amount of PEG was used to modify the membranes. This could be explained by the fact that PEG is highly soluble in the water and they are mainly leached out from the membrane matrix during fabrication process that used large amount of water to initiate phase inversion. The presence of the remaining PEG in small quantity is thus not easy to be detected by FTIR spectroscope.

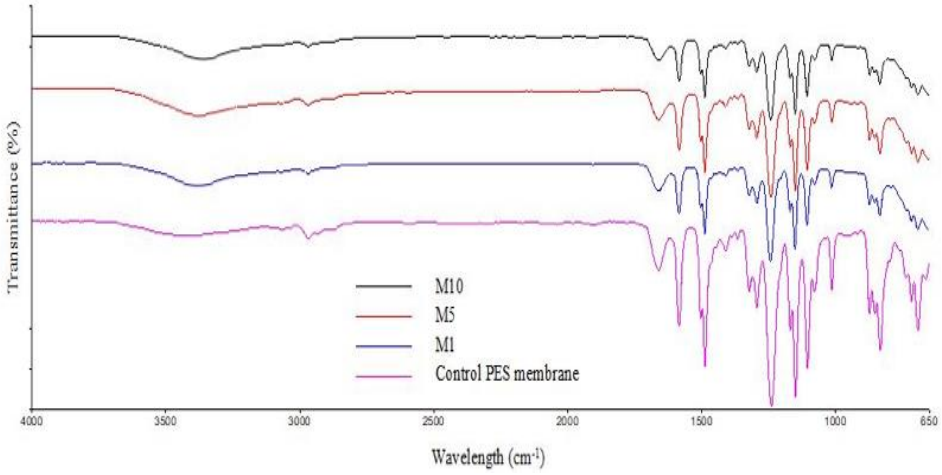

Fig. 1 FTIR spectra of control PES membrane and MMMs

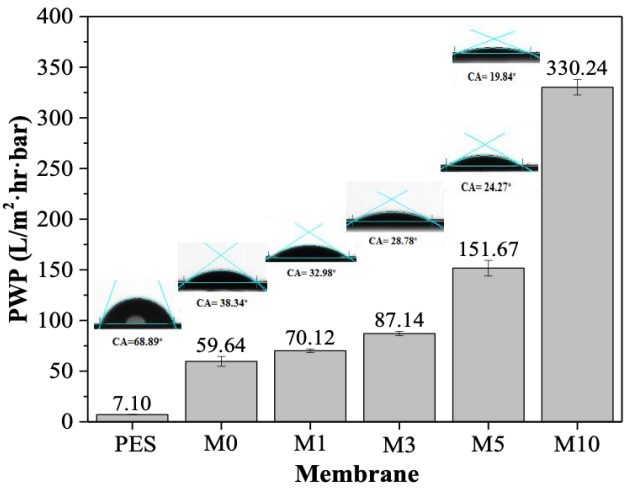

Fig. 2 PWP and contact angle of self-fabricated membranes

The impacts of HMO addition and PEG quantity on the pure water flux and contact angle of PES membrane were further studied and the results are presented in Fig. 2. As shown, the water flux of control PES membrane is significantly enhanced from 7.10 to approximately 60 L/m^2.hr.bar upon incorporation of HMO nanoparticles as found in the M0 membrane. This remarkable flux improvement is greatly attributed to the incorporation of hydrophilic nanomaterial in the membrane that has high affinity towards water molecules. This statement is further supported by the great reduction in the membrane water contact angle. Further flux increment is able to achieve by adding PEG in the MMMs in which the higher the amount of PEG added the greater the water flux produced. The increasing water flux from M0 to M10 membrane could be related to the improved structural integrity (will be further discussed in Fig. 3) and greater surface hydrophilicity (lower contact angle).

Fig. 3 shows the SEM images of the entire cross-sectional structure and top surface of the membranes. There is distinct difference between the morphology of the control PES membrane and

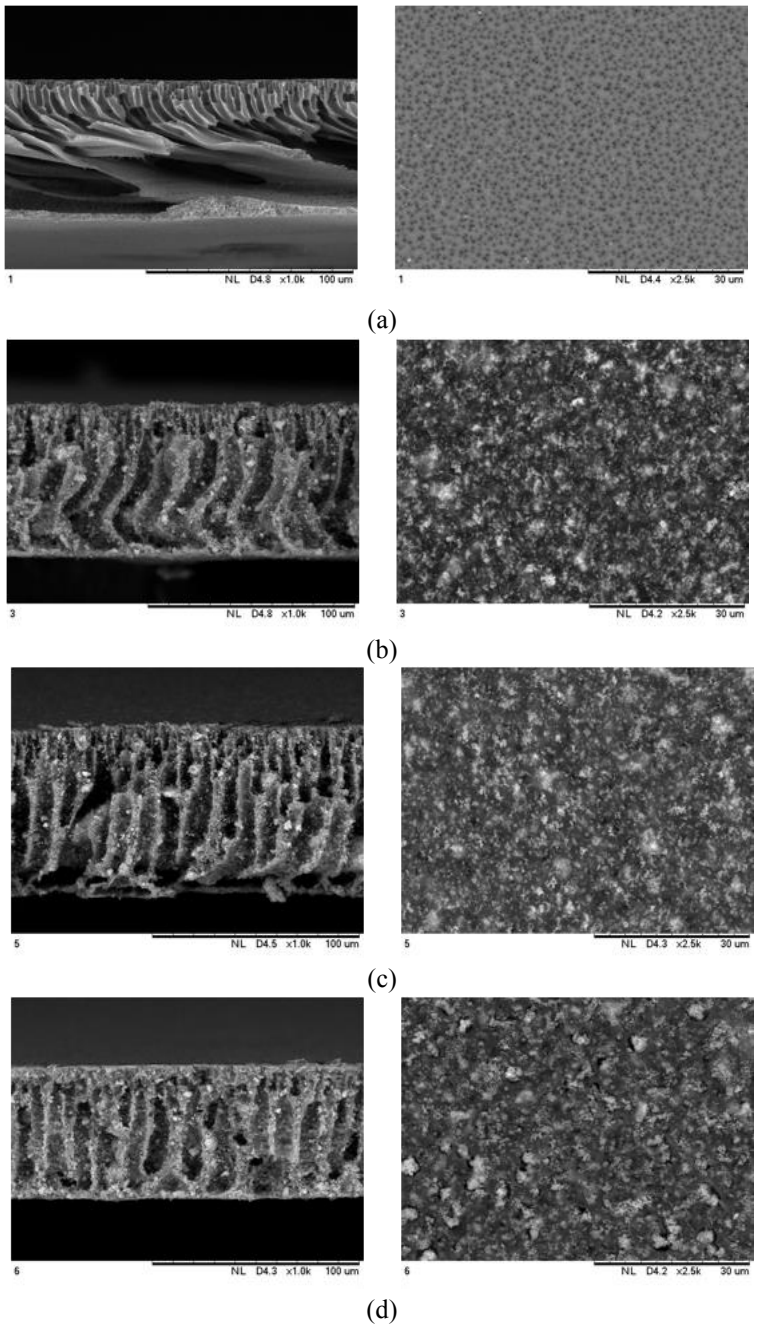

Fig. 3 SEM images of cross-section (left) and top surface (right) of membrane, (a) PES, (b) M1, (c) M5 and (d) M10

the MMMs. Upon addition of HMO nanoparticles, the irregular microvoids on the bottom section of the control membrane are suppressed and extended finger-like structure (from top to bottom section of membrane) is developed. This is mainly due to the faster solvent/non-solvent exchange

rate during membrane fabrication that is promoted by the presence of hydrophilic nanomaterials. As a result, the formation of extended finger-like structure reduces water transport resistance, leading to improved water flux (see Fig. 2). By increasing PEG amount in the membrane from zero to 10%, one can see that a higher integrity of finger-like structure is formed that reduces the structural tortuosity and further enhances water permeability. On the other hand, the surface of the MMMs is significantly rougher compared to the control PES membrane. The result agrees with the presence of inorganic HMO that form nanocomposite membrane structure (organic-inorganic). Because of the existence of large number of HMO on the membrane surface, the membrane surface hydrophilicity is greatly improved.

The filtration performance of the resultant membranes was further evaluated by subjecting the membranes directly to the treatment of highly concentrated oily solution composed of 30,000 ppm oil molecules and the results are shown in Fig. 4. The use of UF membrane for oily solution treatment has been widely reported in the literature, but the filtration results are limited to low concentration of oily solution. In most of the cases, the researchers employed oily solution with <2000 ppm oil concentration as feed for the membrane evaluation (Jamshidi Gohari *et al.* 2014a, Ong *et al.* 2015, 2014). In the real environment, much higher oil concentration could be found. From the figure, all MMMs exhibit higher water permeability than that of control PES membrane and the higher the PEG amount used for membrane modification, the greater the water flux. Compared to the respective pure water flux of each membrane in Fig. 2, the water flux is greatly reduced during oil solution treatment. These results are due to the presence of large amount of oil molecules in the feed solution which deposits and forms thick oil layer on the surface of membranes, creating significant resistance for the water molecules to permeate. Owing to the improved properties of the M10 membrane, approximately 80% higher water flux than the control PES membrane is achieved. In terms of oil rejection, all the developed membranes demonstrated almost complete elimination of oil molecules. It is interesting to note that even though the M10 membrane achieves much higher water flux, its separation efficiency for oil removal is not compromised.

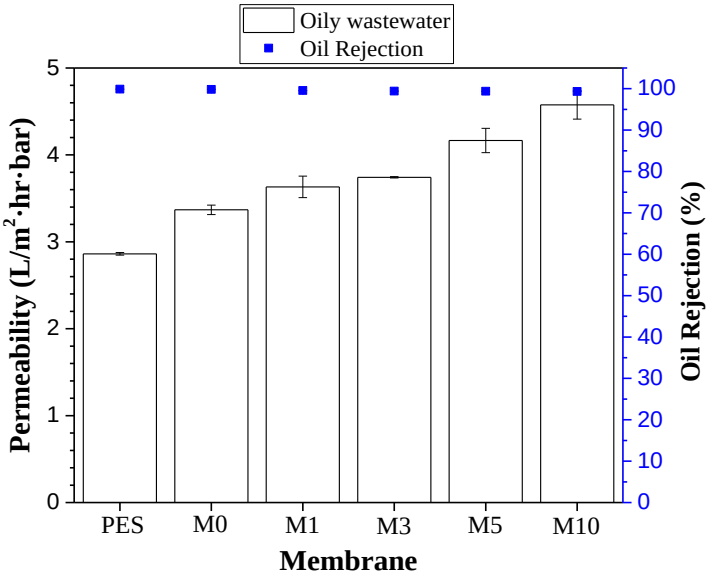

Fig. 4 Membrane performance for the treatment of highly concentrated synthetic oily solution (30,000 ppm)

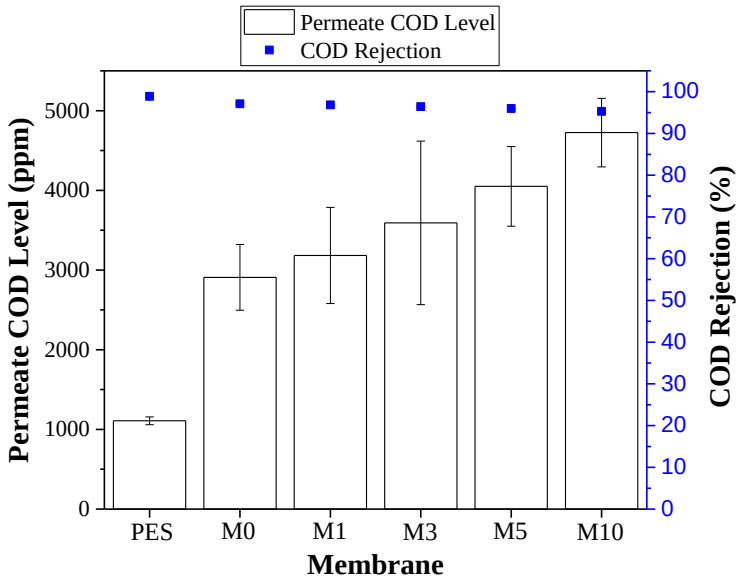

Fig. 5 Permeate COD level and COD rejection of membrane for the treatment of highly concentrated synthetic oily solution (Feed COD level: 100,400±1,533 ppm)

The quality of permeate produced by each membrane was further analyzed in terms of COD value and the findings are presented in Fig. 5. As can be seen, the developed membranes achieve at least 95% COD rejection when they are used to treat synthetic oily solution with COD concentration approximately 100,000 ppm. Since the COD level of the feed solution is extremely high, the COD detection of 1000-5000 ppm in the permeate samples is generally acceptance. Compared to the oil rejection as shown in Fig. 4, it is found that the MMMs shows slightly lower COD rejection in comparison to the control PES membrane. The reduced separation efficiency could be caused by the larger surface pore size of the MMMs that makes them not able to separate oil molecules with relatively smaller size.

4. Conclusions

In the work, the performance of mixed matrix membrane composed of PES and HMO nanoparticles for oily solution treatment was further improved by adding pore forming agent - PEG into dope solution.

- The developed MMMs are potential to be used for handling highly concentration solution (30,000 ppm oil concentration) by achieving excellent removal rates.
- The best performing membrane (M15) that was modified by 15% PEG could achieve ~100% oil rejection and ~95% COD rejection. These results are comparable with the control PES membrane. Nevertheless, it must be pointed out that the oil water flux of the M15 membrane was 80% higher than the value shown by the control membrane.
- The improved filtration performances of MMM are mainly attributed to the improved surface hydrophilicity of the membrane coupled with greater structural integrity (extended finger-like structure) that draw water molecules at a faster rate.

• The findings of this work revealed the potential use of MMM for the treatment of highly concentrated oily wastewater.

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References

Al-Husaini, I.S., Yusoff, A.R.M., Lau, W.J., Ismail, A.F., Al-Abri, M.Z. and Wirzal, M.D.H. (2019), "Iron oxide nanoparticles incorporated polyethersulfone electrospun nanofibrous membranes for effective oil removal", *Chem. Eng. Res. Des.*, **148**, 142-154.

Doraisammy, V., Lai, G.S., Kartohardjono, S., Lau, W.J., Chong, K.C., Lai, S.O., Hasbullah, H. and Ismail, A.F. (2018), "Synthesis and characterization of mixed matrix membranes incorporated with hydrous manganese oxide nanoparticles for highly concentrated oily solution treatment", *Can. J. Chem. Eng*., **96**, 1612-1619.

Jamshidi Gohari, R., Halakoo, E., Lau, W.J., Kassim, M.A., Matsuura, T. and Ismail, A.F. (2014a), "Novel polyethersulfone (PES)/hydrous manganese dioxide (HMO) mixed matrix membranes with improved anti-fouling properties for oily wastewater treatment process", *RSC Adv*., **4**, 17587-17596.

Jamshidi Gohari, R., Halakoo, E., Nazri, N.A.M., Lau, W.J., Matsuura, T. and Ismail, A.F. (2014b), "Improving performance and antifouling capability of PES UF membranes via blending with highly hydrophilic hydrous manganese dioxide nanoparticles", *Desalination*, **335**, 87-95.

Jamshidi Gohari, R., Korminouri, F., Lau, W.J., Ismail, A.F., Matsuura, T., Chowdhury, M.N.K., Halakoo, E. and Jamshidi Gohari, M.S. (2015), "A novel super-hydrophilic PSf/HAO nanocomposite ultrafiltration membrane for efficient separation of oil/water emulsion", *Sep. Purif. Technol*., **150**, 13-20.

Jamshidi Gohari, R., Lau, W.J., Matsuura, T. and Ismail, A.F. (2013), "Effect of surface pattern formation on membrane fouling and its control in phase inversion process", *J. Memb. Sci*., **446**, 326-331.

Lai, G.S., Yusob, M.H.M., Lau, W.J., Gohari, R.J., Emadzadeh, D., Ismail, A.F., Goh, P.S., Isloor, A.M. and Arzhandi, M.R.D. (2017), "Novel mixed matrix membranes incorporated with dual-nanofillers for enhanced oil-water separation", *Sep. Purif. Technol*., **178**, 113-121.

Lau, W.J., Ismail, A.F., Matsuura, T., Nazri, N.A. and Yuliwati, E. (2015), *Chapter 2 - Advanced Materials in Ultrafiltration and Nanofiltration Membranes in Handbook of Membrane Separations: Chemical, Pharmaceutical, Food and Biotechnological Applications*, CRC Press, 7-34.

Ong, C.S., Lau, W.J., Goh, P.S., Ng, B.C. and Ismail, A.F. (2015), "Preparation and characterization of PVDF-PVP-TiO_2 composite hollow fiber membranes for oily wastewater treatment using submerged membrane system", *Desalin. Water Treat*., **53**, 1213-1223.

Ong, C.S., Lau, W.J., Goh, P.S., Ng, B.C. and Matsuura, T. (2014), "Effect of PVP molecular weights on the properties of PVDF-TiO_2 composite membrane for oily wastewater treatment process", *Sep. Sci. Technol*., **49**, 2303-2314.

Ikhsan, S.N.W., Yusof, N., Aziz, F., Misdan, N., Ismail, A.F., Lau, W.J., ... & Hairom, N.H.H. (2018), "Efficient separation of oily wastewater using polyethersulfone mixed matrix membrane incorporated with halloysite nanotube-hydrous ferric oxide nanoparticle", *Sep. Purif. Technol*., **199**, 161-169.