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PREPARATION AND CHARACTERIZATION OF SUPERHYDROPHILIC NANOCOMPOSITE ULTRAFILTRATION MEMBRANES FOR TREATMENT OF HIGHLY CONCENTRATED OIL-IN-WATER EMULSION

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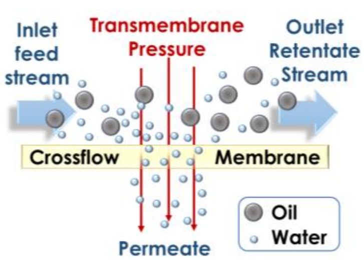
G. S. Lai[a,b], W. J. Lau[a,b*], P. S. Goh[a,b], Y. H. Tan[a,b], A. F. Ismail[a,b], U. Zaik[c], H. Basri[c], R. Jamshidi Gohari[d]

[a]Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[c]Department of Science, Faculty of Science, Technology and Human Development, Universiti Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat 86400, Johor, Malaysia
[d]Department of Chemical Engineering, Islamic Azad University, Bardsir Branch, Bardsir, Iran

*Corresponding author
lwoeijy@utm.my

Graphical abstract



Abstract

In oily wastewater treatment using membrane technology, surface fouling is the major issue that could deteriorate membrane flux and shorten its lifespan. Therefore, nanocomposite membranes were developed in this study by incorporating titanium dioxide (TiO_2) and hydrous manganese oxide (HMO) nanoparticles into polymeric membrane matrix. Three different types of membranes were fabricated. They were pristine PES and membrane incorporated with TiO_2 or HMO. With respect to pure water flux, TiO_2- and HMO-incorporated membranes showed value of 57 and 40 L/m^2.h, respectively. These values were 33-90% higher than that of control PES membrane. In treating 500 ppm oily solution, TiO_2 membrane exhibited the highest water flux. However, the membrane's oil removal rate was slightly compromised. When tested with higher concentration of oily solution (5,000 or 10,000 ppm), TiO_2- and HMO-incorporated membranes still showed promising water flux with 94.5-99.6% oil removal rate. This proved that ultrafiltration membrane incorporated with suitable nanomaterials could improve the water flux of pristine PES membrane and is of more practical for industrial applications.

Keywords: Nanoparticle, ultrafiltration, hydrophilicity, oil removal, hydrous manganese oxide

1.0 INTRODUCTION

In oil and gas industries, a huge amount of wastewater that contains high concentration of oil and grease are produced. These contaminants will eventually cause severe water pollution and endanger the aquatic life. Hence, the wastewater must be properly treated until it achieves the acceptable condition before discharging into any receiving water body in order to protect our environment [1]. Typical oily wastewater contains total oil and grease (TOG) with concentration between 50 and 1000 ppm (mg/L), however, extremely high content of TOG such as 100,000 pm could be detected in certain case [2]. According to United State Environmental Protection Agency (US EPA), the emission limit value for TOG in wastewater discharge is 25 ppm. Nevertheless, stricter local regulation is enforced which only allows 1 to 10 ppm of TOG to be present in discharged water [3]. Hence, many efforts had been done to separate the oil and grease from wastewater.

Generally, the oily wastewater is in the form of oil-in-water emulsion that contains oil droplets of less than 10 mm. The conventional techniques such as gravity separation, centrifugation and air flotation are ineffective in oil removal. In view of this, ultrafiltration membrane technology provides a potential alternative solution to tackle this problem. The significant advantages of using UF technology for oily wastewater treatment are high efficiency in removing oil droplets (even in micron size), low energy consumption, minimum chemical used (only for cleaning process) and production of no by-product. Nevertheless, the separation performance of UF membrane is hindered by fouling issue. In brief, the membrane water lux deteriorating associated with fouling problem that resulted from the absorption and accumulation of oil molecules on the membrane surface [4, 5].

To tackle the problem of membrane fouling caused by the hydrophobic oil molecules, hydrophilic additives are always incorporated into polymeric membranes to enhance their antifouling behavior. Although polyethersulfone (PES) is one of the several main polymer materials used in making commercial UF membranes, its hydrophobic nature is the main factor leading to low water flux and high fouling tendency, particularly when it is used in removing oil molecules. In order to improve membrane surface hydrophilicity and increase its fouling resistance against oil molecules, inorganic hydrophilic nanoparticles are always attempted [6].

In this study, titanium dioxide (TiO_2) and hydrous manganese oxide (HMO) nanoparticles were used as hydrophilic additives during UF membrane fabrication for oily wastewater treatment. Previous studies showed that the incorporation of both typed of nanoparticles (TiO_2 and HMO) have successfully enhanced the membrane water flux and antifouling properties for oily wastewater treatment [5, 7-9]. With respect to oil separation efficiency, both kinds of nanocomposite membranes also exhibited good oil removal. However, these two types of nanocomposite membranes were in fact individually evaluated in different works under different feed conditions. Hence, the main objective of this study was to investigate the type of nanoparticles which is more suitable to be used for nanocomposite UF membrane making for oil-in-water emulsion treatment process among the mentioned nanoparticles. Three different membranes including neat PES membrane and membrane containing either TiO_2 or HMO were fabricated. Characterization and separation performance evaluation on the membrane were performed in order to achieve the goal of the study.

2.0 METHODOLOGY

2.1 Materials

Polyethersulfone Radel® A-300 in pellet form (PES, Solvay) and 1-methyl-2-pyrrolidinone (NMP, 99%, Acros Organics) were used for fabrication of PES ultrafiltration membrane. Polyvinylpyrrolidone (PVP K20, Fluka) was added into the dope solution as pore forming agent. In this study, two types of inorganic nanoparticles were used as additive in preparation of dope solution for fabrication of nanocomposite membrane, which were HMO and TiO_2. HMO nanoparticles were synthesized through oxidation of manganese ions by permanganate according to Parida's method as reported [9, 10]. In brief, potassium permanganate ($KMnO_4$) solution was added into manganese(II) sulfate monohydrate ($MnSO_4 \cdot H_2O$) solution which initially adjusted to pH 12.5. The formed brownish precipitates were HMO. HMO was then washed until neutral prior to use. The synthesized HMO contains flake-like shape particles (particle size <6 nm) and needle-shaped particles (diameter ~12 nm). The commercial TiO_2 (P25 Degussa, diameter ~21 nm, Evonik) were used as the second inorganic nanoparticles to compare with HMO nanoparticles. Crude oil obtained from Terengganu Crude Oil Terminal, Malaysia (Location: RE110) and sodium dodecyl sulfate (SDS, Merck) were used to prepare synthetic oily wastewater for filtration experiment. Milipore reverse osmosis (RO) water (ASTM Type III) was using in nanoparticles synthesis and feed preparation.

2.2 Preparation of UF Flat Sheet Membranes

Three different PES UF flat sheet membranes were fabricated according to dope solution formulation as shown in Table 1. The amount of inorganic nanoparticles that added into dope solution for nanocomposite UF membrane making was an optimized loading reported in previous work [9]. To prepare dope solution, an appropriate amount of PVP and nanoparticles (for nanocomposite membrane) were first added into NMP, followed by 30 min of ultrasonication to disperse nanoparticles well and also minimize agglomeration. Then PES pellets were added slowly into the mixture under vigorous stirring. The mixture was stirred overnight to ensure a homogenous solution was obtained. To remove any air bubbles trapped inside the dope solution, the solution was subjected to 1 h of ultrasonication, followed by at least 24 h storage at room condition before being used for casting process.

All the membranes were fabricated using phase inversion (i.e. immersion precipitation) method under room condition. Basically, membrane with thickness of

110 ± 5 µm was casted on a dry and clean glass plate using a glass rod. The cast membrane was immersing immediately into a water coagulation bath for phase inversion to take place. The membrane was then transferred to another clean water bath once it was peeled off from the glass plate by itself. All the membranes must be kept in water bath for 24 h to remove residual solvent and PVP. At last, the membrane was washed with RO water and dried in room temperature prior to use. These membranes are hereafter denoted as PES, TiO_2 and HMO according to the presence of nanoparticles in the casting dope as shown in Table 1.

Table 1 Dope formulation for UF membranes

Membrane	Dope Formulation (wt%)				
	PES	PVP	NMP	TiO_2	HMO
PES	15.00	1.5	83.5	–	–
TiO_2	11.54	1.15	64.23	23.08	–
HMO	11.54	1.15	64.23	–	23.08

2.3 Membrane Characterization

The element composition of the fabricated membranes was analyzed using energy-dispersive X-ray spectroscopy (EDX, X-Max^N Oxford) with aids of variable pressure scanning electron microscope (VP-SEM, JSM-IT300LT JEOL). The surface hydrophilicity of the membranes was determined by conducting the static contact angle (CA) measurement with contact angle goniometer (DataPhysics OCA 15Pro) using RO water as the probe liquid.

2.4 Evaluation of Performance of UF Membranes

A laboratory-scale crossflow filtration unit (Sterlitech™ CF042P) was used to assess the separation performance of the fabricated membranes. The effective surface area of the membrane was 42 cm^2. Prior to any measurements, the membranes were compacted at pressure of 2 bar for 30 min and followed by the operating pressure of 1 bar for 15 min using RO water as feed to achieve flux steady state condition. The pure water flux (PWF) of the membrane was first calculated before subjecting to oil rejection test.

The synthetic oily wastewater was prepared by mixing crude oil sample, SDS and RO water together. SDS was used as the surfactant to solubilize oil in water to form stable oil-in-water emulsion. The ratio of crude oil sample to SDS used in the oily wastewater preparation was 9:1. Three different concentrations of oily wastewater (i.e. 500 ppm, 5,000, 10,000 ppm) were prepared using a blender. The oil rejection experiments were performed using operating pressure of 1 bar. Permeates were collected for further analysis after the experiments were run at constant pressure for 15 min. Membrane water flux, J (LMH) was calculated using Eqs. (1).

$$J = \frac{\Delta V}{A_m \Delta t} \quad (1)$$

where ΔV is the permeate volume, A_m is the effective surface membrane area and Δt is the time taken to collect permeate.

An ultraviolet-visible (UV-VIS) spectroscopy (Hach DR5000) and chemical oxygen demand (COD) test were conducted to determine the oil concentration and COD level, respectively in the feed and permeate solution. The membrane oil and COD rejection, R were determined using the Eq. (2).

$$R = \left(1 - \frac{C_p}{C_f}\right) x100\% \quad (2)$$

where C_f and Cp are the oil concentration (for oil removal test) or COD level (for COD removal test) of feed and permeate solution, respectively.

3.0 RESULTS AND DISCUSSION

Table 2 tabulates the composition of element present in the membranes that obtained using EDX elemental analysis. In brief, all the membranes contain carbon, oxygen and sulfur due to PES was used as the raw material in preparing the UF membrane. Due to the incorporation of inorganic nanofillers, TiO_2 and HMO membranes have extra one element present in them, where were Ti and Mn respectively. For both membranes, the composition of Ti or Mn were almost the same since the same loading of inorganic nanofillers were used.

The dispersion of inorganic nanofillers in the membranes were visualized using EDX mapping as shown in Figure 1. Only elemental mapping of Ti or Mn were shown in this case. For PES membrane, there was no Ti and Mn were detected. Meanwhile, for nanocomposite membranes, the elemental mapping of Ti and Mn were done for TiO_2 and HMO membranes, respectively. Obviously, both types of inorganic nanofillers were well dispersion in the polymeric membrane matrix from Figure 1(b) and (c).

The separation characteristics of membranes were investigated by subjecting the membranes to the treatment process of oily solution. Figure 3 presents the performance of the membrane in separating oil molecules from the oily solution of 500 ppm. With the presence of oil molecules in the feed solution, the water flux of membranes was found to be much lower than their respective pure water flux shown in Figure 2.

Table 2 Composition of element in membrane

Membrane	Element (wt %)				
	C	O	S	Ti	Mn
PES	68.4	17.1	14.5	0.0	0.0
TiO_2	37.6	25.7	6.7	30.0	0.0
HMO	44.7	19.0	7.2	0.0	29.0

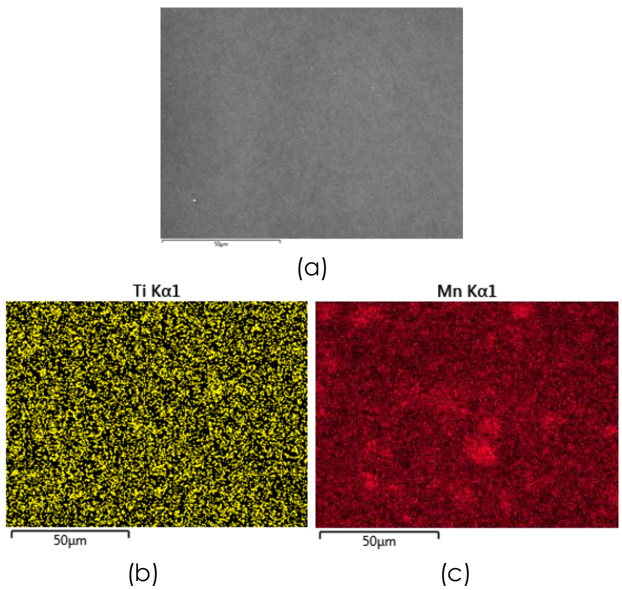


Figure 1 (a) SEM image of PES membrane surface. EDX elemental mapping of (b) element Ti for TiO_2 membrane and (c) element Mn for HMO membrane

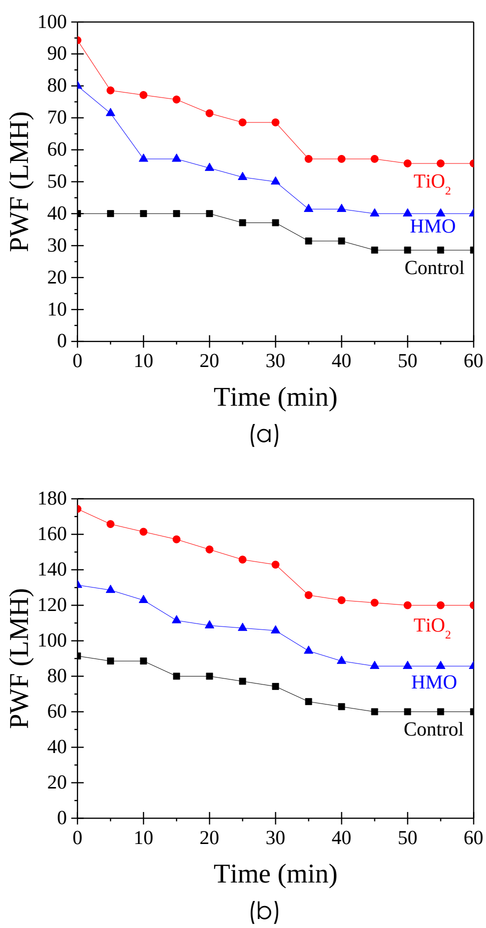


Figure 2 Pure water fluxes of synthesized UF membranes as a function of time at different operating pressure, (a) 1 bar and (b) 2 bar

The reduction in water flux is mainly due to the deposition of oil molecules on the membrane surface, forming an additional layer to resist the permeation of water molecules. Overall, TiO_2 membrane was reported to have the highest water flux followed by HMO membrane and control membrane. The surface hydrophilicity of the membrane surface was further investigated as shown by the contact angle results as shown in Table 3. It is found that the contact angle of the membranes followed similar trend as the PWP, i.e. CA(Control) > CA(HMO) > CA(TiO_2). Hence, the incorporation of hydrophilic nanoparticles into the membranes in general improved membrane hydrophilicity which in turn enhanced membrane water flux [11, 12].

With respect to oil rejection rate, it was found that the excellent-flux TiO_2 membrane was suffered with lower oil removal rate, recording 90.8% rejection. As a comparison, control and HMO membrane displayed 99.5% and 98.2% oil rejection, respectively. This phenomenon could be explained by the trade-off effect between membrane flux and selectivity, i.e. high flux coupled with lower selectivity and vice versa [13].

Table 3 Contact angle of fabricated UF membranes

Membrane	Contact angle
Control	65.2°
TiO_2	44.1°
HMO	47.1°

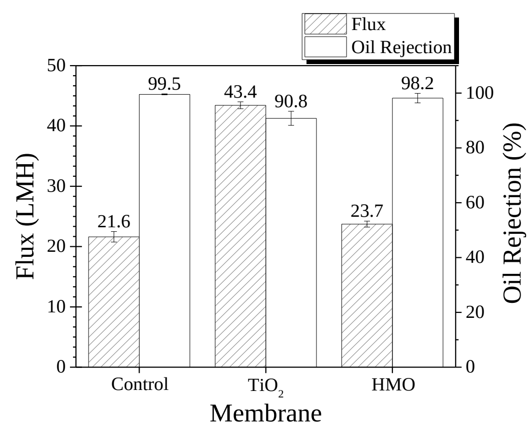
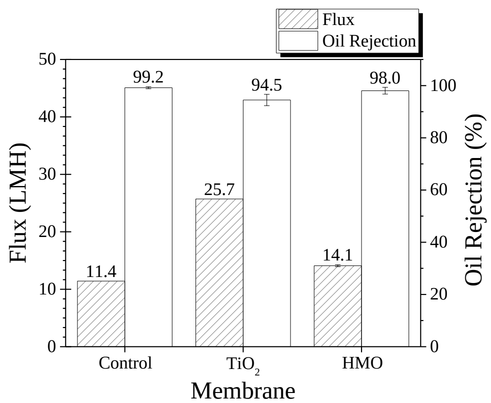


Figure 3 Water flux and oil rejection of synthesized UF membranes when tested with low concentration of oily wastewater (500 ppm) at operating pressure 1 bar

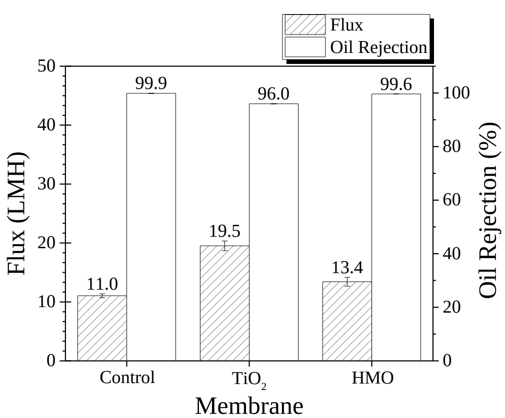
The performances of membranes in treating oily solution were further assessed using feed solutions containing significantly higher oil concentration and the results are shown in Figure 4. By subjecting the membranes to higher concentration of oily solution (5,000 and 10,000 ppm), it was found that fluxes of all these membranes were remarkably reduced. The higher the concentration of oily solution, the lower the membrane water flux. The results showed that TiO_2, HMO and control membrane recorded water fluxes of

25.4, 14.1 and 11.4 LMH, respectively at 5,000 ppm and 19.5, 13.4 and 11.0 LMH, respectively at 10,000 ppm. These values were significantly lower when they were tested with 500 ppm, i.e., 43.4, 23.7 and 21.6 LMH, respectively.

Although the membrane fluxes were negatively affected by high concentration of oily solution, the membrane separation efficiencies were improved. For instance, the oil rejection of TiO_2 membrane was improved from 90.8% to 94.5% and 96.0% with increasing oil concentration from 500 to 5,000 and 10,000 ppm. The possible explanation for the improved rejection rate is due to the formation of denser and thicker oil layer on membrane surface and/or blocking of larger surface pores by oil molecules that create additional barrier to filter oil molecules [14-15].



(a)



(b)

Figure 4 Water flux and oil rejection of synthesized UF membranes when tested with high concentration of oily wastewater at operating pressure 1 bar, (a) 5,000 ppm and (b) 10,000 ppm

Table 4 and 5 summarizes the COD values of feed and permeate samples treated by three different types of UF membranes together with the respective COD removal rate. Compared to the oil rejection determined based on light absorbance method, the COD values obtained from chemical reagent method showed 1-3% difference in terms of oil removal. This could be possibly due to the use of different method in analyzing the content of oil in the samples. Referring to the results shown in the table, it can be said that the membranes could achieve promising COD removal (96.7-98.6%) regardless of type of membrane and oil concentration. Nevertheless, the membranes incorporated with nanofillers in general are more potential for industrial applications, owing to the improved surface hydrophilicity which could lead to higher flux and lower degree of membrane fouling.

Table 4 Performance of synthesized UF membranes in removing COD of 5,000 ppm oily solution

Membrane	5,000 ppm Oily Solution		
	COD (ppm)		Removal
	Feed	Permeate	(%)
Control		97	98.6
TiO_2	6,920	149	97.85
HMO		226	96.73

Table 5 Performance of synthesized UF membranes in removing COD of 10,000 ppm oily solution

Membrane	10,000 ppm Oily Solution		
	COD (ppm)		Removal
	Feed	Permeate	(%)
Control		417	97.47
TiO_2	16,500	321	98.05
HMO		568	96.56

4.0 CONCLUSION

In this work, it is demonstrated that the water flux of PES-based UF membrane could be further improved using hydrophilic nanomaterials as inorganic fillers without significantly affecting the oil removal rate. The successful incorporation of nanomaterials was confirmed by the EDX mapping in which specific element (Ti or Mn) belonging to the respective fillers was detected on membrane surface. Using hydrophilic nanomaterials as the fillers, the newly developed UF membranes could achieve pure water flux of 40-57 LMH with oil removal rate maintained at 96.0-99.6%, even though they were tested with highly concentrated oily solution (10,000 ppm). Control PES membrane meanwhile showed 33-90% lower pure water flux with oil removal rate of 99.9%. The findings of this work showed that the UF membrane incorporated with suitable nanomaterials could overcome the poor water flux of pristine PES membrane and is of more practical for industrial applications.

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