Jurnal
Teknologi

Full Paper

PVDF MEMBRANE FOR OIL-IN-WATER SEPARATION VIA CROSS-FLOW ULTRAFILTRATION PROCESS

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Article history
Received
26 April 2015
Received in revised form
1 July 2015
Accepted
16 November 2015

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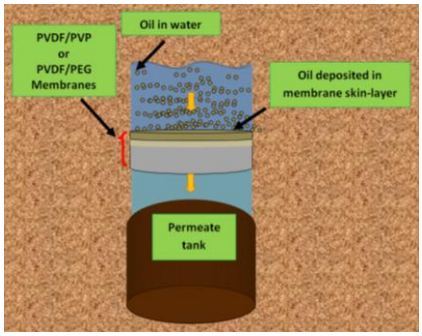
Graphical abstract



Abstract

The objective of this study is to investigate the potential of ultrafiltration polyvinylidene fluoride (PVDF)-titanium dioxide (TiO2) membrane for oil-in-water separator. PVDF polymeric matrix membrane is excellent in term of chemical and thermal stabilities, which make it very promising to be used as a membrane matrix for water separation. However, poor hydrophilic property of the PVDF has led to the severe fouling during operation. Thus, current work was performed to investigate the effect of incorporation of two additives i.e. polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) in PVDF-TiO_2 membrane, which fabricated using dry/wet phase inversion technique. Membranes characterizations were performed using field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), contact angle and UV-vis spectrophotometer. Accordingly, modified PVDF membrane possessed good hydrophilicity property when the additives were added into PVDF-TiO_2 membrane matrix. In term of filtration performance, the experimental results showed that oil rejection using PVDF-TiO_2/PVP membrane were ~99.7%, which met the requirement for discharge. On the other hand, PVDF-TiO_2/PEG membrane was shown more enhancement in terms of permeate flux by given over 64 (L/m2h) at pressure of 2 bar gauge.

Keywords: PVDF, membrane, UF, oil in water, separation

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1.0 INTRODUCTION

Oily wastewater created from oil extraction process [1-3], which mainly contains different types of hydrocarbon, such as benzene, phenols, humus and polycyclic aromatics [4]. Treatment of this wastewater is required prior to release into the environment to avoid the pollution on the seashore, estuaries, rivers, soil, and even the air via organic content [5]. Membrane technology has been widely used to filter organic substances, such as dissolved oil in untreated oil field wastewater before desalination [1, 2, 6]. The volume of oily wastewater generated yearly in the USA onshore estimated at 33 billion barrels for oil and gas onshore, which cannot be re-injected to oil wells or discharged to the environment, since they contain high concentrations of different types organic materials [7, 8]. According to the Clean Water Act (CWA) of the United States of America, the grease and oil concentration in discharge water should not be more than 15 ppm, hence, oil emulsified in water in the range of 100-1000 ppm is considered as a major water pollutant [8-10]. Hence, particles and oil droplets treatment from oil-field wastewater is necessary before discharging or reusing the water [11-14]. While, conventional-techniques in wastewater treatment like coalescer plates and gravity separators may not produce the high purity water for environment discharging or re-injection purposes. Many researchers have attempted to enhance the process in this

approach [15-17]. Among them, membrane ultrafiltration (UF) has been showed in wide number of cases efficient treatment for oil-field wastewater [15, 18-20].

Accordingly, UF membrane technology provides a very viable alternative as conventional technology for oil-field wastewater purification [21, 22]. On the other hand, in the long-term process UF membranes may not productively treat oil-field wastewater [23, 24]. This is due to membrane fouling which lead to membrane flux drop directly, as a result of oil adsorption and accumulation of rejected oil, suspended solids, and other components of oil-field wastewater on the membrane surface (external fouling) or in the membrane pores (internal fouling) [25-28]. Hence, several techniques were used to produce anti-fouling UF membrane for the long-term process [29]. One of the recent techniques is UF nanocomposite membrane production [3, 30, 31].

This study reports the PVDF-TiO2/PVP and PVDF-TiO2/PEG membranes for the oil-field wastewater treatment aiming to enhance permeate flux and rejection. The oil-field wastewater treatment performance by UF nanocomposite membrane filtration was studied by an in-house designed UF cross-flow system.

2.0 EXPERIMENTAL

2.1 Materials

Polyvinylidene fluoride (PVDF) Solef 6012 in pellet form was purchased from Solvay Advanced Polymers, dimethylacetamide (DMAc, >99.5%) solvent was procured from Merck. Poly(vinylpyrrolidinone) (PVP) and poly(ethylene glycol) (PEG) was purchased from Sigma Aldrich and titanium-dioxide (TiO2) P25 nanoparticles with specific surface area of 50±15 m2g-1 from Evonik Degussa were used.

2.2 Membrane formulation and fabrication

Flat sheet membranes was formulated for two different polymeric solutions as follow; PVDF-TiO2/PVP/DMAc (M1), PVDF-TiO2/PEG/DMAc (M2). In order to obtain optimal dispersions of particles in the polymer solutions, agitation was required for at least 24 h and then kept in the oven at 65 oC till 5 h before casting the membrane. PVP and PEG concentration in M1 and M2 was 1 wt% inside dopes, which consisting of PVDF-TiO2 (14+1 wt%, by weight of the solution), DMAc (84 wt%), which is more in detail and listed in Table 1. The polymeric solution was casted uniformly on a glass substrate by means of a hand-casting knife with the thickness of 250 µm [32]. After casting the membrane, it was immersed into the distilled water (for 3 days) and mixture of methanol distilled water 2:1 bath (for 5 hr), respectively [33].

Table 1 Casting solution compositions

Membrane	Membrane code	(w/w) %		
		PVP or PEG	PVDF-TiO2	DMAc
PVDF-PVP	M1	1.0	15.0	85.0
PVDF-PEG	M2	1.0	15.0	85.0

2.3 Characterization of the Nanocomposite Membranes

The cross-section and the top surface of the membrane were observed by field emission scanning electron microscope (FESEM, Jeol JSM 6701-F) combined with energy dispersive X-ray (EDX- Jeol JED-2300F). The water contact angle was measured by contact angle analyzer (model IMC-159D by IMOTO Machinery Co. Ltd.) by dropping of 5 µl de-ionized water to the membrane surface. Atomic force microscopy (AFM) was conducted to analyze the surface morphology and roughness of the prepared membranes by using the AFM device SPA-300 HV (Seiko) equipped with a Nano-Navi software (version 5.01). Small pieces of the prepared membranes (approximately 1 to 2 cm) were cut. The membrane surfaces were imaged in a scan size of 5µm×5µm. The average roughness (Sa), the root mean square of Z data (Sq)the mean difference between the highest peaks and lowest valleys (Sz) and the root mean quare. The mean pore size, μ_p (nm), was also determined from the atomic force microscopy (AFM) image of the membrane surface by the method developed by Singh *et al*.

In membrane filtration experiments, permeation flux (J) was measured gravimetrically by Eq. (1):

$$J = \frac{V}{A \times t} \quad \text{Eq. (1)}$$

where volume of permeate was V (L), membrane effective area was A (m2), and sampling time was t (h). oil rejection percentage R(%) was calculated by Eq (2):

$$R(\%) = 1 - \left(\frac{C_P}{C_F}\right) \times 100 \quad \text{Eq. (2)}$$

where CP (ppm) is oil concentration in permeate and CF (ppm) is the oil concentration in the PMR, which remained almost the same during the entire PMR operation.

2.4 Procedure and Analysis

Oil in water original sample was collected from one of the eastern Malaysian offshore. The oil concentration in water was originally 300 ppm and kept it constant during filtration process. Before the experiment, the oil-

field wastewater has been well mixed at 37 oC using sonicator for 12 h. Moreover, no surfactant was used to stabilize the emulsification as the natural surfactant present in the crude oil stabilizes the mixture. The emulsion was stable with respect to coalescence and homogeneous nature of the solution for at least 12 days. During this period, the droplet size distribution and pH of the interval were found to be almost the same. However, after 12 days, a thin film of oil was seen to come out of the solution gradually and formed a ring at the top of the solution which may be due to the effects of buoyancy and may be considered as an indication of beginning of coalescence of oil droplets. The physical specifications of this oil-field wastewater are listed in Table 2.

Table 2 Characterization of refinery wastewater

Parameters	Data
Concentration of oil in oil-field wastewater	300 (ppm)
Viscosity of oil-field wastewater	1.92 (centipoises)
initial oil droplet in feed tank	0.23-0.69 (μm)
Retentate oil droplet	2.81-3.16 (μm)

Figure1 was illustrated the schematic diagram of cross-flow ultrafiltration system for this experiment. Accordingly, 500 mL of the oil-field wastewater with concentration of 300 ppm was loaded to the cross-flow ultrafiltration system by opening the valve 1 and valve 2, which were controlled by operating pressure gauge via opening the valve 3 as well. 25 cm3 permeate was collected every half an hour to know the flux and the hydrocarbon separation. The experiment was continued by increasing the pressure stepwise from 0.5 to 2 bar gauge with 0.5 bar interval. All experiments were conducted at ambient temperature of 28 oC.

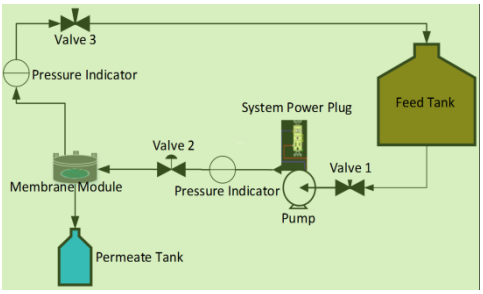

Figure 1 Cross-flow UF system

The original samples and collected samples from the cross flow ultrafiltration system were subjected to UV-VIS spectrophotometric analysis using HACH, DR/5000,wavelength 685 nm to know the organic contents hydrocarbon concentration in each sample.

3.0 DISCUSSION

3.1 Membrane Characterization

Figure 2 depicts the FESEM cross-sectional images of M1and M2, respectively. Accordingly, finger-like voids of M1 membrane is not much different compared to finger-like voids of M2. On the other hand, the sponge-like region has not seen for both M1 and M2, which indicates that both M1 and M2 were shown approximately the same morphology. Thus, it could be predicted that the overall porosity of the membrane is also almost the same range. From overall observation of both membranes, it can be concluded that M1 has more agglomeration into the polymer matrix compare to M2, which probably may affect on the flux performance. This agglomeration may due to the TiO_2. Hence, the configuration of PVDF-TiO_2/PEG was given higher compatibility.

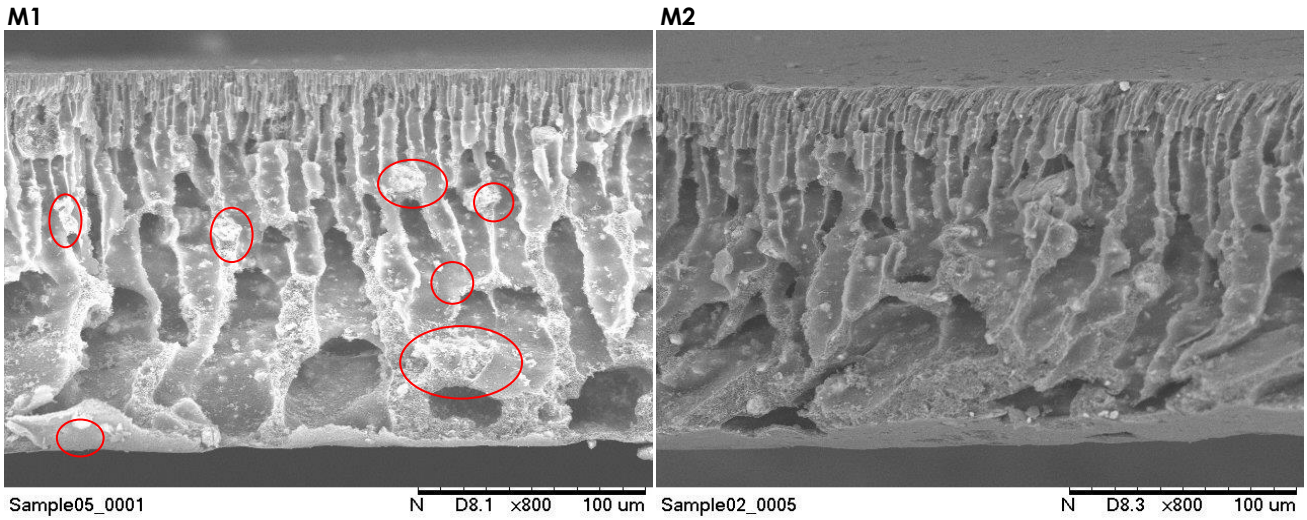

Figure 2 FESEM cross-sectional images of M1 and M2

Table 3 Roughness parameters, average pore size and contact angle at the membrane surface

Membrane	Contact angle (o)	Mean Pore size (rm, nm)	AFM roughness parameters		
			Sa (nm)	Sq (nm)	Sz (nm)
M1	61.73±0.95	12.12	17.81±1.5	24.1±1.9	131.1±1.4
M2	58.74±1.12	59.16	10.9±2.1	19.2±3.1	103.7±3.6

The hydrophilicity of the membranes surface was further investigated by contact angle and atomic force microscope. Mean pore radius size and membrane roughness are summarized in Table 3. Membrane roughness (Sa) was higher for the membrane with the incorporation of PEG compared to PVP. This was due to existence of PVP agglomeration in the PVDF matrix. On the other hand, Sz was redeemably higher for M2. Moreover, contact angle was decreased by the presence of PEG due to hydrophilic property of PEG. Thus, the membrane surface became more hydrophilic by using PEG compared to PVP. The stated results for contact angle and mean pore size were shown a promising specification for M2, which may affect the membrane performance [33].

3.2 The Performance of Nanocomposite Membranes in the Filtration Process

3.2.1 Permeation Flux

Figure 3 shows the fluxes measured by the flat sheet membranes under different transmembrane pressure drops. The flux decreased with time due to membrane fouling, likely caused by the oil layer formation on the membrane surface or by the adsorption of highly hydrophobic oil to the membrane pore wall, blocking the pore partially. The figure shows that the flux of M2 is higher than M1. This is due to better hydrophilicity property (see contact angle data in Table 3) and bulk porosity of M2. Flux changed only marginally, when the transmembrane pressure difference was increased from 0.5 to 2 bar. This is often observed for UF membrane and interpreted by the formation of a cake layer deposited on the surface of the membrane. In this study the thickness of the deposited oil layer has increased progressively with an increase in transmembrane pressure difference, offsetting the increase in the driving force. As mentioned earlier, pump was turned on to collect the permeate from the membrane for the ~2.0 h, during which period the permeate flux, decreased gradually due to membrane fouling.

3.2.2 Oil Rejection

The rejection percentage (%R) of hydrocarbons in oily wastewater after separation process has been calculated by Eq. (2) and is depicted in Figure 4. It is found that both membranes (M1and M2) have more than 97.0% rejection in all applied pressures. Moreover, the rejection percentage dropped as the transmembrane pressure difference increased, since higher pressure forced the hydrocarbon droplets to pass through the membrane pores and would block the smaller pore after some time. The rejection of M2 was lower than M1, which can be attributed to the higher hydrophilicity and the superior morphological structure in the top- and sub-layer of membranes, especially for the oil separation. It is also worth to note that, according to the standard set by the European Union (EU), the oil and grease (source of hydrocarbons) in the wastewater should not be more than 5 mg/L. Hence it can be concluded that the nanocomposite membranes have met the EU requirement. However, M1 showed higher rejection compared to M2 with 99.7% hydrocarbon rejection of oily wastewater at 0.5 bar applied pressure.

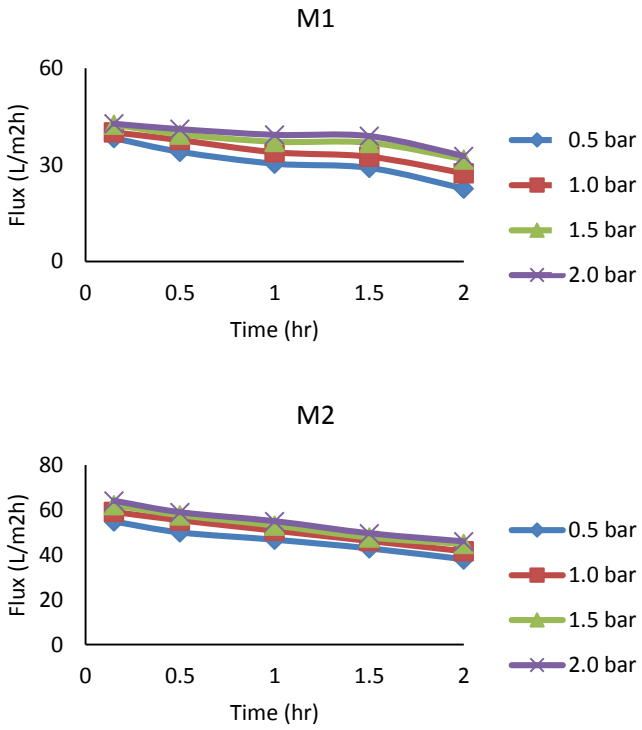

Figure 3 Effect of membranes and transmembrane pressures on flux

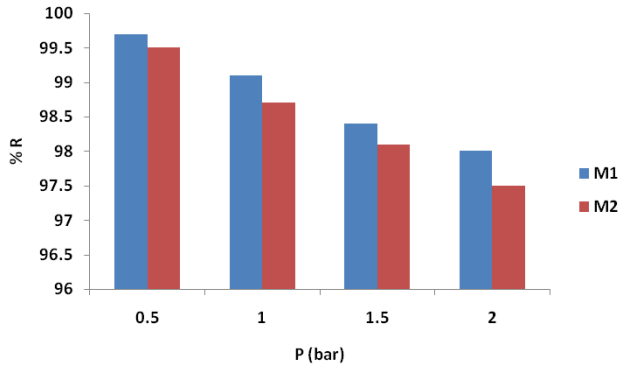

Figure 4 Rejection of oil via nanocomposite membranes at different transmembrane pressure difference

4.0 CONCLUSION

A novel cross-flow UF system was used for the removal of oil-field wastewater hydrocarbon. Four PVDF membranes with different additives (PVP and PEG) were fabricated and tested. From the experimental results, the following conclusions can be drawn:

1. More than 97.0% of the oily wastewater hydrocarbon was removed by the 1 wt% of additives using UF cross-flow system.

2. More than 99.7 of the oily wastewater hydrocarbon rejection was achieved by adding 1% PVPat 0.5 bar operating pressures.

3. Comparing the fabricated membranes in terms of a parameter permeate flux M2 membrane that contained PEG in the PVDF matrix has better performance compared to M1 due the excellent material composition and preparation.

Acknowledgement

The authors gratefully acknowledge financial support from the European Commission FP7 - LIMPID (Project number: NMP3-SL-2012-310177) and technical support from both Aquakimia Sdn. Bhd. and Research Management Centre, Universiti Teknologi Malaysia. The authors also acknowledge Solvay Specialty Polymers Italy and Johnson Matthey PLC UK for providing materials used in this work.

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