Journal of Membrane Science and Research 6 (2020) 390-394

Journal of Membrane Science & Research

journal homepage: www.msrjournal.com

Research Paper

Demulsification Performance of Superhydrophobic PVDF Membrane: A Parametric Study

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Article info

Received 2020-03-08
Revised 2020-06-19
Accepted 2020-06-23
Available online 2020-06-23

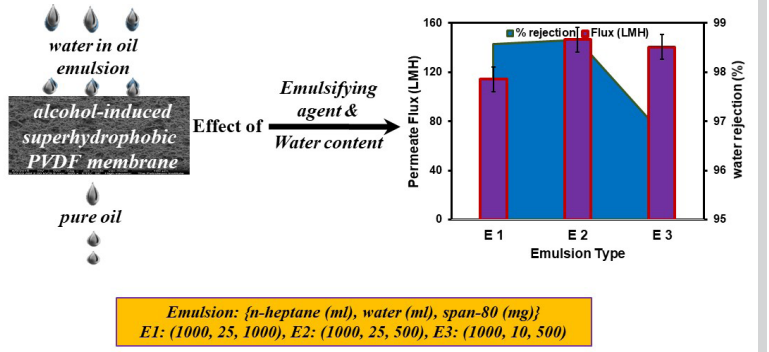
Keywords

Water in oil emulsion
Polyvinylidene difluoride (PVDF)
Superhydrophobic membranes
Permeate flux
Surfactant concentration
Operational stability

Highlights

- Superhydrophobic alcohol-induced PVDF membrane was developed.
- The influence of feed parameters on membrane performance was investigated.
- Emulsifier concentration has a significant impact on permeate flux and rejection.
- The developed membranes are suitable for water-in-oil separation processes.

Graphical abstract



Abstract

Oil-water separation using hierarchical-structured superhydrophobic and superoleophilic membranes have been recently received remarkable attention. In this study, a polyvinylidene difluoride (PVDF) based membrane was prepared by a non-solvent induced phase inversion method for oil-water emulsions separation. The influences of the two key parameters, namely the concentration of emulsifying agent and water content of the feed emulsion, on the membrane performance were investigated in terms of the permeate flux and water rejection. Span-80, distilled water and n-heptane were employed as an emulsifying agent, dispersed phase and continuous phase, respectively. Results showed that an increase in the emulsifier concentration led to a decrease in the oil permeate flux and water rejection. The emulsifier concentration had the most significant effect on the oil-water separation compared with the water content in the feed emulsion. In a continuous experiment lasted for 120 h, more than 95% water rejection was maintained but with a significant drop in oil flux. The well-structured superhydrophobic PVDF membrane showed promise for water-in-oil emulsion separations.

1. Introduction

A large amount of micro and nano-size emulsified-liquid waste is generated by various production plants such as petrochemical, metallurgical and transportation industries [1]. These pollutants are in the form of water in oil (w/o) or oil in water (o/w) emulsions through which they affect the environment when disposed of without treatment [2]. Specifically, during crude oil processing, a dispersed phase (water) encounters the continuous phase (oil), resulting in a w/o emulsions [3]. The emulsions concentration in the crude increases significantly with the aging of oil-wells. Therefore, the demulsification and subsequent removal of water from w/o emulsion are the focal constraints in enhanced oil recovery and gas processing facilities [3]. A variety of conventional processes, namely gravity settling [4], centrifugation [5], chemical demulsification [6], ultrasonication [7], heating [8], superhydrophobic filter and electrostatic coalescers [9] are currently employed for the separation of emulsions. However, all these techniques have certain limitations for the effective w/o emulsions separation [3]. For instance, the chemical demulsification requires a large amount of chemicals, heating is highly energy-intensive, while centrifugation and/or gravity settling are protracted time scale methods. The separation of w/o emulsions using electrostatic coalescers in the petroleum industries entail extremely high applied potentials of 10-20 kV and may possess serious process hazards for the emulsion treatment [10]. In summary, the aforementioned processes are costly, energy-demanding, or consumes large amounts of chemicals and/or

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DOI: 10.22079/JMSR.2020.122768.1353

possess process hazards [3]. Therefore, a cost-effective and efficient w/o emulsion separation process would be an attractive and promising alternative to the current commercial technologies.

Membrane technology is considered to be an economical and effective technique for heavy metal removal and water-in-oil or oil-in-water emulsions separation [11–13]. Comparatively, membrane separation process has several advantages over other conventional separation techniques such as ease of handling without any specific safety considerations, absence of moving parts, and low operational and capital cost [14,15]. Recent studies confirmed that the cross-flow membrane module continuously and effectively treated the surfactants stabilized w/o and o/w emulsions [16]. The efficiency of the emulsion separation depends explicitly on the wettability and surface energy of the developed membranes [17]. Membranes with distinct wettability selectively separate the oil or water phase from the emulsion, depending on the hydrophobic/oleophilic or hydrophilic/oleophobic surface nature. In general, the surface wettability is measured in terms of water contact angle (WCA). Membrane surface with WCA>150º is termed as the superhydrophobic and deployed for w/o emulsion separation because of superior water repellency [13,18]. The superhydrophobic membranes are usually synthesized by plasma polymerization/etching, electrospinning, layer-by-layer approach, phase inversion, sol-gel process and chemical vapor deposition [19]. Amongst them, the phase inversion process is a simple, clean, one-step, and cost-effective process. Various polymeric materials have been studied for membrane synthesis towards w/o emulsions separation applications. For instance, plasma polymerized nanoparticles [20] and polydopamine (PDA) and poly(dimethylsiloxane) (PDMS) modified fiberglass [21] were tested for the development of highly porous superhydrophobic membranes for w/o emulsions separation. Similarly, hydrophobic membranes were synthesized by phase inversion process using poly(vinylidene fluoride-*co*-hexafluoropropylene), P(VDF-*co*-HFP) for gravity-driven w/o emulsion separation process [22]. In our previous study [13], we have reported a superhydrophobic and superoleophilic PVDF based membrane on non-woven support, intrinsically prepared by alcohol-induced phase inversion process for w/o emulsion separation. It was reported that the developed membrane has improved flux and fouling resistance compared to water-induced PVDF membranes. However, the effects of emulsifier concentration and water content of the feed emulsion on the membrane performance were not addressed before and it is quite imperative to understand these effects under similar experimental conditions.

In this study, an eco-friendly non-solvent (ethanol) was used for the preparation of polyester supported superhydrophobic PVDF membrane via phase inversion method for w/o emulsions separation. Different types of feed emulsions were prepared by varying the amount of emulsifying agent (span-80) and dispersed phase (deionized water). The effects of the feed solution parameters were thoroughly investigated in terms of permeate flux and water rejection using the as-developed membrane. Additionally, the fouling nature of the synthesized membrane was also investigated by a 120 h continuous demulsification run.

2. Experimental

2.1. Materials and methods

Ethanol, *n*-heptane, *N*-methyl-2-pyrrolidone (NMP) and span-80 were purchased from Sigma-Aldrich-Germany, while PVDF (M_w: 250-450 kDa) and polyester nonwoven support were supplied by Alfa-Aesar and Hirose paper-Japan, respectively. Deionized (DI) water was used for washing and emulsion preparation. All the chemicals were used without any further treatment or purification.

2.2. Membrane preparation and characterization

Ethanol-induced PVDF membrane was synthesized by a well-known non-solvent induced phase-inversion technique. The detailed membrane synthesis procedure is reported elsewhere [13,23]. Typically, a known mass of PVDF (16 wt.%) in NMP solvent was thoroughly stirred at 50°C and degassed in a vacuum oven (Model: 3608-6CE, ThemoFisher Scientific, Germany) to obtain the desired bubble-free polymer solution, which was then poured and cast on the polyester support of specific dimensions using the doctor blade at room temperature. The film was then immersed in the bath filled with ethanol for phase inversion, followed by drying at ambient temperature.

The morphological characteristics and the WCA of the developed membrane were analyzed using a scanning electron microscope (SEM) (FEI Quanta 200) and Biolin Scientific Goniometer, respectively. The static WCA was measured at five different locations on the membrane surface, and the average value was reported. Figure 1 illustrates a schematic representation of the membrane synthesis process and its testing for surfactant stabilized w/o emulsion separation.

2.3. Water in oil (w/o) emulsions preparation

In order to investigate the impact of emulsifying agents and water content in the emulsion on membrane performance, different microemulsions were prepared and characterized. Specifically, 1000 mL of n-heptane was stirred with two different amounts of span-80 surfactant (0.5 g and 1.0 g) and water (10 mL and 25 mL) for 24 h. The synthesized PVDF membranes were then used in a lab-scale cross-flow membrane module to treat the w/o emulsions.

2.4. Experimental setup and analytical method

An in-house fabricated lab-scale cross-flow membrane setup was used for the demulsification of w/o emulsions. The change in the permeate flux due to variations in the surfactant and dispersed phase concentrations were studied over a transmembrane pressure (TMP) of 1-4 psi. The continuously stirred surfactant stabilized emulsions were recirculated to the membrane module by collecting the permeate in the graduated cylinder. The permeate solution was then tested to measure the content of the dispersed phase using Karl Fischer moisture analyzer (Metrohm 851 Titrando system). The setup consisted of an effective membrane area of 25.6 cm^2 between two-speed spacers at the top and bottom of the membrane. Additionally, membrane fouling analysis was carried out by a 120 h continuous w/o emulsion separation in the same setup without any membrane regeneration. Figure 2 illustrates the schematic representation of the cross-flow membrane module setup for surfactant stabilized w/o emulsion separation.

The membrane compaction was carried-out compacted at a high pressure of 4.5 psi using pure water before all experimentations. The oil permeate flux (J_o) was calculated using equation (1):

$$J_0 = \frac{Q}{A \times t} \tag{1}$$

where Q represents the permeate volume, while A and t is the wetted membrane area and sampling time, respectively.
The water rejection efficiency *(%WR*) was evaluated through equation (2):

$$\%WR = \frac{(W_f - W_p)}{W_f} \times 100 \tag{1}$$

where W_f and W_p are the water content in the feed emulsion and permeate oil, respectively.

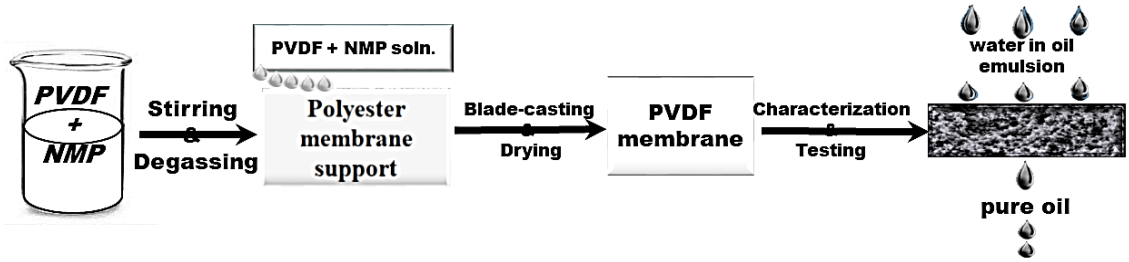


Fig. 1. Schematic illustration of membrane synthesis and testing.

3. Results and discussion

3.1. Morphological characterization

The surface structure and cross-sectional morphology of the as-prepared PVDF membrane are shown in Figure 3(a and b). The SEM images indicate that the developed film consisted of a unified, highly porous and fibrous structure throughout the membrane surface. The heterogeneous configuration of the alcohol-induced PVDF membrane resulted in surface roughness and superhydrophobicity, resulted in better flux and anti-fouling ability for the developed membrane [13]. The pores of the alcohol-induced PVDF-based membrane have size ranging between 100 nm to about 2 µm, and about 80% porosity, as reported in our previous work [13].

Additionally, the superhydrophobic nature of the prepared membrane was also verified through WCA analysis measured immediately after dropping the water at the surface. Remarkably, the alcohol-induced PVDF membrane exhibited a WCA of 155°. The visual image of a water droplet on the developed membrane surface is shown in Figure 3(c).

3.2. Effect of emulsifier concentration and water content on permeate flux

The separation performance of the as-prepared membrane was measured in terms of permeate flux using different types of feed emulsion. To deeply explore the effect of feed solution on permeate flux, various feed emulsions were prepared by varying the emulsifier and water content concentration and subjected to membrane separation. Figure 4 presents the photographic and optical microscopic images of various surfactant stabilized feed w/o emulsions and the permeate (oil) obtained for Emulsion-2 filtration by the membrane separation process.

The surfactant stabilized w/o emulsions were treated by the developed superhydrophobic membrane in a cross-flow membrane module. Figure 5(a and b) illustrates the relationship between the operating pressure and permeate flux obtained for w/o feed emulsions with 2 different values for emulsifier and dispersed phase concentration. As shown, the permeate flux increased with the increase in the applied pressure. The permeate flux increase was small at low TMP but remarkable for higher TMP. As shown in Figure 5(a), an increase in the span-80 emulsifier concentration from 0.5 to 1 gm lowered the permeate flux. In general, the surface tension of the solution decreases with an increase in the concentration of emulsifier as it prevents the coalescence between suspended droplets and the continuous phase [24]. As visually observed, a dense layer on the membrane surface was developed at high emulsifier concentration, which retarded the oil transport across the membrane and resulted in low permeate flux. Therefore, 500 mg of span-80 was selected for further experimentation.

Moreover, membrane flux was also affected by the amount of water in surfactant stabilized w/o emulsions. Results for the effect of dispersed phase concentration on the permeate flux are shown in Figure 5(b). Two different emulsions were prepared in 1000 mL n-heptane and 500 mg span-80 by adding DI water of 0.01% and 0.025%, respectively. The results revealed an improvement in the permeate flux by increasing the water content in the feed solution (emulsion) under the same experimental conditions in conformance with the reported literature [2]. This can be ascribed to the higher interactions between the dispersed phase of water droplets and the surfactant, which led to the enhanced oil flux through the membrane. Conversely, lower permeate flux was observed at lower water concentration, indicating a coalesce of oil droplets with Span-80 [25].

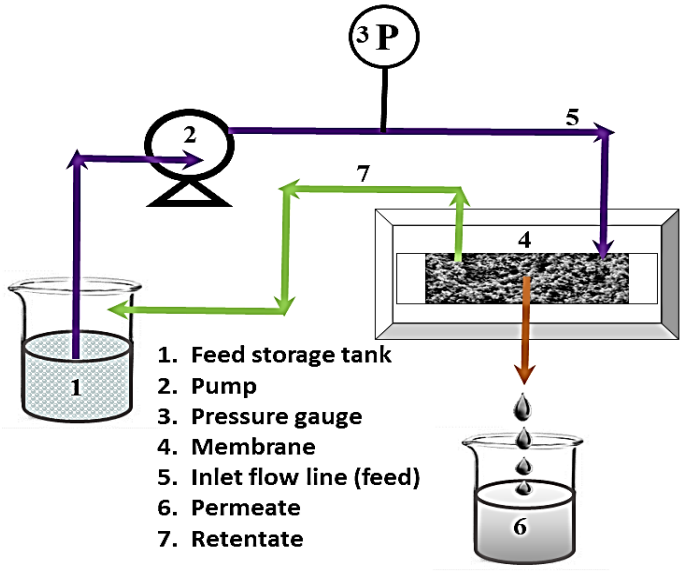


Fig. 2. Schematic representation of membrane module for w/o emulsion separation.

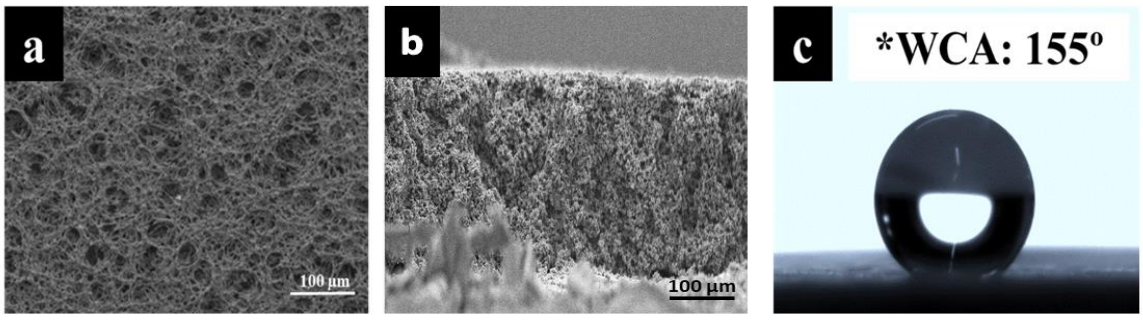
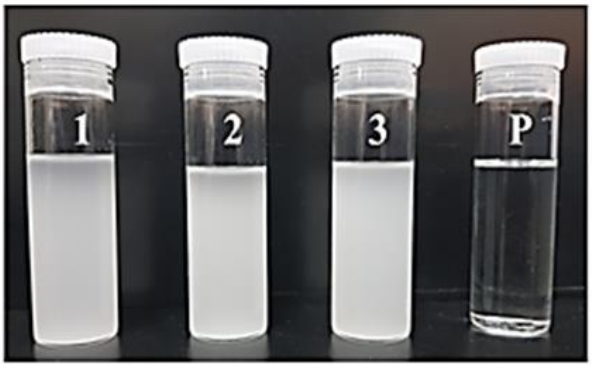


Fig.3. SEM micrographs of alcohol-induced membrane, (a) top-surface (b) cross-sectional area, (c) WCA of PVDF membrane.



Emulsion #	n-heptane (ml)	D.I. water (ml)	Span-80 (mg)
1	1000	25	1000
2	1000	25	500
3	1000	10	500
Permeate	oil	-	-

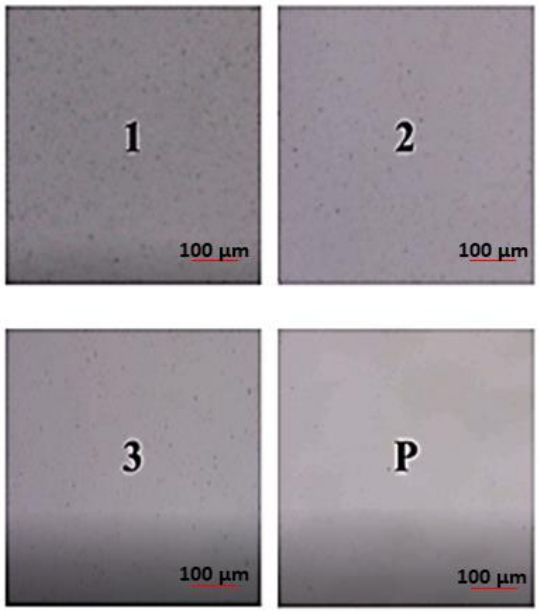


Fig. 4. Photograph (left) and optical microscopic images of w/o emulsions and permeate (right).

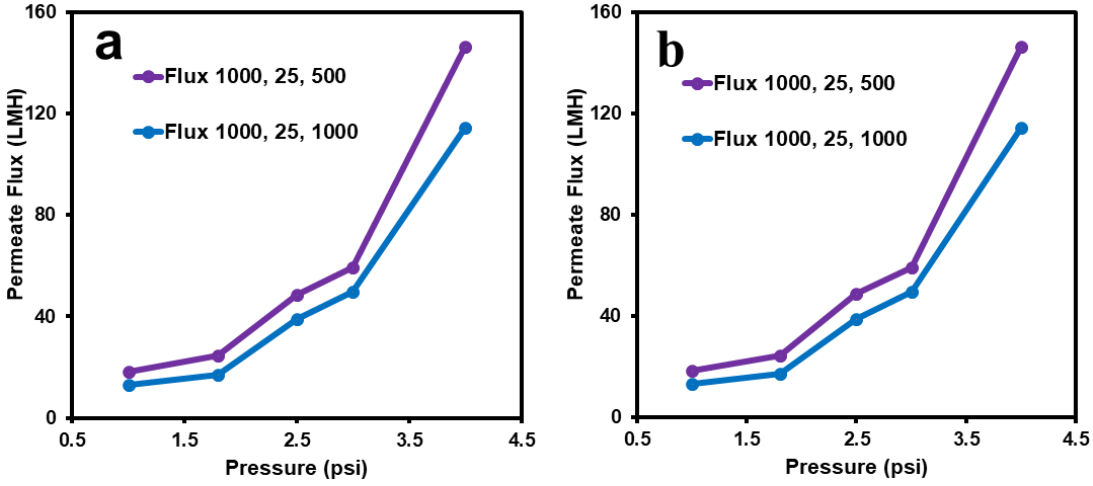


Fig. 5. Effect of (a) emulsifying agent and (b) water content on permeate flux.

3.3. Comparison of water removal in permeates

The membrane performance for w/o emulsions separation was also assessed in terms of water rejection efficiency. The as-prepared micro-emulsion samples (by varying the concentration of emulsifying agent and dispersed-phase), as shown in Figure 4, were treated through PVDF-based membranes, and the permeate oil was evaluated for its moisture content. The results for the variation in water rejection performance for different types of feed emulsions are presented in Figure 6. It can be observed that the amount of moisture content in the permeate oil varied for different feed emulsions. From the results, it can be inferred that the amount of dispersed phase and the emulsifying agent regulated the rejection performance of the PVDF membrane. It was observed that the higher concentration of the emulsifying agent in the feed emulsion led to reduced water rejection efficiency. A low concentration of emulsifier ensured its uniform distribution to produce a highly stable emulsion, which resulted in better water rejection efficiency. However, a high concentration of span-80 in the feed emulsion resulted in significant reduction of the permeate flux due to the potential formation of dense film onto the surface of the membrane [25]. As expected, lowering the dispersed phase in the feed emulsion decreased the moisture content in the permeate oil.

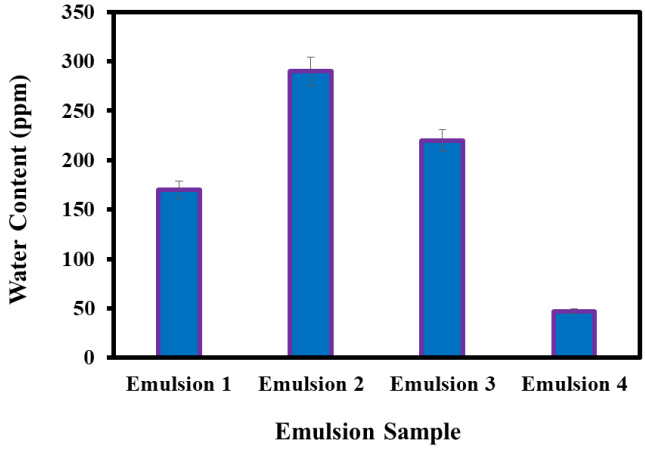


Fig. 6. Emulsions effect on permeate water content.
Emulsion #: {n-heptane (ml), water (ml), span-80 (mg)}
E#1: (1000, 25, 1000), E#2: (1000, 25, 500), E#3: (1000, 10, 500), E#4: (n-heptane).

3.4. Long term membrane testing (membrane fouling resistance analysis)

Considering the higher flux and good water rejection results, emulsion 2 (1000 mL n-heptane, 25 mL DI water, 500 mg span-80) was selected to examine the fouling behavior of alcohol-induced PVDF membrane. A continuous long-term (120 h) operation for w/o emulsion separation was performed using the as-prepared superhydrophobic membrane at 1.5 psi transmembrane pressure without any break or backwashing. Figure 7 shows the variation of oil permeate flux and water rejection over time. The oil permeate flux rapidly decreased in the first 6 h of operation, followed by a sustained decrease to 87% of the initial flux at 120 h. However, the water rejection efficiency of the superhydrophobic PVDF membrane dropped little and remained over 95% to the end of the experiment. The 2% drop of water rejection exhibits the good operational stability of the as-prepared PVDF membrane for demulsification of w/o emulsions. As such, the developed membrane showed promise for the treatment of real-time surfactant stabilized w/o emulsions.

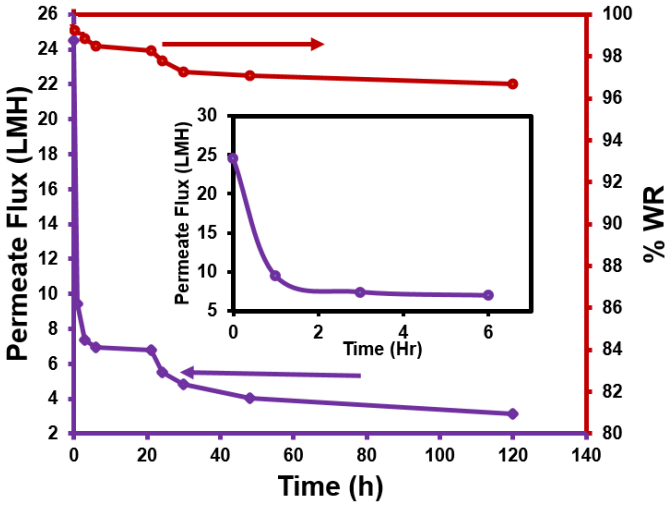


Fig. 7. Influence of long-term emulsion separation process on permeate flux and water content using emulsion # 2 (1000, 25, 500).

4. Conclusions

A highly porous and dense fibrous structured superhydrophobic PVDF membrane was developed and tested for water-in-oil emulsions separation. The surface of the developed membrane showed outstanding superhydrophobicity with WCA of 155°. Results showed that the decrease in the span-80 emulsifier concentration in the feed increased the water rejection and permeate oil flux. Effects of dispersed phase concentration in the feed emulsion were observed to be insignificant. The membrane performance was mainly dependent on the emulsifying agent and water concentration in the feed emulsion. The long term experiment showed a significant reduction in oil flux with a small change in water rejection, indicating a need for regeneration. Overall, the developed membrane showed interesting potentialities for the separation of o/w emulsions.

Acknowledgments

The authors thank Khalifa University of Science and Technology, Abu Dhabi (UAE) for funding the work under Grant No. LTR14013.

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