

An Experimental Study on the Oily Wastewaters Treatment by Polyethersulfone (PES) Nanostructure Hollow Fiber Membranes

Gholamreza Bakeri ^{1,*}, Zeynab Fallahnejad ²

1. Assistant Professor, Faculty of Chemical Engineering, Babol Noshirvani University of Technology, Babol, Iran

2. M.Sc. in Chemical Engineering, Babol Noshirvani University of Technology, Babol, Iran

ARTICLE INFO

Article history:

Received: April 01, 2015

Accepted: October 26, 2016

Keywords:

Oily wastewater treatment
Polyethersulfone (PES) hollow
Fiber membrane
Environmental pollution
Membrane cleaning

* Corresponding author
E-mail: bakeri@nit.ac.ir
Tel.: +98 91 25265739
Fax: +98 11 32334204

ABSTRACT

Oily wastewaters from oil refineries and oil distribution centers are one of the most important environmental concerns in recent decades; therefore, it is critical to treat these types of wastewaters. In this study, the performance of different polyethersulfone hollow fiber membranes in oily wastewaters treatment was investigated and the effects of operating conditions such as transmembrane pressure, oil concentration in the feed and feed cross flow velocity (CFV) on the membrane performance were studied. Increasing the pressure makes more membrane compactness and higher membrane fouling; as a result, higher pressure reduces the membrane performance. The optimum operating conditions for oily wastewaters separation are $P = 1$ bar, low feed concentration (300 ppm) and high feed cross flow velocity (0.18 m s^{-1}). In this study, membrane #M₁ with the mean pore size of 8.29 nm, membrane porosity of 77%, permeation flux of $12.4 \text{ (L m}^{-2} \text{ hr}^{-1})$ and 100% oil rejection showed the best performance in treating the oily wastewaters.

1. Introduction

Due to the impact of oily wastewaters on the environment, the wastewaters from oil refineries and oil distribution centers should be treated before discharging to sewage [1]. Depending on the geographical conditions and characteristics of oily wastewaters, there are varieties of standards in different countries, e.g., in Malaysia the maximum limit is 10 ppm while in the United States, it is 40 ppm [2]. The traditional methods for oily wastewater treatment such as gravity separation and skimming, dissolved air flotation, de-emulsification, coagulation and flocculation are not effective in removing oil droplets and emulsions. These methods have several disadvantages such as low efficiency, high operation costs, corrosion and recontamination of the treated stream. Furthermore, these processes are effective when the size of oil droplet in the oil-in-water emulsion is between 20 μm and 150 μm . All of these disadvantages promoted the development of new processes for the treatment of oily wastewaters especially when the size of the oil droplet is small [3].

Different kinds of membrane-based processes such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have been effectively used for oil/water separation. Membrane-based filtration processes play a major role in the oily wastewater treatment, due to their advantages such as no need to chemical additives to break the emulsion, high COD¹ removal efficiency and the compactness in the equipments used for the oily wastewater treatment [1]. Because of its suitable pore size and its capability in removing the emulsified oil droplets without any de-emulsification processes and low operating pressure which reduce the energy consumption, ultrafiltration has been verified as an efficient method for the treatment of oil-in-water emulsions [4]. Pressure-driven ultrafiltration process is widely used for the separation, purification and concentration of water-soluble solutes or dispersible materials.

According to the existing literature, most studies have focused on the application of ultrafiltration and microfiltration membranes in oily wastewater treatment, where oil droplets are completely retained behind the membrane and the continuous phase permeates [5]. Lipp et al. reported that since the oil droplets are deformable and depending on the applied pressure, the oil droplets can be squeezed through the pores and contaminate the permeate [6]. Nazzal and Wiesner found that if the transmembrane pressure (TMP) was below the critical value, the rejection could be maximized [7]. Hlavacek also reported that the porous structure of the membrane could promote the coalescence of micron-size and submicron-size oil droplets into larger ones that could easily be separated by gravity. In this study, the membranes were used as coalescers rather than as separators [8]. Mueller et al. investigated ceramic and polymeric MF membranes for treating synthetic oil-in-water emulsion, containing 250-1000 ppm heavy crude oil with a diameter of 1-10 μm . They reported that the membranes could make permeate with oil content less than 6 ppm [9]. Kong and Li investigated the effects of feed flow rate, operating pressure, membrane pore size and porosity on the separation of oil-in-water emulsions by flat sheet hydrophobic PVDF membranes [10].

Most of the studies on the application of PES membrane in oily wastewater treatment have been devoted to flat sheet membrane. The objective of this study

¹ Chemical Oxygen Demand (COD)

is the application of polyethersulfone (PES) nanostructure hollow fiber membranes in oily wastewater treatment and investigating the effect of operating parameters such as transmembrane pressure (TMP), feed concentration and feed cross flow velocity (CFV) on the performance of the membranes. The membrane performance is characterized in terms of pure water flux (PWF), permeate flux (PF) and the percentage of the oil rejection (%R).

2. Research method

2.1. Preparation of spinning solutions

A predetermined amount of PES was dissolved in NMP² at 70 °C under gentle mixing to make the PES solution with desired concentration, as has been presented in Table 1.

Table 1: The compositions of the polymer solutions

Solution No.	PES (wt%)	Solvent (wt%)
#M ₁	17	83
#M ₂	19	81
#M ₃	21	79

2.2. Preparation of hollow fibers

The spinning solution was delivered to the annulus of a tube-in-orifice spinneret at constant flow rate while water as the bore fluid was sent to the inner tube of the spinneret. After leaving the spinneret, the nascent fiber entered the coagulation bath (tap water) to complete the phase inversion process. The wet spun fibers were immersed in water for several days to remove the residual solvent and nonsolvent additives and then dried naturally by hanging vertically at room temperature.

2.3. Materials

Commercial grade gas oil and dish washing detergent and deionized water (with a conductivity of 2.9 $\mu\text{s cm}^{-1}$) were used for making the oil-in-water emulsions. Ethylenediaminetetraacetic acid (EDTA) and sodium dodecyl sulfate (SDS) were used for the preparation of the membrane cleaning solution.

2.4. Membrane characterization

Asymmetric porous membranes were characterized by the determination of membrane porosity and mean pore size where the membrane porosity (ϵ) was defined as the volume of the pores divided by the total volume of the porous membrane. Pure water permeation test [11] was used for measuring the membrane mean pore size. The method for the determination of membrane porosity, which is related to the membrane structure, was reported in Yuliwati et al. [12]. The contact angle of water with the membrane surface is a criterion of surface hydrophilicity, that affects the permeance and fouling characteristics of the membrane, and is measured by the sessile drop technique using the contact angle goniometer (model G1, Krüss GmbH, Hamburg, Germany). At least, ten

² N-methyl 2-pyrrolidone (NMP)

points on the surface were used for contact angle measurement and the results averaged.

To measure the membrane porosity, some hollow fibers were immersed in methanol and water respectively, for a few days to completely wet the membranes. Then, the weight of the wet membranes was measured by a balance. Afterward, the free water on the surface of fibers was removed and the water in the lumen side of fibers was discharged through blowing air for a short period and then, the fibers were dried at 45 °C for 12 hours. Next, the weight of the dried membranes was measured. The membrane porosity was calculated by Eq. 1.

$$\varepsilon = \frac{(\omega_1 - \omega_2)}{\frac{\rho_w}{(\omega_1 - \omega_2)} + \frac{\omega_2}{\rho_p}} \quad (1)$$

where w_1 is the weight of wet membrane (g), w_2 is the weight of the dry membrane (g), ρ_p is the density of the polymer (1.55 g cm⁻³ for PES) and ρ_w is the density of the water (1 g cm⁻³).

The mean pore size of the membrane (r_m), that is a representative of pore size along the membrane thickness, was measured by the pure water permeation test. Pure water, with a pressure of 1 bar, was sent to the shell side of the membrane module and the flow rate of water, permeated through the lumen side of fibers, was measured. The mean pore size of the membrane was calculated by Eq. 2 (Guerout–Elford–Ferry equation).

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l Q}{\varepsilon \times A \times \Delta P}} \quad (2)$$

where η is the water viscosity (8.9×10⁻⁴ Pa s), l is the membrane thickness (m), ΔP is the operating pressure (0.1 MPa), Q is the flow rate of the permeated water (m³ s⁻¹) and A is the effective area of the membrane (m²) [11].

2.5. Preparation of oil-in-water emulsion

Gas oil, detergent and deionized water were mixed severely by mechanical stirrer (rpm = 2500) for 5 minutes to make a stable oil-in-water emulsion.

2.6. Cross flow ultrafiltration experiments

The schematic of the ultrafiltration system and the membrane module have been shown in Figure 1 where the synthesized oil-in-water emulsion as the feed solution is sent to the shell side of UF module and the permeate is collected via the lumen side. The feed flow rate is controlled by the valve at the exit of liquid. The permeation flux (J) and rejection (R) are calculated through the Eq. 3-4 below.

$$J = \frac{Q}{At} \quad (3)$$

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (4)$$

where Q is the volume of the permeate (m^3), A is the effective membrane area (m^2), t is the time for the collection of permeate (s), C_P is the concentration of oil in the permeate and C_F is the concentration of oil in the feed.

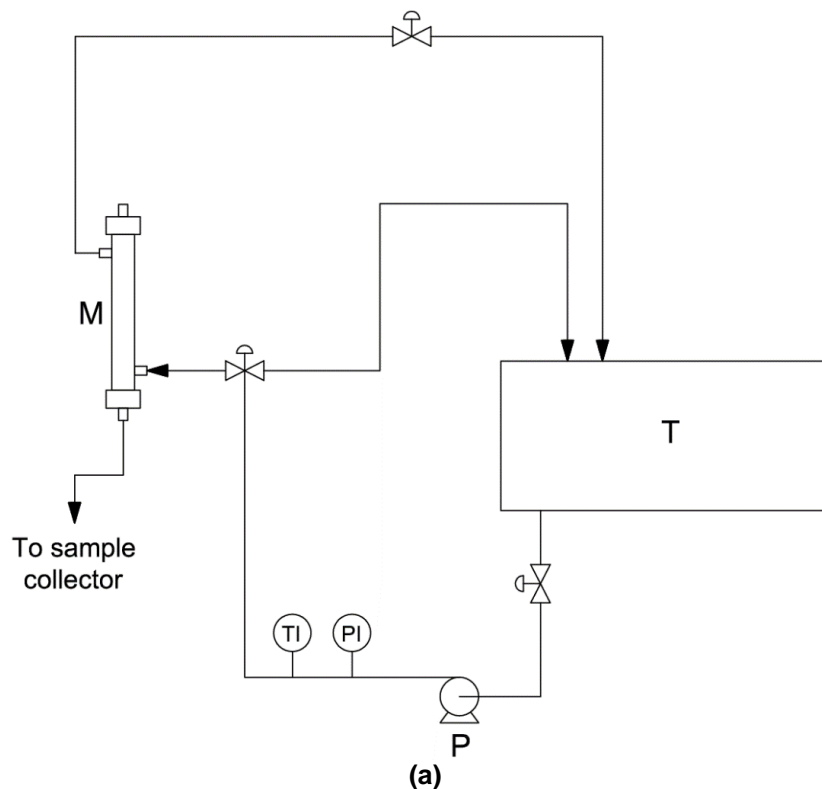


Figure 1: a) Schematic of cross flow ultrafiltration system, T: feed tank, P: pump, PI: pressure gauge, TI: thermometer, M: membrane module. b) Membrane module

The range of the operating parameters for UF experiments has been summarized for each membrane in Table 2.

Table 2: The range of operating conditions for UF experiments

Membrane	Gas oil concentration (ppm)	Pressure (bar)	Temperature (°C)
M ₁	300, 600, 900	1, 2, 3	27
M ₂	300, 600, 900	1, 2, 3	27
M ₃	300, 600, 900	1	27

During the experiments, no separation of oil from water was observed in the feed solution; in other words, the feed solution was stable. The concentration

of gas oil in water was analyzed by UV-VIS spectrophotometer (model: ChromTech) at 200 nm wavelength.

2.7. Cleaning of the fouled hollow fiber membranes

Due to the membrane fouling, flux decreases with time during the filtration process. The membrane cleaning between each run was carried out through the following steps:

Step 1: washing the membrane by the cleaning solution (EDTA + SDS + water) at 45 °C for about 20 minutes. The cleaning solution enters to the shell side of membrane module and exits from the lumen side,

Step 2: washing the membrane by pure water at 50 °C for about 30 minutes,

Step 3: washing the membrane in reverse direction (backwashing) by the cleaning solution (EDTA + SDS + water) at 45 °C for about 30 minutes,

Step 4: backwashing the membrane by pure water at 50 °C for about 30 minutes

2.8. Scanning Electron Microscopy (SEM) test

SEM was used to observe the structure of the membrane cross-section. The fiber was broken in liquid nitrogen to attain a smooth surface and then platinum (Pt) sputtered. The micrographs were taken by SEM (TM 3000, Hitachi) with magnifications of 500 (cross section) and 5000 (surface).

3. Results and discussion

The characteristics tests results of the fabricated membranes presented in Table 3 show that by increasing the polymer concentration in the spinning solution the mean pore size of the membrane decreases. This is a rational conclusion. Furthermore, the porosity of the membrane reduced by increasing the polymer concentration. In addition, the contact angle of the membrane with water increases with polymer concentration. It should be mentioned that the contact angle of the membrane depends on the different surface properties of the membrane such as the pore size and pore size distribution, surface roughness, surface hydrophobicity, etc. In fact, the smaller the pore size, the higher the contact angle.

Table 3: The characteristics tests results of the fabricated PES hollow fiber membranes

Membrane No.	Water contact angle	Mean pore radius (nm)	Membrane porosity (%)	Inner diameter (mm)	Outer diameter (mm)
M ₁	77.13 ± 1.28	8.29	77	0.55	0.75
M ₂	82.17 ± 1.98	7.43	75	0.5	0.75
M ₃	83.16 ± 1.96	6.70	71	0.5	0.80

The SEM micrographs of the surface and cross section for the fabricated membranes have been presented in Figure 2 where all the membranes show skin layers on both inner and outer surfaces and fingerlike macrovoids. They originate from inner and outer surfaces and extend to the middle of the membrane cross section. This structure is related to the low polymer solution viscosity and strong internal and external coagulants (water) that accelerate the phase inversion process.

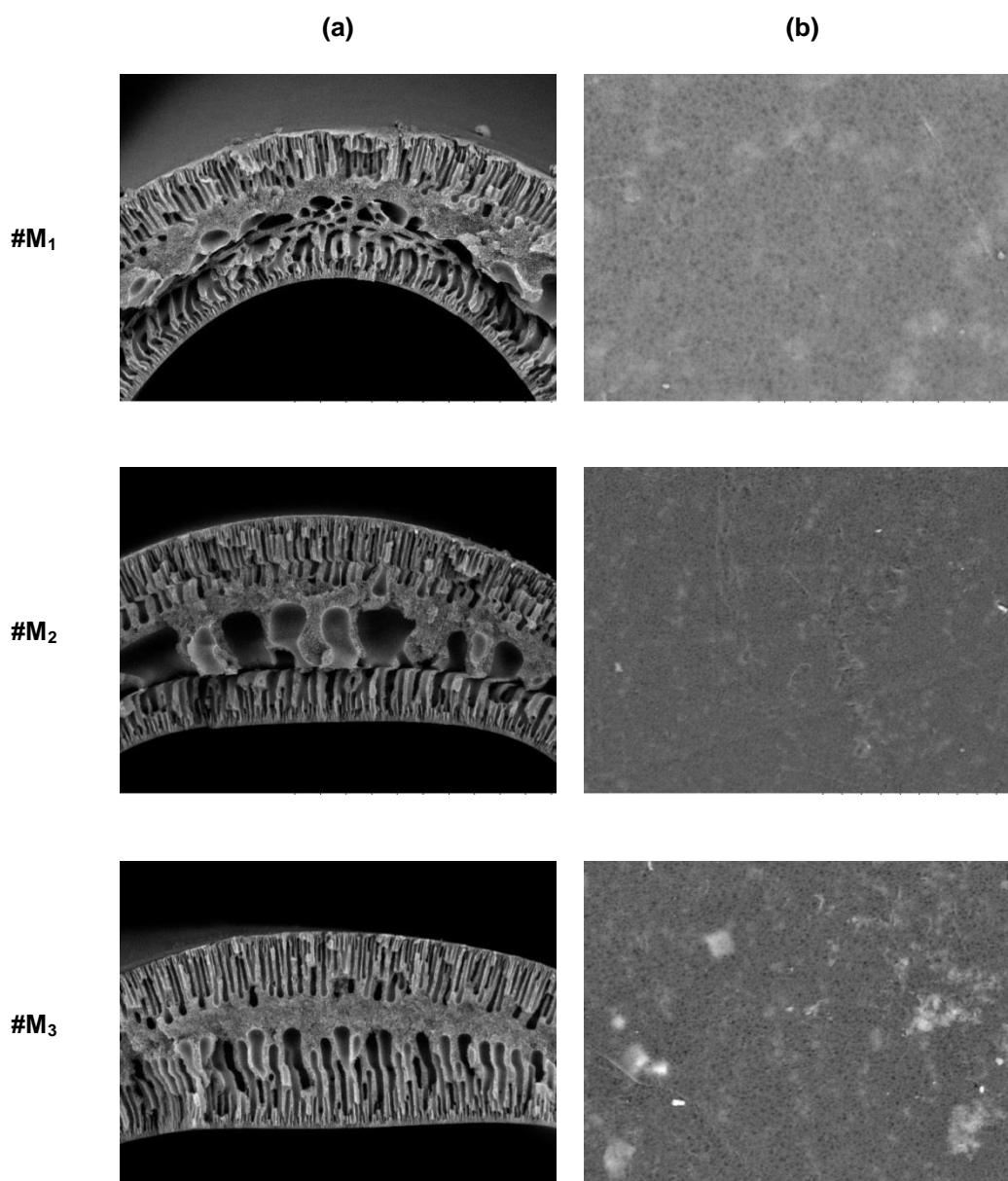
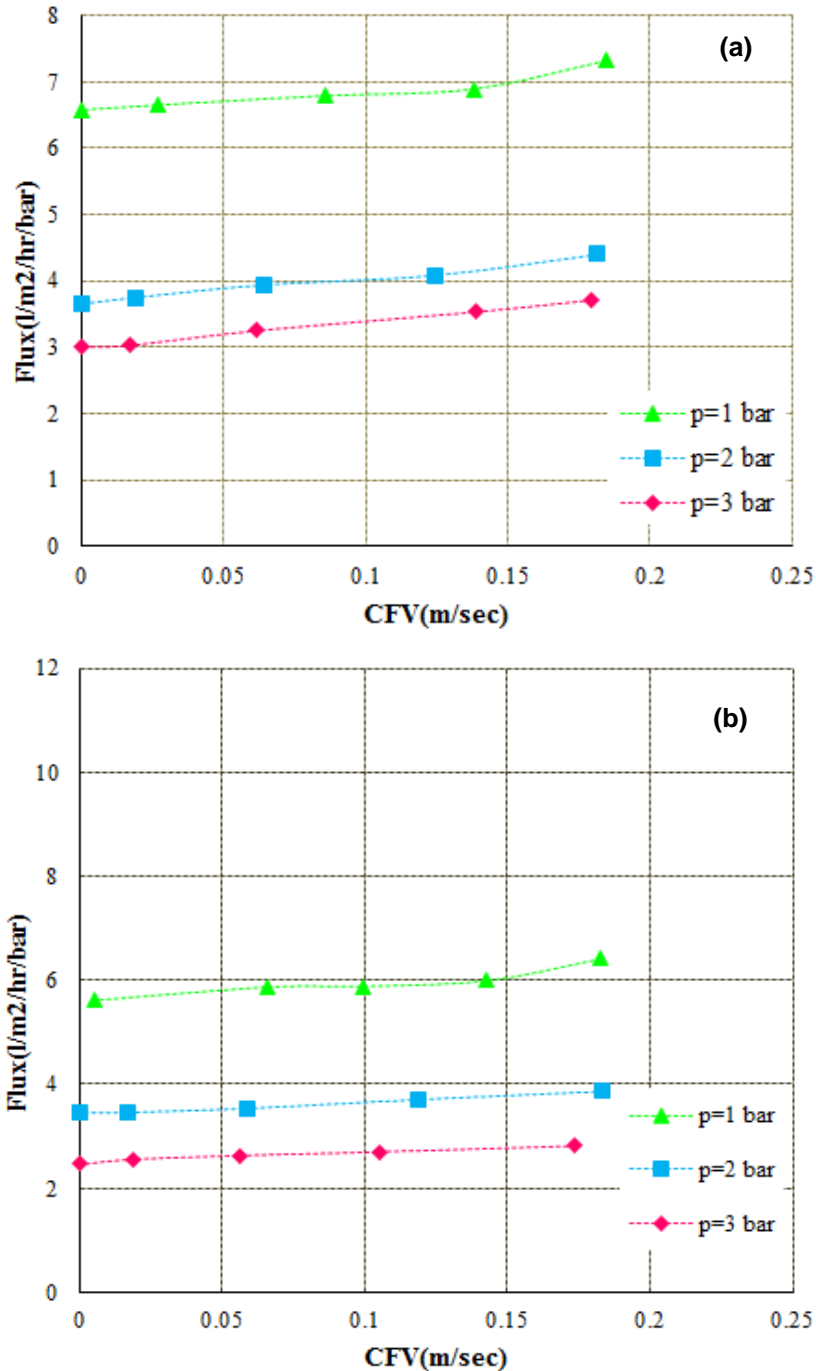


Figure 2: SEM micrographs for the fabricated membranes, a) cross section, b) surface

3.1. The effect of operating pressure on the permeation flux

Membrane permeance and membrane fouling increase by the operating pressure. Higher pressure increases the compactness of oil layer on the surface of membrane which enhances the fouling of the membrane. Furthermore, at higher pressure the oil droplets are pushed into membrane pores which promotes the fouling. Therefore, pressure has an opposite effect on the permeation flux. In Figure 3-4, the normalized permeation fluxes of the membrane #M₁ and #M₂ (in terms of $L\ hr^{-1}\ m^{-2}\ bar^{-1}$) were plotted versus cross flow velocity (CFV) at different feed concentrations which shows the decline in flux as the pressure increases. This can be related to the concentration polarization effect and pore blockage [13]. The flux of the membrane #M₁ is the highest that can be related to the higher porosity and larger mean pore size of this membrane.

At higher pressures, there is more collision between the emulsified oil droplets, which in turn breaks the film between the oil droplet and water, causing oil droplets to coalesce and form larger droplets. A layer containing large oil droplets starts to form just above the membrane surface which in turn, may be compressed on the membrane surface at higher pressure and leads to more membrane fouling [5]. This phenomenon reduces the flux.



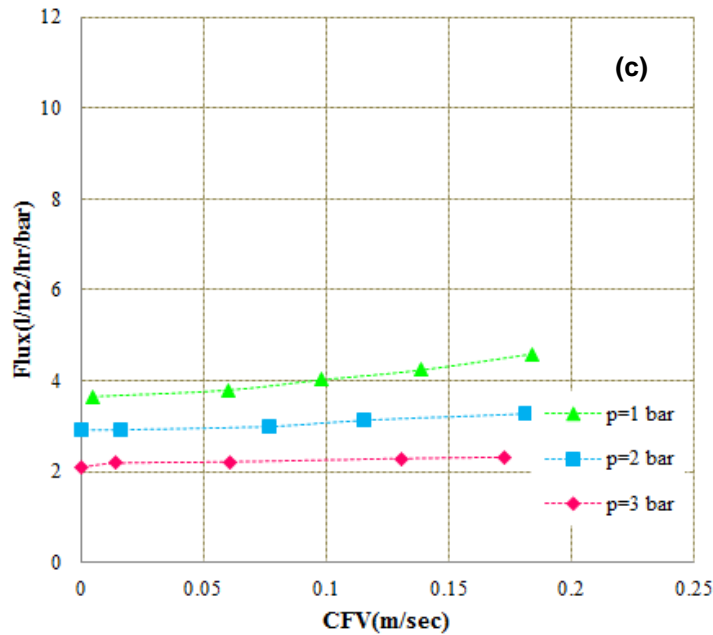


Figure 3: The effect of operating pressure (in terms of bar) on the normalized permeation flux of membrane #M₁ (in terms of L m⁻² h⁻¹ bar⁻¹), oil concentration in the feed: (a) 300 ppm, (b) 600 ppm, (c) 900 ppm

The flux increases with pressure as the pressure is the driving force in the ultrafiltration process but the increase is not exactly linear which can be related to the additional transfer resistances such as the adsorption of oil droplets on the surface of membrane and the concentration polarization effect [15].

The permeation flux versus time for the membranes has been presented in Figure 5 where the permeation flux is leveled off for all the membranes after a specific time that is related to the stabilization of the fouling process on the permeance. The total membrane resistance consists of two main parts: pore blockage and concentration polarization. In the early stages of the filtration process, oil droplets precipitates in the pores of the membrane and causes a rapid decrease in the permeation flux. After the stabilization of the pore blockage phenomenon, the concentration polarization, which is related to the settling of the oil droplets on the surface of membrane, has the major role in the flux reduction [14]. It is interesting that the bigger the pore size of the membrane, the higher the pore blockage effect.

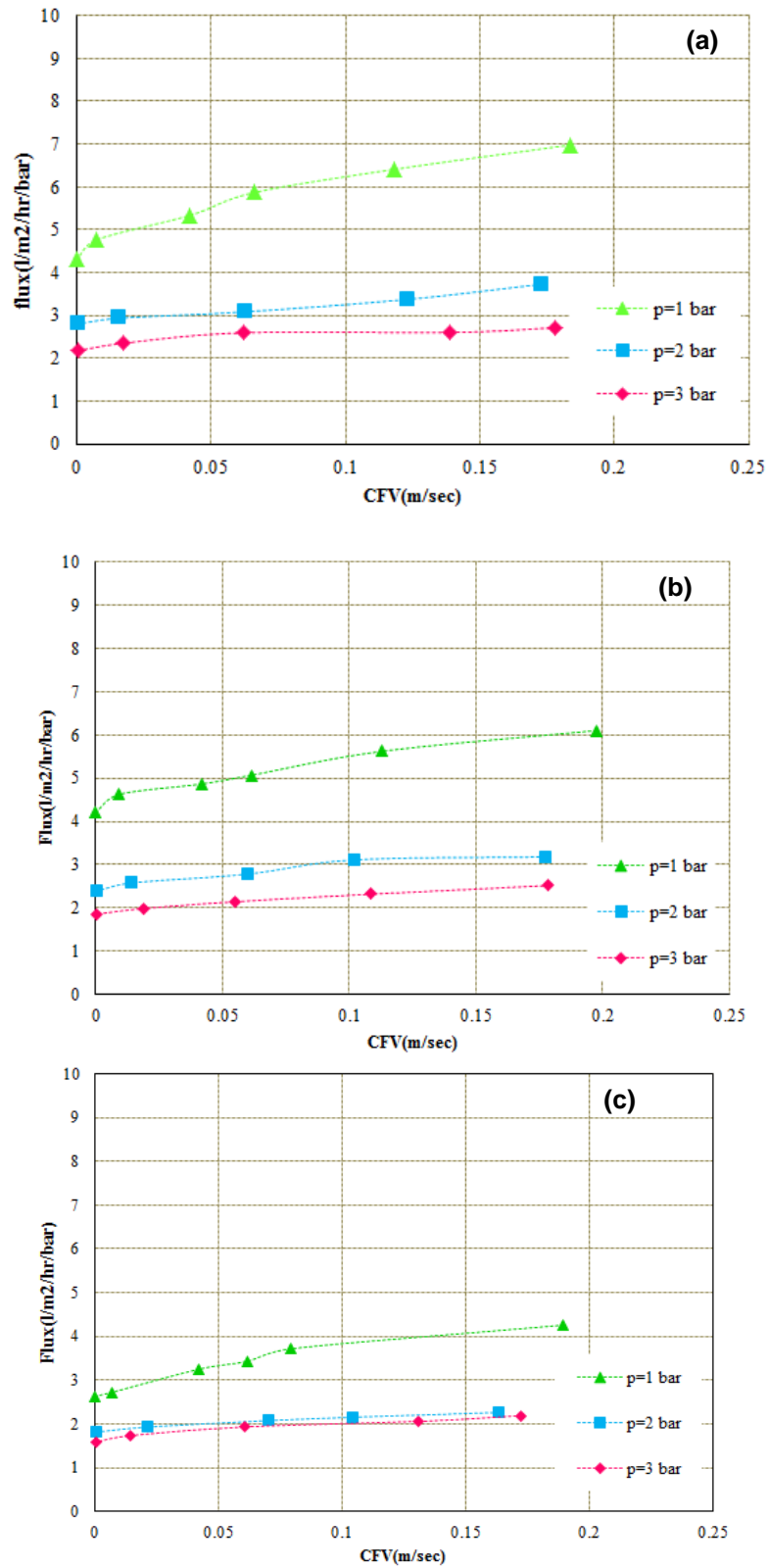


Figure 4: The effect of operating pressure (in terms of bar) on the normalized permeation flux of membrane #M₂ (in terms of L m⁻² h⁻¹ bar⁻¹), oil concentration in the feed: (a) 300 ppm, (b) 600 ppm, (c) 900 ppm

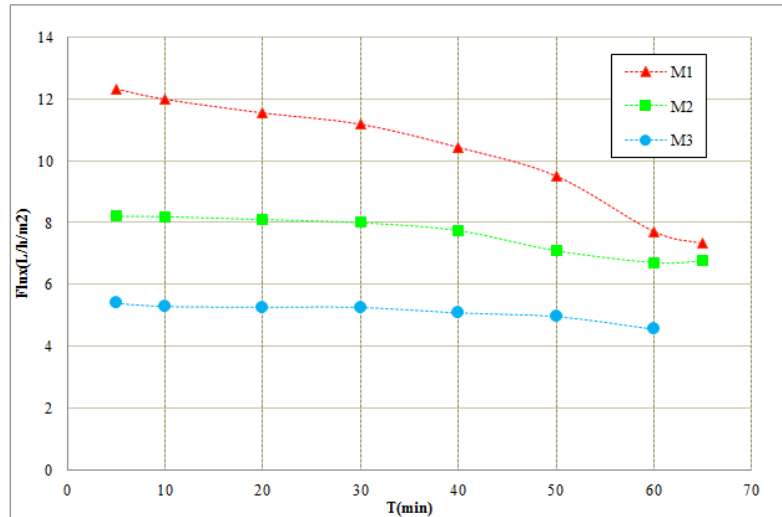
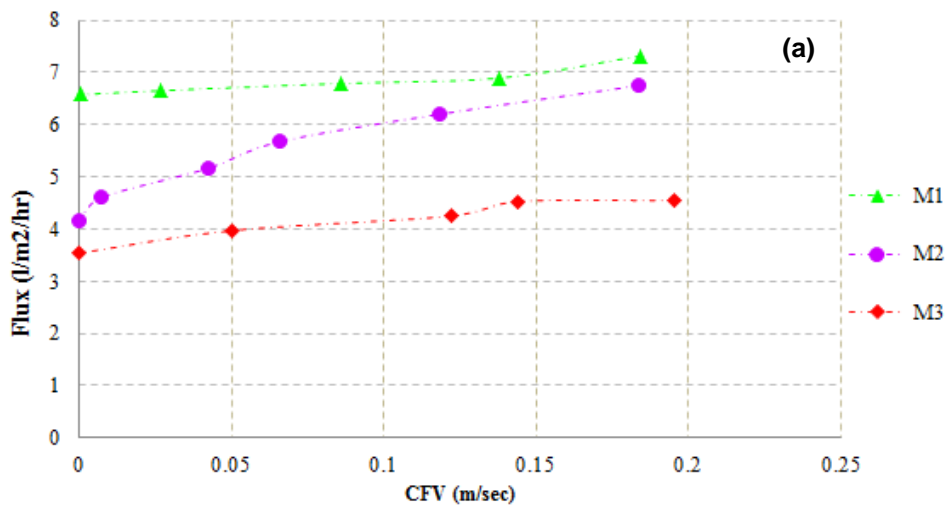


Figure 5: Variation of the permeation flux (in terms of L m⁻² h⁻¹) with time (in terms of minute) for different membranes, feed oil concentration: 300 ppm, P = 1 bar, CFV = 0.18 m s⁻¹

3.2. Effect of feed cross flow velocity on the permeation flux

The effect of feed cross flow velocity (CFV) on the permeation flux of the membranes is shown in Figure 6 where the flux increases with CFV. The reason is the higher turbulence on the surface of membrane which reduces the precipitation of oil droplets on the surface of the membrane; furthermore, it decreases the effect of the concentration polarization.



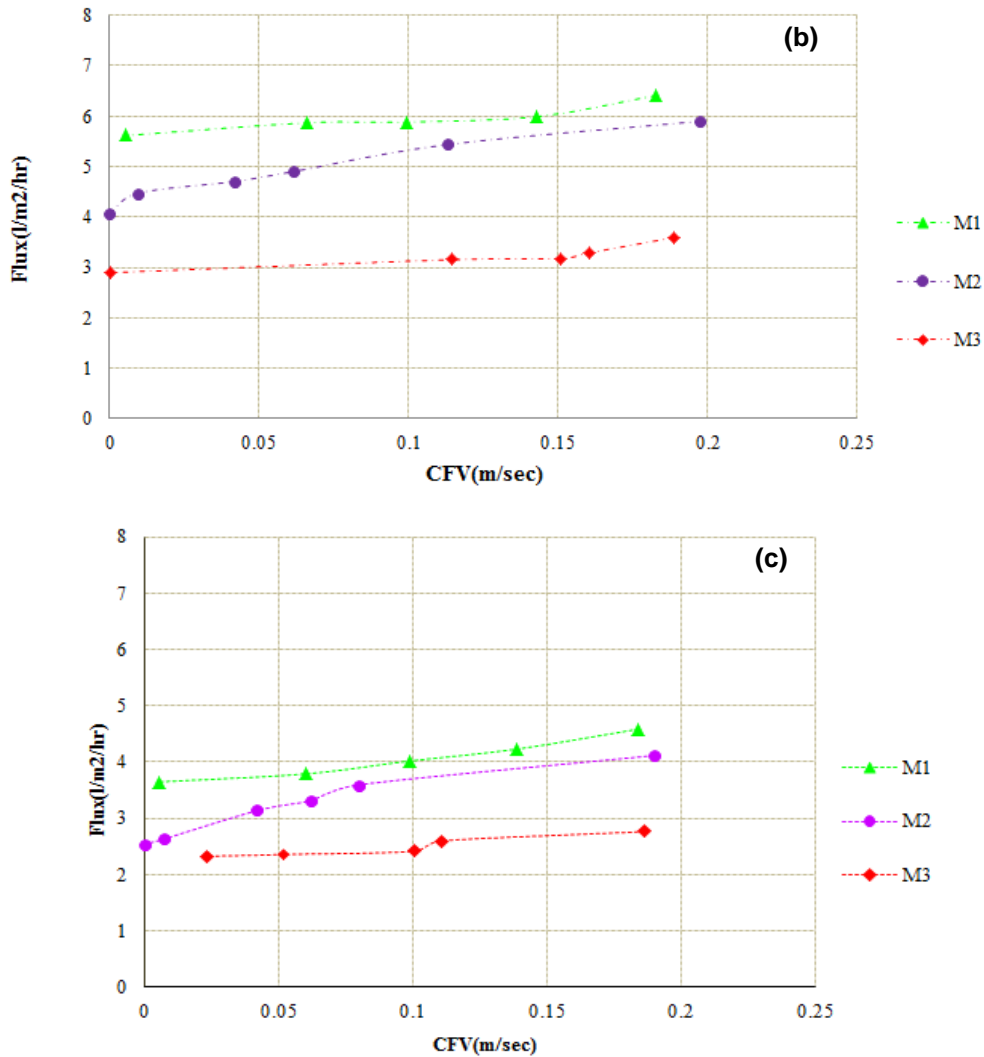


Figure 6: The effect of feed cross flow velocity (CFV) (in terms of m s^{-1}) on the permeation flux (PF) (in terms of $\text{L m}^{-2} \text{h}^{-1}$), $P = 1$ bar, gas oil concentration: (a) 300 ppm, (b) 600 ppm, (c) 900 ppm

3.4. The effect of feed cross flow velocity on the gas oil rejection

Generally, the membrane with a bigger pore size has lower separation performance in the oily wastewater treatment process. Figure 7 shows the effect of feed cross flow velocity on the oil rejection of membranes at the optimum pressure ($P = 1$ bar). Increasing the feed cross flow velocity (CFV) enhances the mass transfer coefficient in the concentration boundary layer on the membrane surface and it may decrease the rejection. All of the membranes show complete separation of the oil from water.

Based on the European standards, the maximum oil content in the treated oily wastewater is 5 ppm [16]; therefore, the PES membranes are suitable candidates for the oily wastewater treatment.

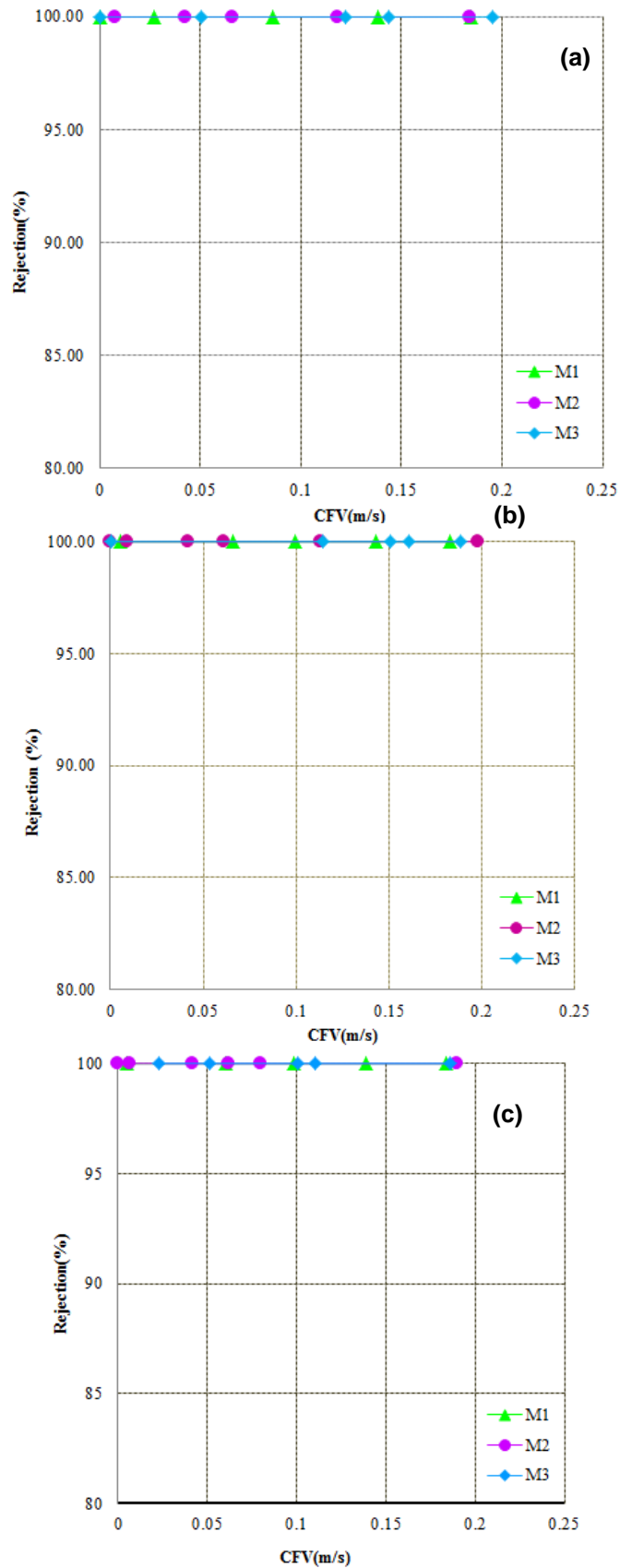


Figure. 7: The oil rejection of PES membranes versus feed cross flow velocity (CFV) (in terms of $m s^{-1}$); $P = 1$ bar, oil concentration in the feed: (a) 300 ppm, (b) 600 ppm, (c) 900 ppm

4. Conclusion

In this study, the treatment of oily wastewaters by nanostructure PES hollow fiber membranes through a cross flow ultrafiltration system was investigated. The effects of membrane pore size and porosity on the permeate flux (PF), gas oil rejection (%) and flux declination were studied. Besides, the effects of transmembrane pressure (TMP), feed cross flow velocity and feed concentration on the membrane performance were analyzed. The conclusions obtained are as follow:

1. The permeation flux increases with the transmembrane pressure (TMP) but due to the existence of other resistances such as the adsorption of oil on the membrane surface and the concentration polarization effect, the flux does not increase linearly with pressure. In terms of flux, the rejection and membrane fouling the optimum transmembrane pressure (TMP) is $P = 1$ bar.

2. The membrane porosity, mean pore size and the structure of the membrane sublayer play a major role in the permeation flux, flux declination (FD) and membrane fouling. The flux of membrane #M₁ is the highest that can be related to the higher porosity and larger mean pore size of this membrane.

3. Permeation flux decreases with the oil concentration in the feed and increases with CFV that is related to the higher turbulency on the surface of the membrane. This in turn reduces the precipitation of oil droplets on the surface of the membrane. In addition, it decreases the effect of concentration polarization. In this study, all of the PES hollow fiber membranes separate the oil from water effectively.

4. Membrane with a bigger pore size has lower separation performance in the oily wastewater treatment process.

References

- [1] Y.S. Li, L. Yan, C.B. Xiang, L.J. Hong. "Treatment of oily wastewater by organic-inorganic composite tubular ultrafiltration (UF) membranes." *Desalination*, vol. 196, pp. 76-83, 2006.
- [2] C.S. Ong, W.J. Lau, P.S. Goh, B.C. Ng, T. Matsuura, A.F. Ismail. "Effect of PVP Molecular Weights on the Properties of PVDF-TiO₂ Composite Membrane for Oily Wastewater Treatment Process." *Separation Science and Technology*, vol. 49, pp. 2303-2314, 2014.
- [3] L. Yan, S. Hong, M.L. Li, Y.S. Li. "Application of the Al₂O₃-PVDF nanocomposite tubular ultrafiltration (UF) membrane for oily wastewater treatment and its antifouling research." *Separation and Purification Technology*, vol. 66, pp. 347-352, 2009.
- [4] W. Chen, J. Peng, Y. Su, L. Zheng, L. Wang Z. Jiang. "Separation of oil/water emulsion using Pluronic F127 modified polyethersulfone ultrafiltration membranes." *Separation and Purification Technology*, vol. 66, pp. 591-597, 2009.
- [5] B. Chakrabarty, A.K. Ghoshal, M.K. Purkait. "Ultrafiltration of stable oil-in-water emulsion by polysulfone (PSF) membrane." *Journal of Membrane Science*, vol. 325, pp. 427-437, 2008.

- [6] P. Lipp, C.H. Lee, A.G. Fane, C.J.D. Fell. "A fundamental study of the ultrafiltration of oil-water emulsions." *Journal of Membrane Science*, vol. 36, pp. 161-177, 1988.
- [7] F.F. Nazzal, M.R. Wiesner. "Microfiltration of oil-in-water emulsion." *Water Environment Research*, vol. 68, pp. 197-203, 1996.
- [8] M. Hlavacek. "Break up of oil-in-water emulsions induced by permeation through a microfiltration membrane." *Journal of Membrane Science*, vol. 102, pp. 1-7, 1995.
- [9] J. Mueller, Y. Cen, R.H. Davis. "Crossflow microfiltration of oily water." *Journal of Membrane Science*, vol. 129, pp. 221-235, 1997.
- [10] J. Kong, K. Li. "Oil removal from oil-in-water emulsions using PVDF membranes." *Separation and Purification Technology*, vol. 16, pp. 83-93, 1999.
- [11] E. Yuliwati, A.F. Ismail. "Effect of additives concentration on the surface properties and performance of PVDF ultrafiltration membranes for refinery produced wastewater treatment." *Desalination*, vol. 273, pp. 226-234, 2011.
- [12] E. Yuliwati, A.F. Ismail, T. Matsuura, M.A. Kassim, M.S. Abdullah. "Effect of modified PVDF hollow fiber submerged ultrafiltration membrane for refinery oily wastewater." *Desalination*, vol. 283, pp. 214-220, 2011.
- [13] A.B. Koltuniewicz, R.W. Field. "Process factors during removal of oil-in-water emulsions with cross-flow microfiltration." *Desalination*, vol. 105, pp. 79-89, 1996.
- [14] C. Zhao, J. Xue, F. Ran, S. Sun. "Modification of polyethersulfone membranes, a review of methods." *Progress in Materials Science*, vol. 58, pp. 76-150, 2013.
- [15] H. Ohya, J.J. Kim, A. Chinen, M. Aihara, S.I. Semenova, Y. Negishi, O. Mori, M. Yasuda. "Effects of pore size on separation mechanisms of microfiltration of oily water, using porous glass tubular membrane." *Journal of Membrane Science*, vol. 145, pp. 1-14, 1998.
- [16] R.V. Lopez, S. Elmaleh, N. Ghaffor. "Crossflow ultrafiltration of hydrocarbon emulsions." *Journal of Membrane Science*, vol. 102, pp. 55-64, 1995.

نتایج تجربی تصفیه پساب‌های نفتی با استفاده از غشاء الیاف توخالی نانوساختار پلی اتر سولفون

غلامرضا باکری^{۱*}، زینب فلاح‌نژاد^۲

۱. دانشکده مهندسی شیمی، دانشگاه صنعتی نوشیروانی بابل، بابل، ایران

۲. دانشکده مهندسی شیمی، دانشگاه صنعتی نوشیروانی بابل، بابل، ایران

چکیده

پساب‌های مراکز توزیع فرآورده‌های نفتی و پالایشگاه‌های نفت یکی از مهم‌ترین آلوده‌کننده‌های محیط زیست در دهه اخیر می‌باشند که باید به رفع این آلودگی‌ها از محیط زیست اقدام نمود. در این مقاله عملکرد غشاءهای الیاف توخالی گوناگونی برای تصفیه پساب‌های نفتی و تأثیر پارامترهای عملیاتی مانند فشار، غلظت خوراک و سرعت جریان عرضی خوراک بر روی عملکرد غشاء مورد بررسی قرار گرفته است. با افزایش فشار، میزان فشردگی و گرفتگی غشاء افزایش و عملکرد غشاء کاهش می‌یابد بنابراین شرایط بهینه عملیاتی برای انجام آزمایش‌ها: فشار ۱ bar و سرعت جریان بالا (۰/۱۸ متر بر ثانیه) و غلظت پایین خوراک (۳۰۰ میلی‌گرم بر لیتر) می‌باشد. در این پژوهش غشاء الیاف توخالی نانوساختار پلی اتر سولفون #M₁ با اندازه حفره ۸/۲۹ نانومتر، تخلخل ۷۷ درصد، فلاکس عبوری ۱۲/۴ (لیتر بر مترمربع در ساعت) و پس دهی ۱۰۰ درصد بهترین عملکرد را در تصفیه پساب‌های نفتی از خود نشان داد.

مشخصات مقاله

تاریخچه مقاله:

دریافت: ۱۲ فروردین ۱۳۹۴

پذیرش نهایی: ۵ آبان ۱۳۹۵

کلمات کلیدی:

تصفیه پساب‌های نفتی
غشاء الیاف توخالی پلی اتر سولفون
آلودگی محیط زیست
شست و شوی غشاء

* عهده‌دار مکاتبات؛

رایانامه: bakeri@nit.ac.ir

تلفن: + ۹۸ ۹۱ ۲۵۲۶۵۷۳۹

دورنگار: + ۹۸ ۱۱ ۳۲۳۳۴۲۰۴