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A hybrid microfiltration/ultrafiltration membrane process for treatment of oily wastewater

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ABSTRACT

In this study, a hybrid microfiltration/ultrafiltration process was employed for treatment of oily wastewaters and the effects of some operating parameters such as transmembrane pressure (TMP), cross-flow velocity and oil concentration on the separation performance were investigated. For this purpose, the cross-flow microfiltration (MF) using a polyvinylidene fluoride membrane and ultrafiltration (UF) with a polyethersulfone (PES) membrane that was fabricated by a non-solvent-induced phase inversion method were conducted in series mode. The separation performance of the hybrid process was compared with the performance of single MF and UF processes for the treatment of an industrial oily wastewater. The results showed that the permeate flux increased and the oil rejection decreased by an enhancement in both TMP and cross-flow velocity. The analysis of variance confirmed the experimental results and indicated that the individual effect of TMP and cross-flow velocity is more important than the interactional effect of these operating parameters on the permeate flux and oil rejection. The permeate of the hybrid process had better quality in terms of total organic carbon, chemical oxygen demand, total dissolved solids, total suspended solids, oil and grease content as well as turbidity compared with the treated water by single MF and UF methods.

Keywords: Oily wastewater; Hybrid process; Ultrafiltration; Microfiltration; Oil rejection; Discharge waters

1. Introduction

Oil and grease are one of the major sources of water pollution in a wide range of industries such as military, automotive, chemical, petrochemical, food, metallurgical, textile and leather. Various physical, chemical and biochemical technologies have been used for the treatment of oily wastewaters [1]. Selection of appropriate methods for separation of oil–water mixtures depends on different parameters

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such as amount of pollutants, permitted level of remaining pollutants in the treated water, presence of other pollutants such as ions, heavy metals, organic compounds as well as dissolved and suspended solids, operating variables, etc. On the other hand, environmental regulations require that maximum total oil and grease concentration in discharge waters to be 10–15 mg/L [2].

Physical methods like dissolved air flotation [3], gravity separation [4] and centrifugal settling [5] as well as chemical methods using surfactants [6] are the most common technologies for the treatment of oil–water mixtures. The traditional methods are mostly not efficient enough for treating stable oil in water emulsions especially when the oil droplets are finely dispersed and the concentration is very low [7]. Due to restrictions and problems with the traditional methods, technologies such as adsorption [8], UV radiation [9], chemical oxidation [10], biological processes [11] and membrane processes [12] have received a lot of attention.

Membrane based separation processes, especially microfiltration (MF) and ultrafiltration (UF) have proven to be promising alternatives for conventional industrial separation methods, since they offer numerous advantages like high selectivity, easy separation, mild operation, continuous and automatic operation, economic and fast operation, as well as relatively low capital and running investment [13–15]. Previous studies [16–21] showed that treatment of domestic and industrial oily wastewaters using the MF and UF processes satisfied the environmental standards and reuse of wastewater. The microfiltration and ultrafiltration are pressure-driven membrane processes that use porous membranes for the separation of contaminants from fluids primarily due to size exclusion. The MF process is frequently employed as a pre-treatment step before ultrafiltration or reverse osmosis (RO) in order to reduce membrane fouling. The possibility of using the microfiltration [22–25] and ultrafiltration [26–29] processes to treat the oil in water emulsions have been previously examined. For example, the cross-flow microfiltration process using a ceramic membrane was employed by Hua et al. [22] to treat the oily wastewater. Zhong et al. [23] studied the treatment of oily wastewater using flocculation and MF process with zirconia membrane. Effect of pH and cross-flow velocity on the performance of ceramic membranes in ultrafiltration of oil in water emulsion was studied by Lobo et al. [29]. Also, Wu et al. [23] used a polyvinyl alcohol membrane in a pilot-scale cross-flow ultrafiltration for treatment of synthetic oily water. Recently, Masoudnia et al. [30] employed the cross-flow microfiltration using polyvinylidene fluoride (PVDF) membrane for separation of oil–water emulsions and investigated the effects of feed flow rate and transmembrane pressure (TMP) on the separation performance of MF process.

Furthermore, various combined membrane processes have been reported for treatment of various wastewaters. Gryta et al. [7] applied a combination of ultrafiltration and membrane distillation processes to the treatment of oily wastewater. The combinations of MF/UF and UF/RO were used to the treatment of textile wastewaters by Yang et al. [31] and Boleda et al. [32], respectively. Yu et al. [33] studied the possibility of the treatment of a vegetable oil wastewater using an integrated MF/RO process. Salahi et al. [34] used UF/RO process for treatment of an oily wastewater.

In this study, a hybrid microfiltration/ultrafiltration process was employed for complete removal of oil from industrial and synthetic wastewaters. For this purpose, the cross-flow microfiltration using a commercial PVDF membrane was employed for oil separation from relatively concentrated oil–water emulsions and then the ultrafiltration with a laboratory made polyethersulfone (PES) membrane was applied for further purification of the MF permeate stream. Besides, the effects of some operating parameters such as cross-flow velocity and TMP on the flux decline and separation performance were investigated.

2. Materials and methods

2.1. Feed solutions

Two feed solutions were used in the experiments, synthetic oil in water emulsion and an industrial oily wastewater. Synthetic oil in water emulsion was prepared by mixing a commercial grade gas–oil and de-ionized water. A Homogenizer (WiseTis-HG-15D, Daihan Co., Korean) was utilized to homogenize the oil–water mixtures at high shear rates (12,000 rpm) for 60 min. The oil concentration of synthetic feed was 3,000 ppm for all experiments.

Also, the desalter plant wastewater of Tehran Oil Refining Company without further treatment was used as the industrial oily wastewater. Analysis of the industrial oily wastewater is presented in Table 1.

2.2. Membranes

Hydrophilic PVDF membrane (Durapore, HVLP, Millipore Co., USA) with an average pore size of 0.45 μm was used in the experiments for the MF process.

The PES membrane used in the UF process was prepared in the laboratory using phase inversion

Table 1
Analysis of the desalter plant wastewater of Tehran Oil Refining Company and the permeate of single MF and UF processes as well as the hybrid MF/UF process

Characteristic	Unit	Feed	MF	UF	MF/UF
TOC	mg/L	1,222	71.9 (94.1%)	25.5 (97.9%)	Trace (100%)
COD	mg/L	2,698	151 (94.4%)	52.7 (98.0%)	1.5 (99.9%)
TDS	mg/L	1,598	1,154 (27.7%)	424 (73.4%)	8.4 (99.4%)
TSS	mg/L	350	9 (97.4%)	5 (98.5%)	Trace (100%)
Oil and grease	mg/L	3,591	21.5 (99.4%)	18.5 (99.5%)	0.4 (99.9%)
Turbidity	NTU	255	3.1 (98.7%)	1.5 (99.4%)	Trace (100%)

induced by the immersion precipitation technique according to a procedure presented by Sadeghi et al. [35]. Casting solutions were prepared by dissolving 16 wt.% PES and 10 wt.% polyethylene glycol (PEG) as a pore forming additive in dimethylacetamide (DMAc) as solvent at room temperature. For preparation of the UF membrane, the commercial PES with molecular weight of 58,000 g/mol (Ultrason E 6020 P) was provided by BASF (Ludwigshafen, Germany). DMAc and PEG with an average molecular weight of 600 g/mol were purchased from Merck Co. (Darmstadt, Germany). The characterizations of the prepared membrane are listed in Table 2. The membranes were cut into 15 × 20 cm piece and held in a flat-frame membrane module.

2.3. Sample analysis

The size of oil emulsion droplets in the synthetic feed solution was measured by a laser diffraction particle size analyser, Nano ZS (red badge) ZEN3600 manufactured by Malvern Co. (UK). Droplet size distribution of the oil in water emulsion with oil concentration of 3,000 ppm is presented in Fig. 1. As observed, the size range of oil droplets varies within ~0.18–1.7 μm with a mean size of 0.90 μm. The size distribution of oil droplets in the feed right after preparation of the sample and also 2 h after preparation were similar, which demonstrate the good stability of the solution.

The oil content of the feed and permeate solutions were determined by the chemical oxygen demand (COD) test according to the opened reflux method [36]. Total organic carbon (TOC), total dissolved solids (TDS), total suspended solids (TSS), oil and grease content as well as turbidity of the treated wastewater were also analysed according to the APHA standard methods [36]. TOC was measured using a TOC Analyser (Model DC-190 TOC Analyser, Texas, USA). TDS and TSS were determined by gravimetry method using Whatman 2.5 cm GF/C-Class Microfiber. Oil and grease content was analysed using Infracal TOG/TPH Analyser (Model CVH, Wilks Enterprise, Inc., South Norwalk, CT, USA). Turbidity was estimated by a Turbidimeter (Model 2100A, HACH Co, Colorado, USA).

Table 2
The characteristics of the PES membrane

Characteristic	Value
Membrane thickness, μm	95
Average pore size, nm	23
Pure water flux[a], kg/m^2 h	195.38
Porosity, %	20

[a] at TMP = 3 bar and Re = 2,500.

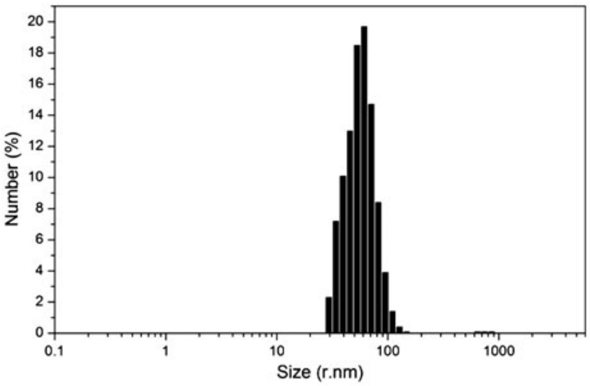

Fig. 1. The particle size distribution of the oily wastewater.

2.4. Experimental apparatus

The experimental apparatus consists of a microfiltration and an ultrafiltration set up. A scheme of the experimental set up is shown in Fig. 2. The MF set up consists of an eight lit feed tank equipped with a temperature controller during the experiments with a precision of ±0.5˚C. The feed tank was connected to a variable speed rotary vane pump (Hypro 4001XL 4-Roller Pump (USA)) to conduct the feed to a

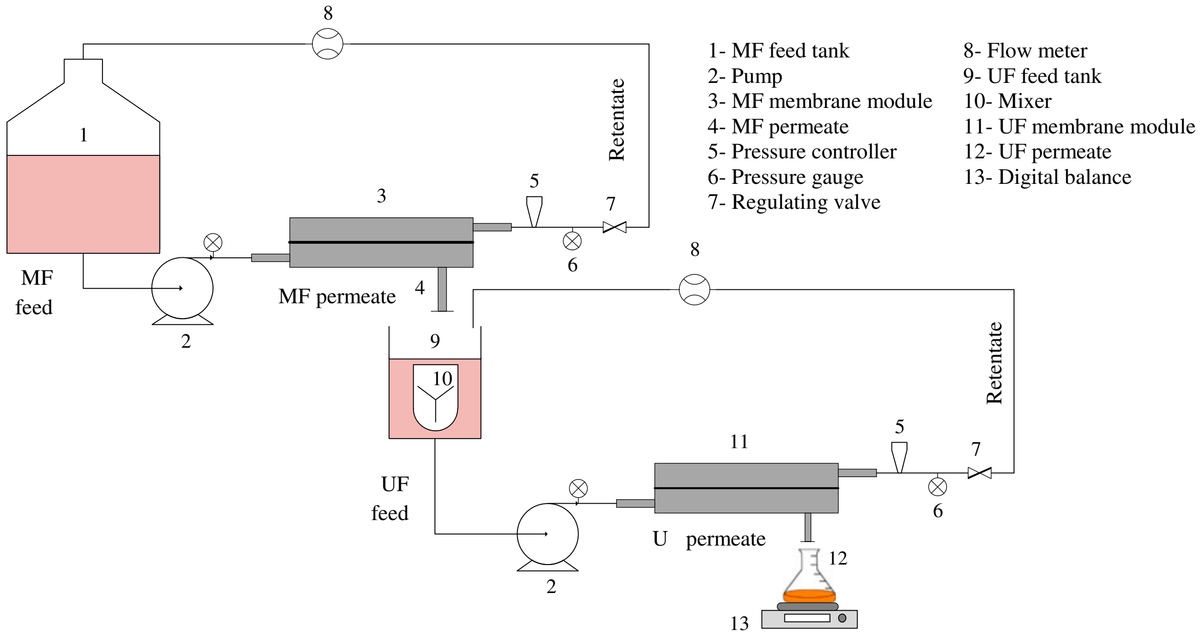

Fig. 2. The scheme of the MF/UF process experimental setup.

flat-frame stainless steel membrane module (Osmonics Inc., Minnetonka, MN, USA). A pressure controller and a pressure gauge were used to set pressure at a given value, and feed flow rate was adjusted by a flow meter and a regulating valve. The retentate coming out of the membrane module was recycled to the feed tank. The permeate was assembled in the UF feed tank and agitated with a high speed mixer. The UF set up was also equipped with a membrane module, temperature and pressure controller as well as a flow meter similar to the MF set up. The UF permeate was continuously collected and weighed by a digital balance.

The permeate flux (J) was calculated by dividing the weight of the permeate sample (W) by the product of membrane area (A) and time duration of the experiments (t) as follow (Eq. (1)):

$$J = \frac{w}{A \times t} \tag{1}$$

also, oil rejection (R) was calculated using the following Eq. (2):

$$\%R = \frac{C_F - C_P}{C_F} \times 100 \tag{2}$$

where C_F and C_P are the concentration of oil in the feed and permeate solution, respectively.

In the present work, the influence of TMP which varied from 1 to 3 bar above the atmospheric pressure for the microfiltration and 3–8 for the ultrafiltration process, and the feed flow rate which corresponds to a Reynolds number (Re) of 500, 1,500 and 2,500 on the separation performance of the MF/UF process for 3,000 ppm oil in water emulsion was investigated. Also, the effect of feed concentration of 500, 700, 1,000, 2,000 and 3,000 ppm for the MF process was studied. The feed temperature was fixed at $30 \pm 0.5^\circ\mathrm{C}$ during the experiments.

The Re is a well-known dimensionless description of the hydrodynamic conditions in the feed flow and can be calculated as follows (Eq. (3)):

$$\mathrm{Re} = \frac{u d_h}{v} \tag{3}$$

where u, v and d_h are velocity and kinematic viscosity of feed and hydraulic diameter of membrane module, respectively. Flow regimes into a channel are laminar, transient and turbulent at Reynolds numbers of Re <500, 500< Re <2,000 and Re >2,000, respectively [37].

The TMP determines the driving force of the MF and UF processes, and is defined as the pressure difference between the retentate and the permeate side (Eq. (4)):

$$\mathrm{TMP} = \frac{P_{\mathrm{in}} + P_{\mathrm{Out}}}{2} - P_p \tag{4}$$

2.5. Statistical analysis

A 3^2 full factorial design was used to investigate the effect of cross-flow velocity and TMP on the performance of the integrated MF/UF process. The independent variables were converted to dimensionless ones (x_1, x_2), with the coded values at three levels: −1, 0 and +1. Selection of the operating variable levels was based on the results obtained through pre-tests. The arrangement of factorial design for the MF and UF processes are shown in Table 3. All experimental conditions were repeated three times and the average values were reported. A regression equation with two parameters and their interaction with each other were used to describe the importance of operating variables and their interactional effects. This equation can be given with the following expression (Eq. (5)):

$$y_i = B_0 + B_1X_{1i} + B_2X_{2i} + B_{12}X_{1i}X_{2i} + B_{11}{X_{1i}}^2 + B_{22}{X_{2i}}^2 \tag{5}$$

The regression coefficients are computed as follows (Eqs. (6)–(11)):

$$B_0 = \frac{1}{9}(-y_1 + 2y_2 - y_3 + 2y_4 + 2y_5 + 2y_6 - y_7 + 2y_8 - y_9) \tag{6}$$

$$B_1 = \frac{1}{6}(y_1 + y_2 + y_3 + y_7 - y_8 - y_9) \tag{7}$$

$$B_2 = \frac{1}{6}(y_1 - y_3 + y_4 - y_6 + y_7 - y_9) \tag{8}$$

$$B_{11} = \frac{1}{6}(y_1 + y_2 + y_3 - 2y_4 - 2y_5 - 2y_6 + y_7 + y_8 + y_9) \tag{9}$$

$$B_{22} = \frac{1}{6}(y_1 - 2y_2 + y_3 + y_4 - 2y_5 + y_6 + y_7 - 2y_8 + y_9) \tag{10}$$

$$B_{12} = \frac{1}{4}(y_1 - y_3 - y_7 + y_9) \tag{11}$$

where y_i shows the amount of the permeate flux and oil rejection, X_{1i} and X_{2i} values indicate the corresponding parameters in their coded forms according to Table 3, i is the index of experiments ($i = 1, 2, 3, \ldots 9$); B_0 is the average value of the result; B_1 and B_2 are the linear coefficients that show the effect of Reynolds number and TMP, respectively; B_{11} and B_{22} represent the linear combination of all responses and B_{12} represents the interacting effect of Reynolds–TMP variables.

3. Results and discussion

3.1. Effect of TMP and cross-flow velocity on the MF process

The changes of the permeate flux during 90 min of running the microfiltration process with an oil in

Table 3
The coded values of the experimental data at three levels for a 3^2 design matrix for the MF and UF process

		Independent variables		Dependent variables	
Process	Serial number	TMP, bar X_1 (x_1)	Re X_2 (x_2)	Permeate flux, kg/m^2 h	Oil rejection, %
MF	1	1 (−1)	500 (−1)	463.5 ± 37	84.7 ± 0.4
	2	1 (−1)	1,500 (0)	580.1 ± 41	84.6 ± 0.2
	3	1 (−1)	2,500 (1)	800.2 ± 46	81.2 ± 0.3
	4	2 (0)w	500 (−1)	587.6 ± 31	83.6 ± 0.3
	5	2 (0)	1,500 (0)	684.1 ± 37	83.1 ± 0.2
	6	2 (0)	2,500 (1)	906.2 ± 42	80.6 ± 0.2
	7	3 (1)	500 (−1)	861.1 ± 29	81.5 ± 0.3
	8	3 (1)	1,500 (0)	983.3 ± 34	80.9 ± 0.2
	9	3 (1)	2,500 (1)	1,151.2 ± 39	80.0 ± 0.3
UF	1	3 (−1)	500 (−1)	77.7 ± 4	99.46 ± 0.1
	2	3 (−1)	1,500 (0)	89.5 ± 4	99.25 ± 0.1
	3	3 (−1)	2,500 (1)	98.3 ± 6	99.14 ± 0.2
	4	5 (0)	500 (−1)	99.4 ± 5	99.14 ± 0.3
	5	5 (0)	1,500 (0)	118.5 ± 5	98.93 ± 0.3
	6	5 (0)	2,500 (1)	126.4 ± 6	98.82 ± 0.1
	7	7 (1)	500 (−1)	113.0 ± 9	98.82 ± 0.2
	8	7 (1)	1,500 (0)	128.3 ± 8	98.71 ± 0.1
	9	7 (1)	2,500 (1)	138.6 ± 10	98.60 ± 0.1

water emulsion containing 3,000 ppm of oil at Reynolds number of 2,500 and various TMPs are shown in Fig. 3. A decrease of the permeate flux was observed during the operation of the MF plant. The permeate flux decline with time is the main problem in practical applications of the microfiltration process. The existence of a limiting flux can be related to the membrane fouling that arises as the feed solution is convected toward the membrane where the separation of oil droplet from bulk solution takes place. A concentration profile from bulk solution to the membrane surface is generated by the rejected oil accumulated on the membrane. The formation of a viscous and gelatinous-type layer is responsible for an additional resistance to the permutation flux in addition to that of the membrane and causes the flux decline. Fig. 3 indicates that the higher TMP caused faster fouling while significantly decreasing the permeation rate of the fouled membrane. Based on Darcy's law (Eq. (12)), increasing TMP enhances the permeate flux. However, increasing TMP can be a compensated fouling layer compression [22,38,39]. At lower pressure, the permeate flux is directly proportional to TMP. Higher TMP results in droplets to pass rapidly through the membrane pores, so more oil droplets accumulate on the membrane surface and consequently in the membrane pores, leading to the membrane fouling [40].

$$Q = \frac{P \times A}{\mu \times R_t} \tag{12}$$

where Q is flow rate, P is the TMP, A is the membrane area, R_t is the transport resistance and μ is the solution viscosity.

The effects of cross-flow velocity on the permeate flux and oil rejection of microfiltration treatment of the oil–water emulsion are indicated in Fig. 4. As shown in Fig. 4(a), increasing cross-flow velocity increases steady permeate flux [22]. Increasing cross-flow velocity promotes the turbulency and mass transfer coefficient. This can reduce aggregation of feed components in the gel layer, and as a result, the aggregated materials on the membrane surface diffuse back to the bulk feed solution, and this weakens the effect of concentration polarization and enhances the permeate flux [38,39]. The cross-flow velocity affects the shear stress at the membrane surface and, consequently, reduces the concentration polarization and accumulation of retained solutes by increasing the mass transfer coefficient.

Fig. 4(b) shows the effect of TMP on the oil rejection at various Reynolds numbers. It can be seen that the oil rejection decreases as TMP goes to higher levels. Increasing the operating pressure affects the selectivity of the filtration process and increases the oil passing through the membrane. Also, an enhancement in the TMP leads to an increase of the mass transfer driving force and, consequently, the transport of oil droplets through the membrane are facilitated and the oil rejection decreases. In addition, it is observed in

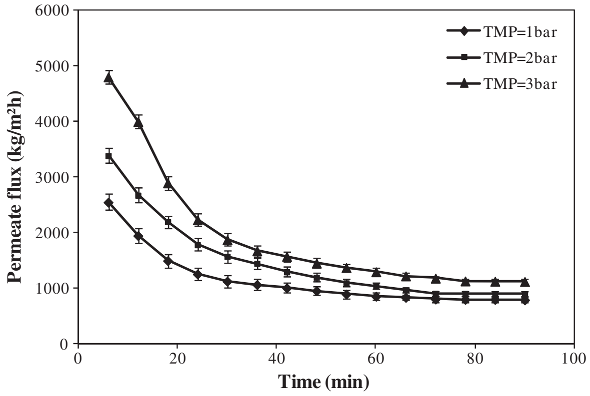

Fig. 3. The time dependency of the permeate flux of the MF process for various TMPs at Reynolds number of 2,500.

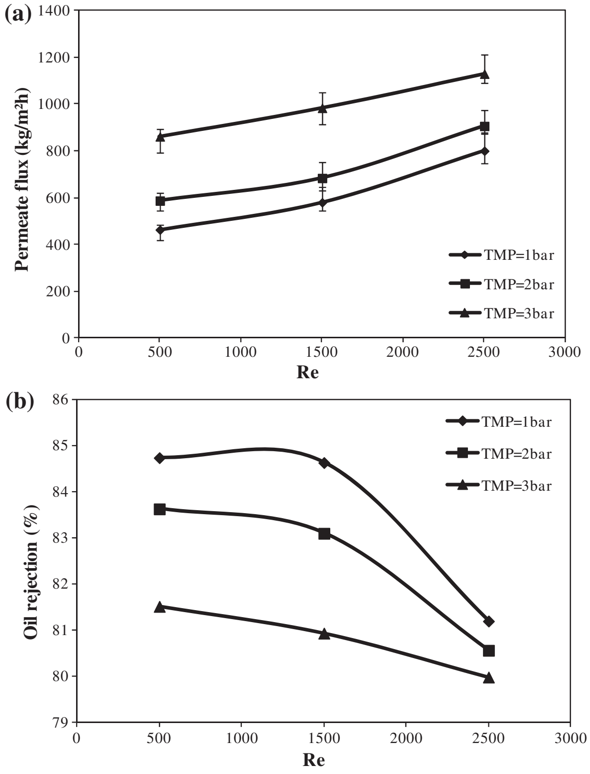

Fig. 4. The effect of Reynolds numbers on the permeate flux (a) and oil rejection (b) of the MF process at different TMPs.

Fig. 4(b) that as the Reynolds number increases the oil rejection is reduced. This can be due to the fact that the membrane fouling and the cake resistance reduces with an increase in the cross-flow velocity, so more oil droplets could pass across the membrane, and therefore the oil rejection decreases.

Moreover, the effects of TMP and cross-flow velocity on the permeate flux and oil rejection were analysed by analysis of variance (ANOVA) to assess the validation of data. The ANOVA table for the permeate flux and oil rejection as a function of TMP, Reynolds number and their interaction effects are presented in Table 4. Statistical analysis indicates that R^2 values for the permeate flux and oil rejection are 0.997 and 0.927, respectively. The P values reveal that all terms were significant at 95% confidence. The obtained values of regression coefficients are inserted in Eq. (5) and the final regression equations for the permeate flux and rejection can be expressed as follows (Eqs. (13) and (14)):

$$J = 659.49 + 95.70P + 157.92\mathrm{Re} - 11.66P\mathrm{Re} + 80.60P^2 + 45.79\mathrm{Re}^2 \tag{13}$$

$$R = 83.06 + 28.53P + 1.36\mathrm{Re} + 0.50P\mathrm{Re} - 0.26P^2 - 0.95\mathrm{Re}^2 \tag{14}$$

These equations reveal the effect of individual operating parameters and interactional effects on the permeate flux and oil rejection. The TMP and feed flow rate have a positive effect on the permeate flux in order of Reynolds number > TMP as can be seen from Eq. (13). A similar trend is observed for the effect of the operating parameters on the oil rejection from Eq. (14). The negative values for the permeate flux coefficient indicate a reverse relation between interactional effect of Reynolds number and TMP on the permeate flux. Fig. 5 shows the contour map for the effect of the independent variables on the permeate flux and oil rejection. As shown in this figure, 85.8 and 72.6% enhancement in the permeate flux is observed when the TMP increases from 1 to 3 bar and the Reynolds number increases from 500 to 2,500, respectively.

3.2. Effect of feed concentration on the MF process

In order to determine the effect of variation in the feed concentration on the separation performance of the microfiltration process, different oil in water emulsions with the oil concentration of 500, 700, 1,000, 2,000 and 3,000 ppm were used in the experiments at TMP of 3 bar and Reynolds number of 2,500 and the results are depicted in Fig. 6.

Fig. 6(a) shows the effect of feed concentration on the permeate flux of the MF process. It can be seen that an increase in the oil feed concentration leads to reduction in the permeate flux. This behaviour can be attributed to an increase in the thickness of the gel layer on the membrane surface due to the concentration polarization phenomenon at high oil concentrations. It holds that at higher concentration the phenomenon of the accumulation of oil drops on the surface of the membrane is more likely to occur. Consequently, the gel layer formed resists against the permeate flow from the membrane and reduces the permeation rate through the membrane. At lower concentrations, an oil layer formed on the membrane surface can be removed by hydrodynamic action of the flow. But at higher oil concentrations, the hydrodynamic action cannot remove the oil layer. By increasing the operation time, this layer becomes

Table 4
The ANOVA of the permeate flux and oil rejection for the MF process

Dependent variables	Source	Degrees of freedom	Sum of squares	Main squares	F	P
Permeate flux	TMP	2	234,137	117,069	417.7	0
	Re	2	153,196	76,598	273.3	0
	Re–TMP	4	2,342	4,311	11.43	0
	Residual Error	4	1,121	280	–	–
	Total	12	390,797	–	–	–
	R	0.997	–	–	–	–
Oil rejection	TMP	2	11.096	5.5478	12.07	0.02
	Re	2	12.409	6.2044	13.5	0.017
	Re–TMP	4	2.341	0.763	1.253	0.011
	Residual Error	4	1.838	0.4594	–	–
	Total	12	27.684	–	–	–
	R	0.927	–	–	–	–

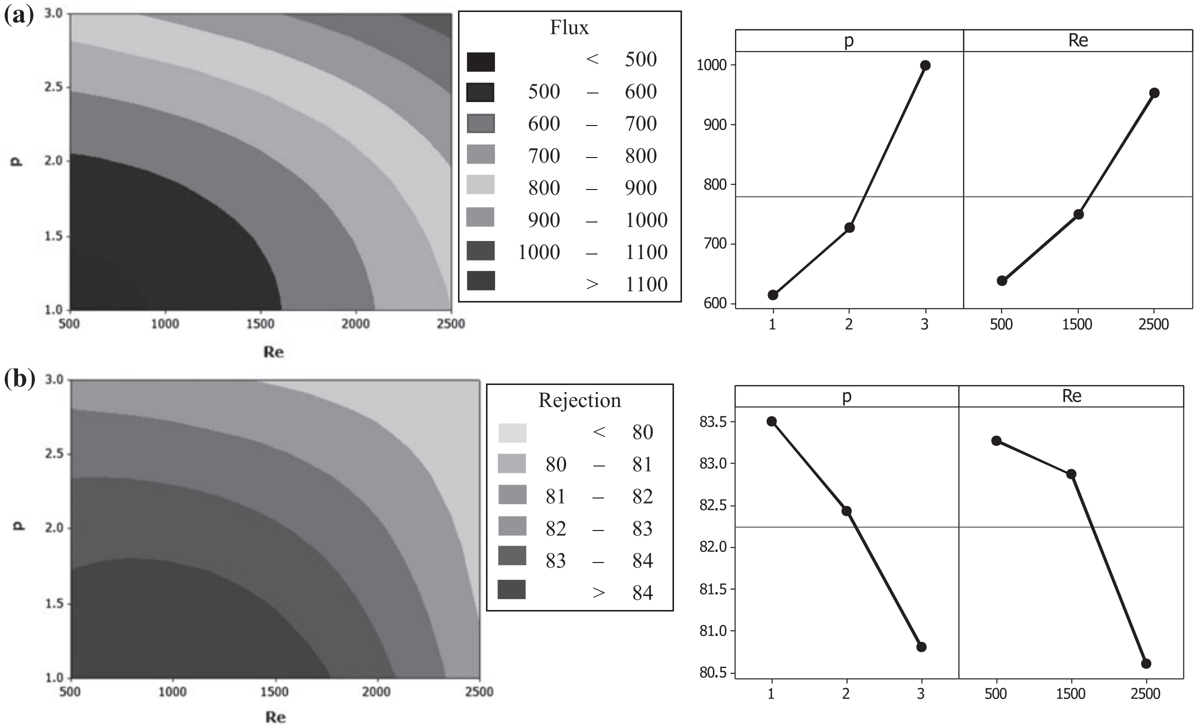

Fig. 5. Contour map for the effect of independent variables on the permeate flux (a) and oil rejection (b) of the MF process.

thicker and the permeate flux decreases. Similar observations have been reported in the previous literature [41,42].

The effect of oil feed concentration on the oil rejection is presented in Fig. 6(b). This figure shows that the oil rejection decreases with an increase in the feed concentration. For example, the oil rejection reduces from 96.1 to 79.98% as the oil content of feed solution varies from 500 to 3,000 ppm. When the feed concentration increases, the number of oil droplets interacting with the membrane enhances and consequently, the oil droplets pass through the membrane more easily and the oil rejection decreases.

3.3. Effect of TMP and cross-flow velocity on the UF process

The permeate of the MF process which had an oil concentration of ~500 ppm was collected in the feed tank of the UF process and purified by the PES membrane. In the following, the effects of the main operating parameters on the separation performance of the UF process, i.e. the permeate flux and oil rejection, are presented.

Fig. 7 shows the time dependency of the permeate flux of the UF process at Reynolds number of 2,500 and various TMPs. As shown in this figure, the flux sharply decreases at the early period of filtration and then very slowly approaches a steady state limit value after ~40 min. Due to the membrane blocking by the oil droplets and deposition of these droplets on the membrane surface, the permeate flux rapidly decreases at the initial time of filtration. It is also found that the steady permeate flux is highly dependent on the TMP.

The effects of TMP and cross-flow velocity on the permeate flux and oil rejection of ultrafiltration treatment of the oil in water emulsion is indicated in Fig. 8. A maximum point can be seen in Fig. 8(a) at TMP ~8 bar for various Reynolds numbers. When TMP increases from 3 to 7 bar, the permeate flux enhances, while the flux decreases as TMP varies from 7 to 8. In addition, the increase in the permeate flux under lower TMP was greater than that under higher TMP. As mentioned earlier, higher TMP facilities transport through the membrane, thus enhancing the permeation rate. On the other hand, higher pressure causes more oil droplets to accumulate on the membrane surface as well as in the membrane pores which leads to the membrane fouling; decreasing the permeation flux as a result. These two opposite phenomena result in lower enhancement in the permeate flux at higher TMP in comparison with lower TMP. In other words, the critical flux occurs at TMP ~8 bar. Similar

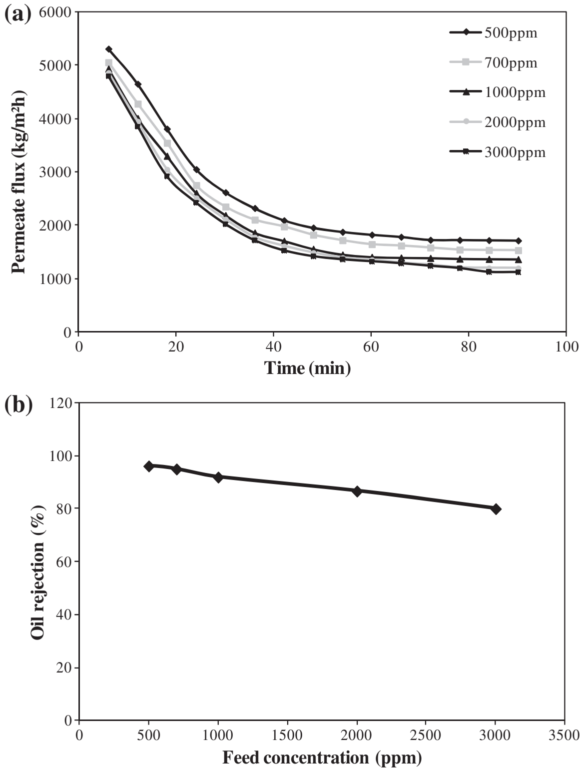

Fig. 6. The effect of feed concentration on the permeate flux (a) and oil rejection (b) of the MF process at Reynolds number of 2,500 and TMP of 3 bar.

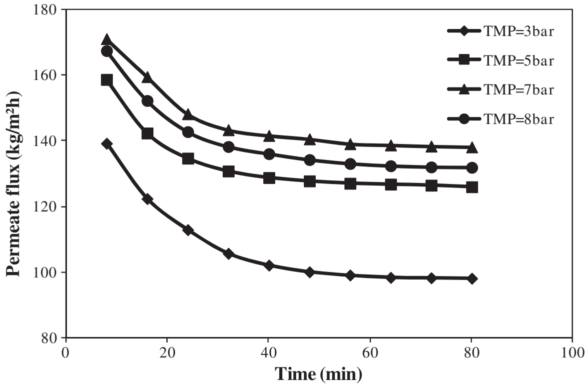

Fig. 7. The time dependency of the permeate flux of the UF process for various TMPs at Reynolds number of 2,500.

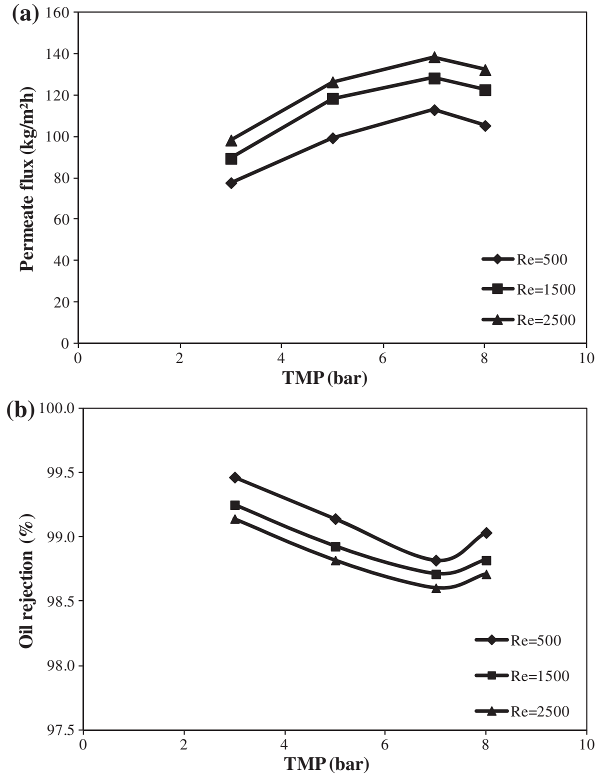

Fig. 8. The effect of TMP on the permeate flux (a) and oil rejection (b) of the UF process at different Reynolds numbers.

behaviours have been reported by other researchers. Field et al. [43] introduced the concept of critical flux for the microfiltration process. According to this concept, a critical flux exists, below which there is no flux decline with time and the flux depends linearly on the TMP. When the pressure is increased above this limit, the membrane fouling and compaction of the gel layer on the membrane occurs, the mass transfer resistance across the membrane enhances and, consequently, the flux does not increase.

From Fig. 8(a) it can also be seen that an increase in the Reynolds number leads to a higher permeate flux and at high pressure the effect of Reynolds reduces. At high TMP, when Reynolds number increases from 1,500 to 2,500, compression of the gel layer increase significantly. Furthermore, as shown in Fig. 8(b), the oil rejection decreases when the Reynolds number and TMP increase. This can be due to the fact that the membrane fouling and the cake resistance reduces with an increase in the cross-flow velocity, so more oil droplets could pass across the membrane, and therefore the oil rejection decreases.

In addition, the effects of TMP and cross-flow velocity on the permeate flux and oil rejection of the UF process are determined by ANOVA to assess the validation of data. The ANOVA table for the permeate flux and oil rejection as a function of TMP, Reynolds number and their interaction effects are presented in Table 5. The P values in these tables indicate that all terms were significant at 95% confidence. Statistical analysis indicates that R^2 values for the permeate flux and oil rejection are 0.995 and 0.993, respectively. The

Table 5
The ANOVA of the permeate flux and oil rejection for the UF process

Dependent variables	Source	Degrees of freedom	Sum of squares	Main squares	F	P
Permeate flux	TMP	2	2,284.91	1,142.45	262.43	0
	Re	2	913.52	456.76	104.92	0
	Re–TMP	4	232.8	112.5	21.3	0
	Residual error	4	17.41	4.35	–	–
	Total	12	3,215.84	–	–	–
	R	0.995	–	–	–	–
Oil rejection	TMP	2	0.4952	0.2476	222.88	0
	Re	2	0.1254	0.0627	56.47	0.001
	Re-TMP	4	0.0235	0.0084	12.54	0.011
	Residual error	4	0.0044	0.0011	–	–
	Total	12	0.6252	–	–	–
	R	0.993	–	–	–	–

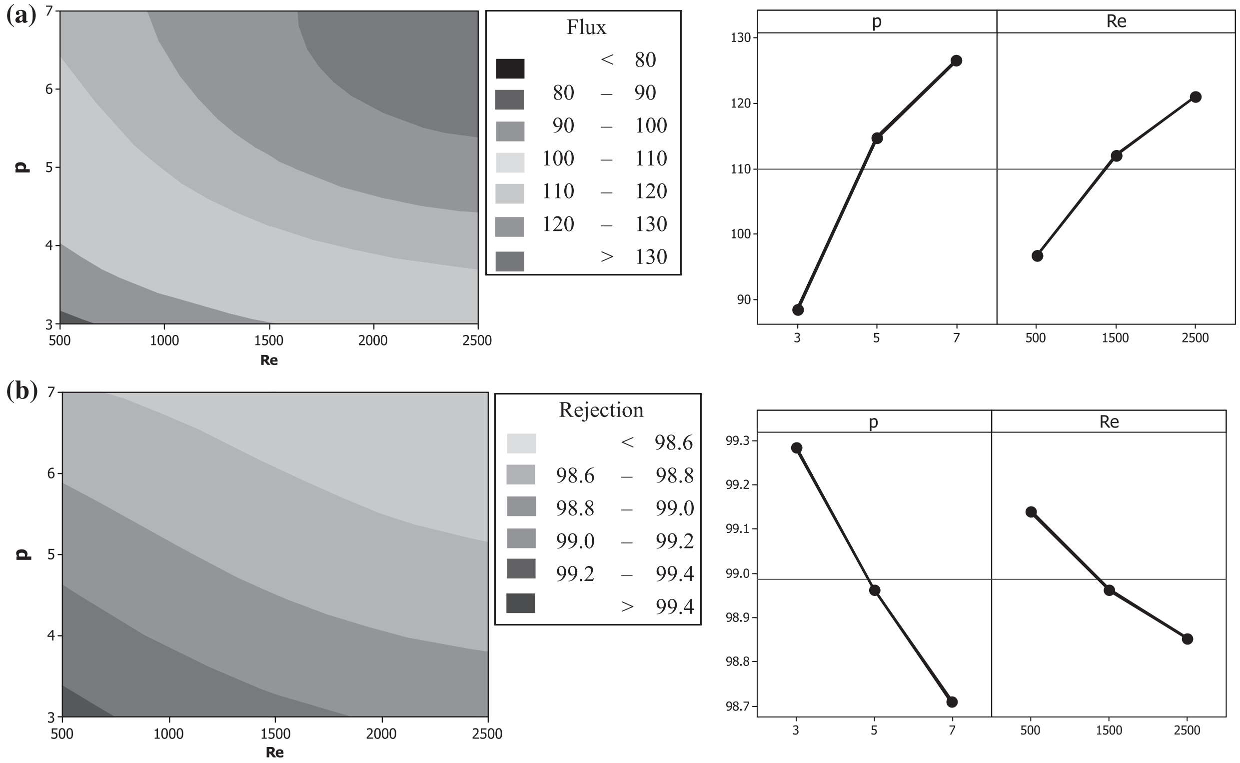

Fig. 9. Contour map for the effect of independent variables on the permeate flux (a) and oil rejection (b) of the UF process.

final regression equations for the permeate flux and oil rejection, after putting values of all coefficients in Eq. (5) can be expressed as follows (Eqs. (15) and (16)):

$$J = 115.86 + 18.59P + 12.21\mathrm{Re} + 1.25P\mathrm{Re} - 7.21P^2 - 3.18\mathrm{Re}^2 \qquad (15)$$

$$R = 98.83 + 33.22P + 0.14\mathrm{Re} + 0.02P\mathrm{Re} + 0.04P^2 + 0.04\mathrm{Re}^2 \qquad (16)$$

The above equations indicate the effect of individual operating parameters and interactional effects on the permeate flux and oil rejection. As can be seen from

Eq. (15), the TMP and Reynolds number have a positive effect on the permeate flux in order of TMP > Reynolds number > TMP–Reynolds. The contour map for the effect of the independent variables on the permeate flux and oil rejection are indicated in Fig. 9. As shown in this figure, 70.9 and 81.5% enhancement in the permeate flux is observed when the TMP increases from 3 to 7 bar and the Reynolds number increases from 500 to 2,500, respectively.

3.4. Treatment of industrial wastewater by the MF/UF process

The proposed hybrid MF/UF process was employed for treatment of the industrial wastewater. The TMP and Reynolds number of the MF process was adjusted at the optimum values which were determined in previous sections, i.e. TMP of 3 bar and Reynolds number of 2,500. The UF process that was performed on the permeate stream of the microfiltration process was conducted at a TMP of 7 bar and Reynolds number of 2,500, i.e. the optimum operating conditions of the UF treatment of the synthetic oily wastewater. In order to compare the performance of the hybrid process with single MF and UF processes, the industrial wastewater was also treated by these membrane processes at the above operating conditions. The analysis of permeate stream of these three separation processes are presented in Table 1. The results reveal that the treated water by the integrated MF/UF has better quality than the permeate of a single MF and UF process. TOC, COD, TDS, TSS, oil and grease content as well as turbidity of the MF/UF permeate is trace, 1.5 mg/L, 8.4 mg/L, trace, 0.4 mg/L and trace, respectively.

4. Conclusions

Treatment of oily wastewater was performed by a hybrid microfiltration/ultrafiltration process and the separation performance of the proposed method was compared with single MF and UF processes. The effects of some operating parameters on the permeate flux and oil rejection were investigated. The results revealed that an increase in the cross-flow velocity led to higher permeate flux and lower oil rejection for both MF and UF processes. The permeate flux increased and the oil rejection decreased as the TMP and the oil content of the feed solution went to higher levels in the cross-flow microfiltration. In the ultrafiltration process, variations of the permeate flux vs. the TMP had a maximum point at which the critical flux occurred. Furthermore, the ANOVA analysis validated the experimental results and indicated that the TMP and Reynolds number have a positive effect on the permeate flux and oil rejection in the order of TMP > Reynolds number > TMP–Reynolds.

Finally, it can be concluded that the proposed integrated MF/UF process would be a useful technique for the treatment of oily wastewater, especially for relatively concentrated stable oil in water emulsions.

Nomenclature

A — membrane area (m^2)
C_F — concentration of oil in the feed (ppm)
C_P — concentration of oil in permeate solution (ppm)
d_h — hydraulic diameter of microfiltration module (m)
J — permeate flux ($kg/m^2\,h$)
P_{in} — initial pressure (bar)
P_{out} — output pressure (bar)
P_p — permeate pressure (bar)
Q — flow rate (m^3/s)
R_t — transport resistance (1/m)
Re — Reynolds number
R — oil rejection (%)
T — time of operation (h)
TMP — transmembrane pressure (bar)
W — weight of collected permeate (kg)
u — velocity of feed (m/s)
v — kinematics viscosity of feed (m/s^2)
μ — dynamic viscosity (kg/m s)

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