Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.842505

53 (2015) 340–351
January

Taylor & Francis
Taylor & Francis Group

A study of a polymeric membrane performance in an ultrafiltration system to use in industrial application

Amin Reyhani[a,*], Forough Rajaei[b], Mousa Shahmoradi[c], Ali Kahkesh[d]

[a]*Young Researchers and Elites Club, North Tehran branch, Islamic Azad University, Tehran, Iran*
Tel. +98 21 22364015; email: aminreyhani@gmail.com
[b]*Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran*
[c]*Department of Chemical Engineering, Sahand University of Technology, Tabriz, Iran*
[d]*Department of Chemical Engineering, University of Sistan and Baluchestan, Zahedan, Iran*

Received 11 July 2013; Accepted 27 August 2013

ABSTRACT

The performance of a polymeric membrane in an ultrafiltration system under the chosen optimum conditions was studied. To achieve this, four real produced waters were dealt with. To find the optimum conditions, Taguchi method was applied. Results showed that PAN350 membrane is a potential candidate for industrial applications for three feeds which contained oil and total organic carbon (TOC) less than 1,500 and 300 ppm, respectively. The values of oil/grease, total suspended solids, and turbidity rejections were approximately 100%. Although TOC could not be entirely removed, the removal values for TOC were acceptable in this study. For the fourth feed due to the values of oil and TOC which were more than 1500 and 300 ppm, the permeation flux approached zero after 10 min. In the long-time experiments, membrane permeability was equal to 37, 40, and 10 $L\,m^{-2}\,h^{-1}\,bar^{-1}$ for feed 1, feed 2, and feed 3, respectively. Also, the mean of particles size distribution of permeates decreased from 500 to 0.9 nm for feed 1, from 425 to 1.2 nm for feed 2, and from 1,225 to 1.1 nm for feed 3. Experimental calculations demonstrated that both cake layer formation and pore-blocking mechanism affected the flux decline effectively during the process.

Keywords: Permeability; Polymeric membrane; Produced water; Rejection; Size distribution; Ultrafiltration

1. Introduction

Oily wastewaters are mostly generated in oil-refining processes [1]. Also, produced water is generated in the petroleum industry as a by-product of various processes in production and refinement [2]. Petroleum refineries attempt to reduce oil content in water discharged into the sea [1]. Conventional approaches to treat oily wastewaters include gravity separation, API unit and skimming, dissolved air flotation, de-emulsion coagulation, and flocculation. The gravity separation process followed by skimming is fairly effective to remove free oil from wastewater. API unit has been widely accepted as an effective, low cost, and primary treatment step. However, these methods are not effective for removing smaller oil droplets and emulsions. Dissolved air flotation process uses air to increase the buoyancy of smaller oil droplets for the enhancement of separation rate. The

*Corresponding author.

emulsified oil in the influent of dissolved air flotation process is removed by de-emulsification with chemicals, thermal energy or both. Dissolved air flotation units typically employ chemicals to promote coagulation and to increase flock size to facilitate separation [3]. Membrane technology in wastewater treatment has significant progress in recent years. There are four filtration methods: microfiltration (MF) [4,5], ultrafiltration (UF) [5,6], nanofiltration (NF), and reverse osmosis (RO) [2]. Membrane processes are widely employed due to their success in reducing effluent concentrations to as low as 5 mg/L. Fouling is generally a problem in membrane processes, especially in a filtration of produced water. This phenomenon is a damaging appearance in the membrane process that can make permeation flux decline as a result of the degeneration of feed water quality [1]. A primary reason for the flux decline during the initial period of a membrane separation process is concentration polarization of solute at the membrane surface. This can occur in conjunction with irreversible fouling of the membrane as well as reversible cake/gel layer formation [7]. Several methods have been developed in various applications of UF to reduce concentration polarization and membrane fouling [8–10].

Another significant agent in membrane process is solutes rejection efficiency. A higher percentage of rejections are desirable for researchers. Like membrane fouling, the solutes rejections efficiency has been the main focus of many studies. Li et al. [11] employed a tubular UF module equipped with polyvinylidene fluoride membranes modified by inorganic nano-sized alumina particles to purify oily wastewater from an oil field. They analyzed the quality of permeation water after UF process using modified and unmodified membranes at transmembrane pressure (TMP) = 0.1 MPa, temperature = 30˚C and flow velocity = 7.8 m/s. These membranes resulted solutes rejections between 87.82 and 98.73%. The results indicate that after UF treatment, oil content was below 1 mg/L, suspended solids content was below 1 mg/L, and solid particle median diameters were less than 2 μm. The quality of the permeation water met the requirements by oilfield injection or drainage.

Experimental design is widely used for controlling the effects of parameters in many processes in order to avoid full factorial experiments which are time-consuming and expensive [10]. Its usage decreases the number of experiments, exploiting the time and the material resources. Furthermore, the analysis performed on the results is easily realized and experimental errors are minimized. Statistical method measures the effects of change in operating variables and their mutual interactions on process through experimental design way. The three steps used in experimental design included statistical design experiments, estimation of coefficient through a mathematical model and analysis of the model's applicability [12].

Table 1
Some researches in which Taguchi approach has been employed to find the optimum conditions

Ref.	System/feed	Controlling parameters/levels	Optimum conditions
[13]	Nanofiltration/CIP waste water	pH, temperature, and TMP/three (low, medium, and high)	Temperature, TMP: first level pH: second level
[15]	Spiral-wound reverse osmosis element/waste water from Exir pharmaceutical Co	Pressure, temperature, and concentrations of ions/three (low, medium, and high)	- For highest flux: Temperature, pressure: third level Concentration: first level - For highest rejection of ions: Temperature, pressure: first level Concentration: third level
[16]	Ultrafiltration/waste water from metal working	pH, oil concentration, temperature, salt (NaCl, $CaCl_2$), feed velocity, and pressure./three (low, medium, and high)	pH, temperature, pressure, flow velocity: third level Oil concentration, $CaCl_2$: first level
[17]	Ultrafiltration/kerosene-water emulsion	Membrane type, TMP, oil concentration, flow velocity, and pH/three (low, medium, and high)	Membrane type: C30F (second level) Pressure: third level Oil concentration: first level
[18]	Hybrid UF/RO/outlet of the API unit of Tehran refinery	Temperature, TMP, cross flow velocity, and pH/three (low, medium, and high)	pH, cross flow velocity: third level Temperature, TMP: second level

Table 2
Characterization of real produced waters employed in this study

Test	Unit	Test method	Feed 1	Feed 2	Feed 3	Feed 4
TSS	mg/L	SM2540 D	115	111	96	44
TDS	mg/L	SM2540 C	64,941	57,197	159,160	65,816
COD	mg/L as O_2	SM5220 B	425	505	560	432
Oil-grease	mg/L	SM5520 C	51	16	816	1,925
Turbidity	NTU	SM1889 D	100	155	204	278
TOC	mg/L	SM5310	114	170	278	380

Taguchi method is a statistical technique introduced by R.A. Fisher in England in the 1920s, which is used for optimization. Taguchi method aims at finding optimum process conditions with a minimized sensitivity to noises. It is a type of fractional factorial design which uses an orthogonal array to study the influence of factors with fewer numbers of experiments [13]. Tippett discovered orthogonal arrays in 1934; however, Taguchi simplified their usage by providing tabulated sets of standard orthogonal arrays and corresponding linear graphs to fit specific projects. In Taguchi method, the experimental response quality is expressed as the ratio of desired factor (signal) compared with uncountable factors (noise) [14]. In Table 1, some research in which Taguchi approach has been applied to find the optimum conditions are listed.

In this paper, the performance of PAN membrane was experimentally studied in the UF treatment of four real produced waters under optimum conditions to meet the expectations of two of the desalination units operating in Iran. The optimum conditions were found using Taguchi approach. To study the performance of the membrane under the optimum conditions, the particles size distribution of all feeds was measured after 4 h, which should be less than 100 nm in solutes size as a demand of the desalination units. Also, the values of rejection of turbidity, oil/grease, total organic carbon (TOC), and total suspended solids (TSS) were calculated after 4 h long experiments.

2. Materials and methods

2.1. Process feed

Different produced waters applied in the experiments were generated in two of the desalination units operating in Iran. These feeds are considered as feed 1, feed 2, feed 3, and feed 4. A detailed analysis of the produced waters is represented in Table 2. The particle size distribution of feeds is illustrated in Fig. 1. The ranges of particles size in the feeds; 190–810 nm for feed 1, 40–770 nm for feed 2, 450–2,000 nm for feed 3, and 700–1,500 nm for feed 4 prove the presence of dissolved oils in feeds 1, 2, 3, and 4, and also the presence of emulsion in feeds 3 and 4 [19].

2.2. Membrane

In this study, a rectangular flat-sheet polymeric membrane (PAN350) purchased from Sepro Co., USA, was used. This membrane has a high hydrophilic feature and is formed from polyacrylonitrile. Its molecular weight cut-off is 20 kDa. PAN350 is formed from two layers called top layer with 1 μm thickness, and sublayer as support. Recommended operating limits by company for PAN350 are as follows: pH range (1.5–10.5), temperature range (0–100˚C), and pressure range (1–10 bar).

2.3. Filtration section

Fig. 2(a) shows the UF module used in experimental setup. It was made of stainless steel with an effective area of 66 cm^2. This module has been

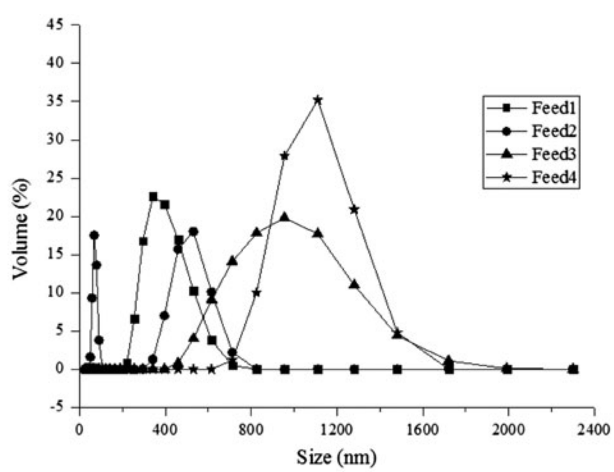

Fig. 1. Size distribution of particles for the all feeds.

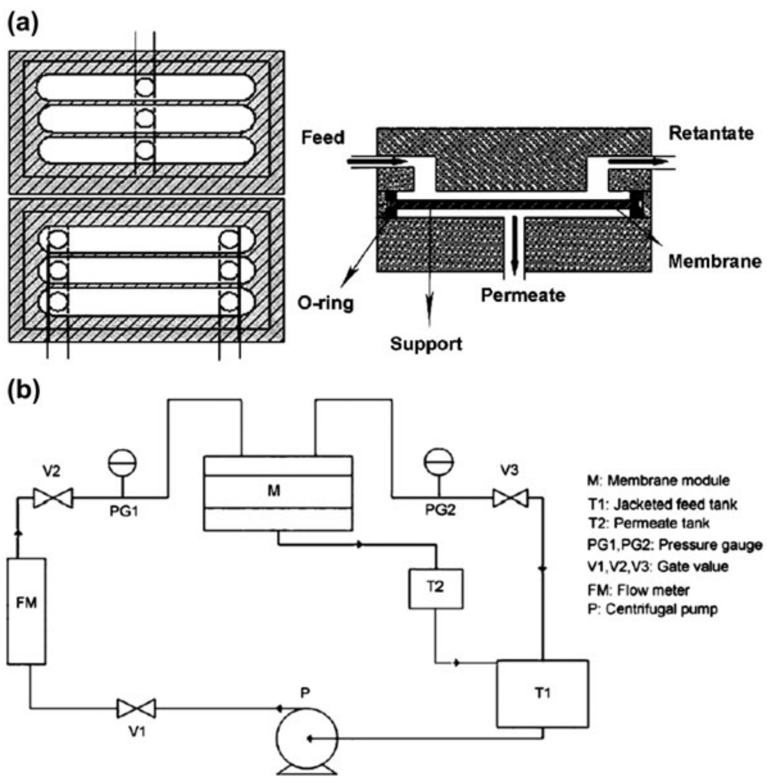

Fig. 2. (a) UF module and (b) diagram of UF experimental setup.

designed in such a way to allow the cross-flow regime. This module is made up of two separate parts, which are joined to each other by nuts and bolts and completely sealed by an O-ring. As demonstrated, the membrane is kept by a support which is located between these two parts. The module has one inlet for feed and two outlets, one for residual component over the membrane (retentate) and the other one for out flowing component (permeate).

Fig. 2(b) illustrates a schematic diagram of UF system in this paper. The feed was pumped to the module by using a centrifuge pump. Feed flow was regulated using valves V1 and V2 and the pressure on the membrane was adjusted by valve V3.

The feed flow was divided into two streams, one is the concentrate which was formed from non-passing components and was returned to the feed tank, and the permeate flow containing the components which passes through the membrane and measured by a balance. The permeate flow, after measurement was returned to the feed tank so as to have a constant concentration of the feed. A cooling/heating system was employed to detect the operating temperature. All experiments were conducted in concentration mode of filtration for 60 min in a cross-flow operation.

2.4. Scanning electron microscopy

The membrane fouling on the pores and the surface of membrane was observed with a scanning electron microscope (SEM). The SEM was operated with maximum voltage of 30 kV (model: XL30, Philips company).

2.5. Particle size distribution measurement

To measure the particle size distribution of emulsified oil droplets in the sample by light scattering method, the LLS instrument (SEMA-633) was used. The measurement range of this instrument is from 0.4 to 10,000 nm.

2.6. Experimental design based on Taguchi method

Taguchi method aims at finding the optimum operating conditions with a minimized sensitivity to noises. Taguchi method is based on several steps including planning the experimental matrix, conducting the experiments, use of signal-to-noise (S/N) ratios to evaluate the results, analysis of variance, selecting the optimum levels of factors, verifying the optimum process parameters through the verification step of the confidence interval [10,20].

Taguchi method employs fractional factorial experimental designs and orthogonal arrays to decrease the number of experiments based on the number of control factors and their levels. The first step for planning of the experimental matrix in the Taguchi method is to determine the number of factors that need to be evaluated [20]. In this study, for treating the all feeds, three factors with three levels were chosen based on the literatures [13,15,18,20] as follows:

- TMP: 1.5, 3, and 5 bar.
- Temperature: 25, 40, and 55˚C.
- Cross flow velocity: 0.5, 1, 1.5 m/s.

Each parameter has two degrees of freedom (DOF). If k_A is considered as the number of levels of parameters, the DOF for each factor is k_A-1.Using L_9 orthogonal array of Taguchi design, the number of experiments required to investigate the important effects can be reduced to nine, whereas full factorial experimentation requires $3^3 = 27$ experiments. L_9 (3^3) orthogonal array of Taguchi design include nine experiments for three factors at three levels. Suggested experimental plan for the L_9 is illustrated in Table 3 which has eight DOF (total DOF). If N is considered as the number of experiments, the total DOF is N-1.

In Taguchi method, "signal" and "noise" determines the acceptable and unacceptable values for outputs, and their ratio (S/N) is used to transform the response parameters (here permeate flux and rejections) to find the optimum conditions, which will be obtained by using the S/N ratio of the results of experimental data. The larger-the-better, the smaller-the-better, and nominal-the-better are three basic S/N ratios [16]. The equation of the S/N ratio depends on the scale for the quality characteristics to be optimized [20]. For high permeation flux and rejection, the "larger-the-better" criteria was chosen.

Table 3
All experiments based on orthogonal array (L_9) by Taguchi method [18]

Trial no.	TMP (bar)	Temperature (˚C)	CFV (cross flow velocity) (m/s)
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

2.7. Calculations

In this section, all of the equations needed for the calculation of permeate flux and rejection rate are given. The value of permeation flux can be obtained from Darcy's law [21]:

$$J = \frac{\Delta P}{\mu \sum R} \quad (1)$$

where J is the out flow permeate flux, ΔP is the pressure difference applied on two sides of membrane, μ is the viscosity, and $\sum R$ is the sum of resistances against fluid permeation. The percentage of oil/grease, TSS, TOC, and turbidity rejections were calculated as follows:

$$\text{rejection } (\%) = \frac{C_f - C_p}{C_f} \times 100 \quad (2)$$

where C_f and C_p are the solutes concentration of permeate and feed flows, respectively.

3. Results and discussion

3.1. Influence of TMP

Based on Darcy's law, increasing the value of TMP increases the permeate flux. However, increasing TMP can be a compensated fouling layer compression. Previous studies show that at low pressures, the flux increases with pressure and concentration polarization takes place. It means permeate flux is directly proportional to TMP. Over this region, 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 membrane fouling. The rejection rate decreased with an increasing pressure. This behavior can be attributed to the permeation of oil droplets through gel layer and membrane surface under the presence of a high pressures [5,22,23].

3.2. Influence of temperature

To investigate the effect of temperature, some experiments were carried out based on L_9 (3^3) array of Taguchi method in the range of 25–55˚C. Previous researches have shown that an increase in temperature causes a rise in the amount of permeate flux [16]. This increase usually is explained through the viscosity of solvent, solvent diffusion coefficient in the membrane, and the extent of thermal expansion in the membrane substance. The increase in temperature causes a reduction in the viscosity of solvent and hence an increase in the solvent diffusion coefficient [24]. The results implied that the values of TOC rejection decreased with increasing the temperature due to the increase in oil permeation and fouling layer reduction.

3.3. Influence of cross-flow velocity

An increase in CFV increases the mass transfer coefficient in the concentration boundary layer and also increases the extent of mixing over the membrane surface. 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 phenomenon weakens the influence of concentration polarization and increases permeate flux [18,23,25]. TOC removal slightly decreased with CFV. This phenomenon might be affected by existence of the fouling resistance. At a lower CFV, the fouling layer is easily developed, and oil and natural organic matters can accumulate on it. The fouling layer acted as another filter layer, and this further restricts passing of natural organic matter through the membrane resulting in higher TOC removal. At a higher CFV, high shear rate and turbulency sweep the deposited particles away from the membrane surface; therefore, the fouling layer on the membrane surface is made thinner. As a consequence, more natural organic matter can pass through the membrane and TOC removal efficiency decreases [23].

3.4. Optimum operating conditions

In this study, all experiments were conducted based on L_9 (3^3) array of Taguchi method. The effect of above-mentioned controlling parameters were studied on the variations of permeate flux and TOC rejection. The values of out flowing permeate flux (J_f) and TOC rejection after 1 h of the UF process are reported in Table 4.

Using Taguchi method [26,27] for analyzing the data reported in Table 4, the optimum conditions were found in the UF treatment of all the mentioned feeds. These conditions are reported in Table 5 for different UF processes of produced waters. As it can been seen, the optimum conditions in treatment of all feeds were different. It can be attributed to the different size distribution of particles and different concentration of solutes in the feeds, and uncontrollable factors during the experiments (noises).

3.5. Performance of PAN350 membrane

Steady-state permeation fluxes in the treatment of all feeds were measured under optimum conditions in 4 h-long experiments, which are reported in Table 6. As it can be seen, the value of permeate flux obtained from UF treatment of feed 4 was nearby zero because of its high content of oil/grease, and TOC. Treated produced waters except feed 4 were analyzed in order to evaluate the values of their TOC, TSS, oil/grease, and turbidity. These values obtained from UF process using PAN350 membrane, and feeds' qualities are reported in Table 6. These results proved that quality of feed 1 in membrane filtration has increased dramatically. Approximately, 64.91% of TOC and 99% of oil/grease reduced. TSS and turbidity values also declined 100 and 99.30%, respectively. The results also show that feed 2 quality has increased in the process. Table 6 demonstrates that 75.29% of TOC, 97% of oil/grease, 100% of TSS, and 99.61% of turbidity were removed by PAN350 membrane. Finally, based on the following table, it can be said that the quality of feed 3

Table 4
Experimental results (permeate flux and TOC rejection values) obtained from UF process for all feeds

Trial no.	Feed 1		Feed 2		Feed 3	
	J_f ($L\,m^{-2}\,h^{-1}$)	TOC rejection (%)	J_f ($L\,m^{-2}\,h^{-1}$)	TOC rejection (%)	J_f ($L\,m^{-2}\,h^{-1}$)	TOC rejection (%)
1	55	56	127	63	20	57
2	80	59	198	62	31	55
3	90	57	256	59	41	53
4	76	57	213	61	34	54
5	93	58	234	67	37	60
6	97	55	238	59	38	52
7	101	58	226	65	35	58
8	99	53	238	58	38	51
9	124	54	358	62	56	55

Table 5
Optimum operating conditions found by Taguchi method

Parameter	Feed 1		Feed 2		Feed 3	
	Value	Level	Value	Level	Value	Level
TMP (bar)	1.5	1	3	2	3	2
Temperature (°C)	40	2	40	2	40	2
Cross flow velocity (m/s)	1.5	3	1.5	3	1	2

Table 6
Characteristics of feeds and treated samples by the UF system

Produced water	Optimum conditions	Permeation flux (L/m^2 h)	Results			
			Parameter	Feed quality	Permeate quality	Removal %
Feed 1	Pressure: 1.5 bar Temperature: 40°C Cross flow velocity: 1.5 m/s	55	Oil and grease (ppm)	51	<1.5	99
			TSS (ppm)	115	Trace	100
			TOC (ppm)	114	40	64.91
			Turbidity (NTU)	100	0.7	99.30
			Size distribution (nm)	190–810	0.9–2.4	–
Feed 2	Pressure: 3 bar Temperature: 40°C Cross flow velocity: 1.5 m/s	120	Oil and grease (ppm)	16	<1.5	97
			TSS (ppm)	111	Trace	100
			TOC (ppm)	170	42	75.29
			Turbidity (NTU)	155	0.6	99.61
			Size distribution (nm)	40–770	0.5–4	–
Feed 3	Pressure: 3 bar Temperature: 40°C Cross flow velocity: 1 m/s	30	Oil and grease (ppm)	816	<1.5	100
			TSS (ppm)	96	Trace	100
			TOC (ppm)	278	94	66.19
			Turbidity (NTU)	204	1.6	99.21
			Size distribution (nm)	450–2,000	0.6–1.1	–
Feed 4	Pressure: 3 bar Temperature: 40°C Cross flow velocity: 1 m/s	Zero (after 10 min)	Oil and grease (ppm)	1925	–	–
			TSS (ppm)	44	–	–
			TOC (ppm)	380	–	–
			Turbidity (NTU)	78	–	–
			Size distribution (nm)	700–1,500	–	–

reached to an acceptable level. Table 6 represents that TOC and oil/grease of feed 3 have decreased 66.19 and 100%, respectively. TSS and turbidity were removed as 100 and 99%, respectively. Thus, PAN350 membrane can be a good choice for rejection of oil materials and grease, solid-suspended salts, organic matters, and turbidity. Additionally, for purifying those produced waters containing oil/grease more than 1,500 ppm and TOC more than 300 ppm, PAN350 is not sufficient selection.

Produced waters are complex compounds containing petroleum and oil materials, salts, emulsifiers, anticorrosion additives, and other chemicals. These compounds are suspended and emulsified in the oily wastewaters [28,29]. Mean particles size distribution of permeates decreased from 500 to 0.9 nm for feed 1, from 425 to 1.2 nm for feed 2, and from 1,225 to 1.1 nm for feed 3. It is shown that size distribution of suspended solid particles and emulsified oil droplets for all three treated samples was reached to less than

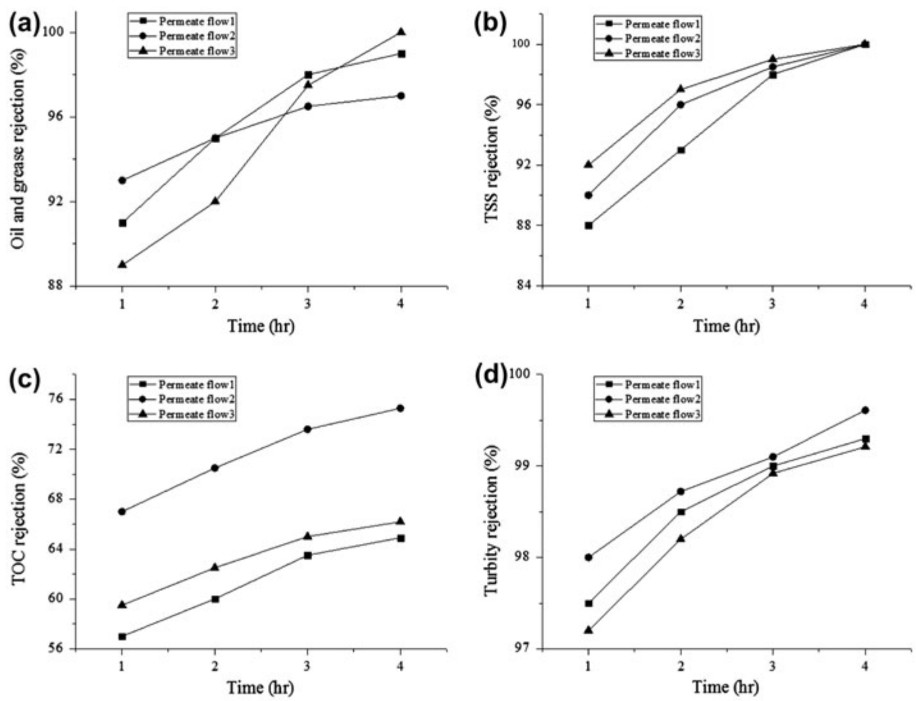

Fig. 3. Variation of (a) oil and grease, (b) TSS, (c) TOC, and (d) turbidity rejections vs time at optimum conditions during 4 h long experiments for three permeate flows 1, 2, and 3.

100 nm after UF process, which is acceptable for the desalination unit.

Fig. 3 shows the variations of rejection for oil and grease, TSS, TOC, and turbidity during the long-time experiment in the three permeate flows. As permeation flux declined versus time during a 4 h-long experiment, the values of rejections increased. Oil and grease, solids, salts, organic components, and other solutes existing in the produced water accumulated on the membrane surface and pores as cake layer and pore blocking, which causes more values of rejections. The range of oil/grease, TSS, TOC, and turbidity rejections were 89–100%, 88–100%, 57–75.29%, and 97.2–99.61%, respectively. According to the obtained results, it is observed that PAN350 membrane is a suitable membrane for the removal of large and suspended solid particles from produced waters.

3.6. Permeability of PAN350 membrane

The permeation fluxes throughout the long-time experiments under optimum conditions were divided by pressures to consider the amount of membrane permeability for different feeds. For instance, permeate fluxes through the membrane divided by 1.5 and 3 bar for feed 1 and feed 2, respectively. Since the optimum conditions for feeds were slightly different, to study under the same conditions, all of the permeation fluxes convert to permeability and then membrane performance was studied. Changes in amount of membrane permeability are illustrated in Fig. 4 for three permeate flows obtained from all feeds. After 4 h, permeability was equal to 37, 40, and 10 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$ for feed 1, feed 2, and feed 3, respectively. As it is shown, permeability is more for

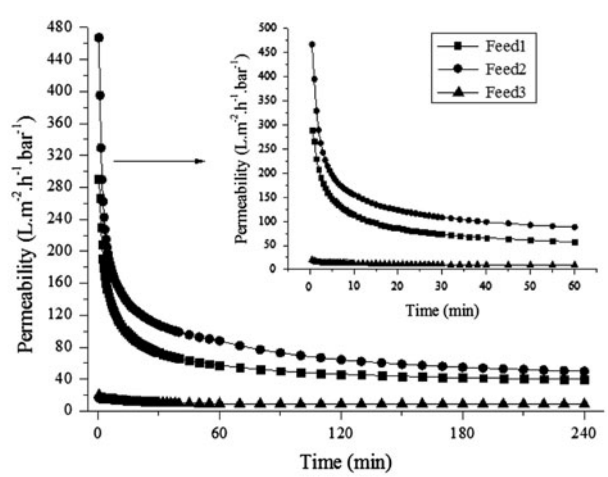

Fig. 4. Membrane permeability variations vs time for feed 1, feed 2, and feed 3 throughout 4 and 1 h of the process of UF.

feeds containing less solid salts, oil/grease. In other words, the flux passing the membrane at TMP = 1 bar is less for those feeds which have a higher percentage of contaminations. Furthermore, in a 60 min scale, Fig. 4 shows membrane permeability versus time under optimum conditions through 1 h of the UF process for feeds.

Undoubtedly, this difference in permeability and flux through the membrane is due to the difference between the amount of blockage of pores, concentration polarization and cake formation for all three feeds [7]. Permeability would decrease by increasing the amount of internal blockage and cake formation [30]. Fig. 5 shows the difference in internal blockages and formed cakes in the UF process between feed 1, feed 2, and feed 3. Fig. 5(a) shows the SEM image of fresh membrane before UF. As it is observed, there is no cake and internal blockage in membrane. The comparison between parts b, c, and d of Fig. 5 corroborates the noted results about amount of permeability. It can be seen in Fig. 5(d1) and (d2) that formed cake on the surface of membrane and internal blockage within pores of membrane resulted from UF treatment of feed 3 are more than feed 1 and feed 2. Even in Fig. 5 (d1), it is quite clear that formed cake and sediments on the surface of membrane is more intensive and greater than Fig. 5(b1) and (c1) after 4 h of UF process. Likewise, from Fig. 5(d2), it is observed that compaction, amount of sediments and internal blockage in pores of membrane for feed 3 is much higher than feed 1, and feed 2. These differences in amount of pore blocking and formed cakes are attributed to the different concentration of oil materials, organic matters, salts, etc., in the feeds [7,31].

It was said that at 10 min of UF process for feed 4, because of high concentration of oil, organic matters and salts, pore blocking occurred such fast that no time remained for cake formation and concentration

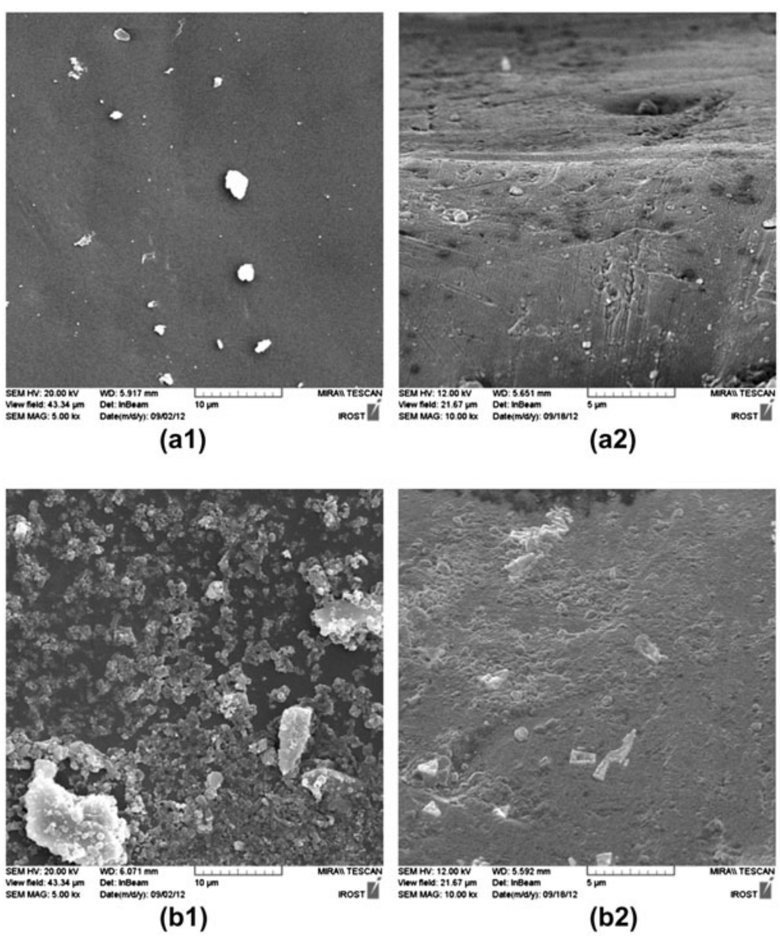

Fig. 5. SEM images of PAN350 membrane, formed cake layer and internal blockage, (a) fresh membrane before UF process, (b) resulted from UF process for feed 1, (c) resulted from UF process for feed 2, (d) resulted from UF process for feed 3, and (e) resulted from UF process for feed 4.

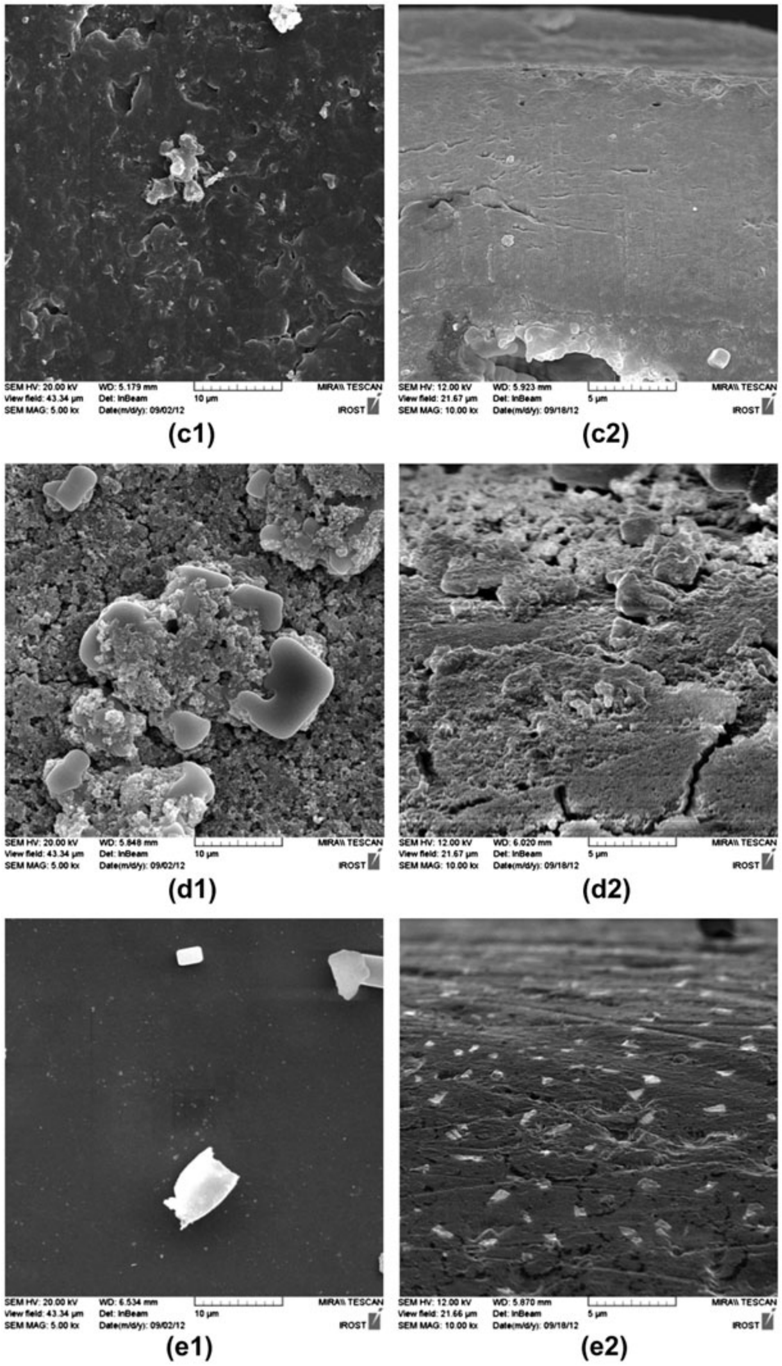

Fig. 5. (*Continued*).

polarization. Comparison of Fig. 5(e1) with Fig. 5(a1) proves it. As it is observed, there is not much difference between SEM image of the surface of membrane resulted from UF treatment of feed 4 and Fig. 5(a1) which is surface of fresh membrane. However, in Fig. 5(e1) it can be seen clearly that an extreme blockage caused by solid, oil etc. particles occurred in the pores of membrane.

3.7. Membrane fouling mechanism

To establish the fouling mechanism of the PAN350 membrane during long-term experiment for four feeds in the experimental manner, the typical methods were employed as introduced in the previous studies [32]. The total fouling resistance (R_t), the natural resistance of fresh membrane (R_m), the pore-blocking resistance

Table 7
The values of different fouling mechanism during the long-time experiments of UF process of four produced water

Feed	$R_t \times 10^{12}\,\mathrm{m}^{-1}$	$R_m \times 10^{12}\,\mathrm{m}^{-1}$ (effect percent %)	$R_p \times 10^{12}\,\mathrm{m}^{-1}$ (effect percent %)	$R_c \times 10^{12}\,\mathrm{m}^{-1}$ (effect percent %)
Feed 1	9.5	0.4 (4%)	3.4 (36%)	5.7 (60%)
Feed 2	8.1	0.4 (5%)	2.5 (30%)	5.2 (65%)
Feed 3	12.9	0.4 (3%)	5.8 (45%)	6.7 (52%)
Feed 4	17.6	0.4 (2%)	16.7 (95%)	0.5 (3%)

and the cake filtration resistance of the fouled membrane (R_p and R_c) are reported in Table 7. Thus, Fig. 5 and the experimental calculations indicate that both pore blocking and cake layer formation contributed quite effectively to the flux decline during the UF process of feed 1, feed 2, and feed 3. However, for feed 4 the pore-blocking resistance accounted for 95% of R_t. The results obtained from the experimental calculations approved the observations from SEM micrographs of Fig. 5. Therefore, it surely could be stated that the nature and amount of sediments depend on several things, such as the kind of pore size distribution, concentration of solutes, flow hydrodynamic, properties of membrane surface, and the interactions between membrane and dissolved materials [10].

4. Conclusion

In this paper, in order to investigate the performance of PAN350 membrane as a polymeric membrane to be used in industrial application, UF treatment of four real produced waters in an attempt to meet the demand of a desalination unit in Iran was performed. Taguchi method was employed to optimize the effects of significant factors on permeation flux, and TOC rejection. As a result, the optimum conditions were chosen as follows: the second level of TMP (3 bar), temperature (40°C), and cross-flow velocity (1 m/s) for feed 3. The values of oil/grease, TSS, and turbidity removals were approximately 100%. Although TOC could not be entirely removed, the removal values of TOC were acceptable based on the demand of desalination unit. As for the fourth feed, because the values of oil and TOC were more than 1,500 and 300 ppm, the permeation flux approached zero after 10 min. In a 4 h-long experiment, membrane permeability was equal to 37, 40, and 10 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$ for feed 1, feed 2, and feed 3, respectively. It was proved that permeability value was more for feeds containing less solid salts, oil/grease, and TOC. Also, mean particles size distribution of permeates decreased from 500 to 0.9 nm for feed 1, from 425 to 1.2 nm for feed 2, and from 1,225 to 1.1 nm for feed 3. Results showed that for three feeds containing oil/grease, and TOC less than 1,500 and 300 ppm, PAN350 membrane would be a good choice for industrial applications. According to the obtained results, the PAN350 membrane successfully passed the request of desalination unit operating in Iran for achieving TSS = nil, size distribution < 100 nm, turbidity < 5, oil/grease < 5 ppm, and TOC > 65%.

Experimentally, the calculations relevant to fouling mechanism indicated that both pore blocking and cake layer formation contributed quite effectively to the flux decline during the UF process. As the values of membrane fouling mechanism were so high, a hybrid MF/UF system is strongly suggested to reduce the membrane fouling.

Symbols

C_f	—	quality values of feed flow
C_p	—	quality values of permeate flow
J	—	outflowing permeate flux
ΔP	—	pressure difference applied on two sides of membrane
$\sum R$	—	sum of resistances against fluid permeation
μ	—	viscosity

References

[1] H. Shokrkar, A. Salahi, N. Kasiri, T. Mohammadi, Prediction of permeation flux decline during MF of oily wastewater using genetic programming, Chem. Eng. Res. Des. 90 (2012) 846–853.

[2] S. Alzahrani, A.W. Mohammad, N. Hilal, P. Abdullah, O. Jaafar, Comparative study of NF and RO membranes in the treatment of produced water-Part I: Assessing water quality, Desalination 315 (2013) 18–26.

[3] A. Salahi, A. Gheshlaghi, T. Mohammadi, S.S. Madaeni, Experimental performance evaluation of polymeric membranes for treatment of an industrial oily wastewater, Desalination 262 (2010) 235–242.

[4] J. Seo, A. Vogelpohl, Membrane choice for waste water treatment using external cross flow tubular membrane filtration, Desalination 249 (2009) 197–204.

[5] S.S. Madaeni, A. Gheshlaghi, F. Rekabdar, Membrane treatment of oily wastewater from refinery processes, Asia-Pac. J. Chem. Eng. 8 (2012) 45–53.
[6] R.S. Faibish, Y. Cohen, Fouling-resistant ceramic-supported polymer membranes for ultrafiltration of oil-in-water microemulsions, J. Membr. Sci. 185 (2001) 129–143.
[7] A. Salahi, M. Abbasi, T. Mohammadi, Permeate flux decline during UF of oily wastewater: Experimental and modeling, Desalination 251 (2010) 153–160.
[8] A. Salahi, T. Mohammadi, A. Rahmat Pour, F. Rekabdar, Oily wastewater treatment using ultrafiltration, Desalin. Water Treat. 6 (2009) 289–298.
[9] N. Xue, J. Xia, X. Huang, Fouling control of a pilot scale self-forming dynamic membrane bioreactor for municipal wastewater treatment, Desalin. Water Treat. 18 (2010) 302–308.
[10] A. Reyhani, F. Rekabdar, M. Hemmati, A.A. Safekordi, M. Ahmadi, Optimization of conditions in ultrafiltration treatment of produced water by polymeric membrane using Taguchi approach, Desalin. Water Treat. (2013) 1–10, doi: 10.1080/19443994.2013.776505.
[11] Y.S. Li, L. Yan, C.B. Xiang, L.J. Hong, Treatment of oily wastewater by organic-inorganic composite tubular ultrafiltration (UF) membranes, Desalination 196 (2006) 76–83.
[12] W. Djoudi, F. Aissani-Benissad, S. Bourouina-Bacha, Optimization of copper cementation processby iron using central composite design experiments, Chem. Eng. J. 133 (2007) 1–6.
[13] Z.B. Gonder, Y. Kaya, I. Vergili, H. Barlas, Optimization of filtration conditions for CIP wastewater treatment by nanofiltration process using Taguchi approach, Sep. Purif. Technol. 70 (2010) 265–273.
[14] S. Aber, D. Salari, M.R. Parsa, Employing the Taguchi method to obtain the optimum conditions of coagulation–flocculation process in tannery wastewater treatment, Chem. Eng. J. 162 (2010) 127–134.
[15] S.S. Madaeni, S. Koocheki, Application of Taguchi method in the optimization of wastewater treatment using spiral-wound reverse osmosis element, Chem. Eng. J. 119 (2006) 37–44.
[16] M. Hesampour, A. Kryzaniak, M. Nystrom, Treatment of waste water from metal working by ultrafiltration, considering the effects of operating conditions, Desalination 222 (2008) 212–221.
[17] A. Rezvanpour, R. Roostaazad, M. Hesampour, M. Nystrom, C. Ghotbi, Effective factors in the treatment of kerosene-water emulsion by using UF membranes, J. Hazard. Mater. 161 (2009) 1216–1224.
[18] A. Salahi, R. Badrnezhad, M. Abbasi, T. Mohammadi, F. Rekabdar, Oily wastewater treatment using a hybrid UF/RO system, Desalin. Water Treat. 28 (2011) 75–82.
[19] S. King, Oily Wastewater Management Study, Final Report (1999). Available from: www.govlink.org/hazwaste.
[20] M. Hesampour, A. Kryzaniak, M. Nystrom, The influence of different factors on the stability and ultrafiltration of emulsified oil in water, J. Membr. Sci. 325 (2008) 199–208.
[21] A. Deriszadeh, M.M. Husein, T.G. Harding, Produced water treatment by micellar-enhanced ultrafiltration, Environ. Sci. Technol. 44 (2010) 1767–1772.
[22] M. Abbasi, M.R. Sebzari, A. Salahi, S. Abbasi, T. Mohammadi, Flux decline and membrane fouling in cross-flow microfiltration of oil-in-water emulsions, Desalin. Water Treat. 28 (2011) 1–7.
[23] S.R.H. Abadi, M.R. Sebzari, M. Hemati, F. Rekabdar, T. Mohammadi, Ceramic membrane performance in microfiltration of oily wastewater, Desalination 265 (2011) 222–228.
[24] I. Kowalska, K. Majewska-Nowak, M. Kabsch-Korbutowicz, Influence of temperature on anionic surface active agent removal from a water solution by ultrafiltration, Desalination 198 (2006) 124–131.
[25] M. Hemmati, F. Rekabdar, A. Gheshlaghi, A. Salahi, T. Mohammadi, Effects of air sparging, cross flow velocity and pressure on permeation flux enhancement in industrial oily wastewater treatment using microfiltration, Desalin. Water Treat. 39 (2012) 33–40.
[26] J.M. Wang, H.J. Yan, J.M. Zhou, S.X. Li, G.C. Gui, Optimization of parameters for an aluminum melting furnace using the Taguchi approach, Appl. Therm. Eng. 33–34 (2012) 33–43.
[27] T. Canel, A. Uğur Kaya, B. Çelik, Parameter optimization of nanosecond laser for microdrilling on PVC by Taguchi method, Opt. Laser Technol. 44(8) (2012) 2347–2353.
[28] M. Ebrahimi, K.S. Ashaghi, L. Engel, D. Willershausen, P. Mund, P. Bolduan, P. Czermak, Characterization and application of different ceramic membranes for the oil-field produced water treatment, Desalination 245 (2009) 533–540.
[29] M. Ebrahimi, D. Willershausen, K.S. Ashaghi, L. Engel, L. Placido, P. Mund, P. Bolduan, P. Czermak, Investigations on the use of different ceramic membranes for efficient oil-field produced water treatment, Desalination 250 (2010) 991–996.
[30] C.Y. Tang, Q. She, W.C.L. Lay, R. Wang, A.G. Fane, Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration, J. Membr. Sci. 354 (2010) 123–133.
[31] F.A.H. Al-Abduwani, P.B. Edrikovetsky, R. Farajzadeh, W.M.G.T. van den Broek, P.K. Currie, External Filter Cake Erison: Mathematical Model and Experimental Study, SEP, 2005, 14p., doi: 10.2118/94635-MS.
[32] M. Li, Y. Zhao, S. Zhou, W. Xing, F.S. Wong, Resistance analysis for ceramic membrane microfiltration of raw soy sauce, J. Membr. Sci. 299 (2007) 122–129.