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Optimization of operating conditions in ultrafiltration process for produced water treatment via Taguchi methodology

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ABSTRACT

This paper describes how to find optimal operating conditions of three controlling parameters, i.e. temperature, transmembrane pressure (TMP), and cross-flow velocity (CFV) for maximizing the permeate flux and total organic carbons (TOC) rejection, and minimizing the fouling resistance using Taguchi method in ultrafiltration (UF) treatment of the real produced water. At first, the optimal operating conditions were found at a temperature of 45°C, TMP = 4 bar, and CFV of 2.25 m/s. To determine the most significant parameters affecting the response parameters, an analysis of variance was employed. In the second stage, performance of applied polymeric membrane in the UF system was studied under an optimum operating condition thus, 100% oil and grease, 100% total suspended solids, 99.78% Turbidity, and 79% TOC removal was obtained. The experimental calculations indicated that both pore blocking and cake layer formation mechanisms of fouling contributed quite effectively to the flux decline during the UF process. It is then concluded that purified produced water has the appropriate qualifications to be used for other necessary applications including irrigation, injection into oil wells, cooling towers, and boilers.

Keywords: Experimental design; Optimization; Polymeric membrane; Produced water; Ultrafiltration

1. Introduction

The produced water contains various materials such as oil, salts, heavy metals, organic acids, and radionuclide, which are considered to be major sources of pollution in oil and gas fields. Therefore, it needs to be properly treated before being employed for any purposes [1,2]. Traditional technologies as for this such as coagulation, flocculation, air flotation, and gravity separation are normally not able to meet the requirements of a high level of purity regarding the discharge of the produced water. There is a growing tendency to use membrane technology for the produced water treatment, and a number of studies have also shown successful treatments of oily water using membranes [1,3]. This is due to the fact that it has plenty advantages such

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as high product selectivity, high separation efficiency, and high system integration flexibility through optimum membrane selection and module design [4].

Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and a mixture of them are often used to purify the produced water [5,6]. Membrane fouling phenomenon, which may markedly reduce the filtration flux and product quality, and consequently increase the operating costs, is an important concern in a membrane filtration process [4,7]. A review of literature revealed that a number of studies have been conducted to control membrane fouling, including optimization of operating conditions like temperature, transmembrane pressure (TMP), pH and velocity, use of various additives, and modification of membranes [4,8].

Hwang and Sz [4] investigated membrane fouling caused by Bovine serum albumin (BSA)/dextran mixtures in cross-flow MF using a hydrophilic flat-sheet membrane made of mixed cellulose acetate. They found that, to decrease the fouling resistance, the concentration of BSA and dextran should be in the lowest quantity. Also, they concluded that the dextran concentration impact was of more significance because, the filtration resistance caused by membrane blocking is much higher than the one caused by cake formation in the majority of conditions.

Moreover, another significant function in the field of membrane filtration is solute rejection efficiency. A higher percentage of rejection is desirable for researchers because treated samples can be reused for different purposes such as in boilers, cooling towers, irrigation, and many others. Like membrane fouling, the solute rejections efficiency has been the cynosure of many studies. Salahi et al. [9] treated the oily waste water using hybrid UF/RO system. Polyacrylonitrile and polyamide membranes were employed as the UF and RO membranes, respectively. Analysis of the treated outlet water of the UF/RO system under obtained optimum operating conditions (TMP = 3 bar, cross-flow velocity (CFV)= 1 m/s, operating temperature = 40˚C, and pH = 9) showed 100, 98, 98, 95, and 100% reductions in the oil and grease content, total organic carbons (TOC), chemical oxygen demand (COD), total dissolved solids (TDS) and the turbidity, respectively.

Membrane filtration research is circumscribed in terms of factors variability. An approach often used in the experimental developments is to identify an important factor to study vs. a response of interest as we neutralizing the other factors by keeping them constant. Certainly, this approach has some drawbacks as well. Statistical experimental designs which are described as the design of experiments can be applied to investigate the effect of all the possible combinations of the conditions, whereby a smaller number of experiments with similar results can be achieved [10]. Taguchi method is a statistical technique introduced by R.A. Fisher in England in the 1920s, which was used for optimization processes. Taguchi method aims at finding optimum process conditions with a minimized sensitivity to noise. It is a type of fractional factorial design which employs an orthogonal array (OA) to study the influence of factors with fewer numbers of experiments. Taguchi method, as an experimental design, provides a systematic approach to meet the optimum conditions [11]. Table 1 lists some papers worked on in the field of membrane filtration applying Taguchi method to find optimal operating conditions. In the fourth column the sign > is used to show the importance of factors in order. For instance, in the first row, the temperature has the most important effect on permeate flux, and in terms of ions rejections, the concentration of ions is more important than the temperature and pressure.

This study concentrates on responding to an important question: "is purified produced water suitable for reusing in irrigation, injection into oil wells, boilers, and cooling towers?"

For this goal, effects of temperature, TMP, and CFV on the amount of permeate flux, TOC removal, and fouling resistance were investigated using Taguchi approach. Moreover, analysis of variance (ANOVA) was employed to find out the significance of the controlling factors. Finally, in order to investigate the performance of the membrane at optimum conditions, an 8-h experiment was conducted.

2. Methodology

2.1. Measurements

In this study, the values of total suspended solids (TSS), turbidity, TOC, and oil and grease of the feed, and permeates were measured by some special standard methods: 2,540 D, 1889 D, 5,310 C, and 5,520 B, respectively. The procedures described in these standards are intended for the examination of waters of a wide range of quality, including water suitable for domestic or industrial supplies, surface water, ground water, cooling or circulating water, boiler water, boiler feed water, treated and untreated municipal or industrial wastewater, and saline water.

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

Table 1
Some researches applying Taguchi method to find out the optimum conditions

Reference	System/ membrane type/ feed	Controlling parameters (Levels)	Most important factors (in order)	Optimum conditions
[12]	RO/Composite polymeric/ Wastewater from Exir pharmaceutical Co.	Pressure (5.75, 6.25, and 6.75 bar), temperature (25, 30, and 35°C), and concentrations of ions (50, 80, and110 ppm).	• On permeate flux: temperature > pressure > concentration of ions. • On rejection of ions: concentration of ions > temperature > pressure.	• For highest permeate flux: Temperature: 35°C, pressure: 6.75 bar, and concentration of ions: 50 ppm. • For highest rejection of ions: Temperature: 25°C, pressure: 5.75 bar, and concentration of ions: 110 ppm.
[13]	UF/Polymeric/ Refinery oily wastewater	Transmembrane pressure (1.5, 3, and 4.5 bar), cross-flow velocity (0.25, 0.75, and1.25 m/s), pH (4, 7, and 10), and temperature (25, 37.5, and 50°C).	–	Temperature: 50°C, pH: 10, cross flow velocity: 1.25 m/s, and transmembrane pressure: 3 bar.
[14]	MF/Polymeric/ Synthetic oil–water emulsion	Pressure (0.5, 1.5, 2.5, and 3.5 bar), residence time (30.6, 15.3, 10.2, and 7.6 s), water content (5, 10, 15, and 20 (%, v/v)); temperature (35, 45, 55, and 65°C), and emulsifier content (0.2, 0.4, 0.6, and 0.8 (%, v/v))	Emulsifier content> temperature> residence time> water content> pressure.	Temperature: 65°C, water content: 20 (%, v/v), residence time: 30.6 s, emulsifier content: 0.2 (%, v/v), and pressure: 1.5 bar.
[15]	NF/Polymeric/ Yeast industrial wastewater	PVA concentration (5, 10, 15, and 20 g/L), glutaraldehyde concentration (10, 30, 50, and 70 ml/L), and TiO_2 nanoparticle concentration (0.5, 1, 2, and 5 g/L)	• On permeate flux: PVA concentration > TiO_2 concentration > GA concentration. • On COD of permeate: PVA concentration > TiO_2 concentration > GA concentration.	• For highest permeate flux: GA concentration: 50 mg/L, PVA concentration: 20 g/L, and TiO_2 concentration: 5 g/L. • For permeate COD: GA concentration: 10 mg/L, PVA concentration: 5 g/L, and TiO_2 concentration: 0.5 g/L.

2.2. Process feed

The actual produced water used in the experiments was generated in one of the desalination units operating in Iran. The feed was taken daily and used immediately so that the error caused by the duration in the characteristics of feed was approximated to zero. The details of the produced water are listed in Table 2. The particle size distribution was below 800 nm, indicating the presence of dissolved oil in the process feed [16]. The result of particle size distribution analysis showed two ranges in feed: the first is from 51 to 92 nm, and the second is from 342 to 712 nm.

2.3. Membrane

In this study, a rectangular flat-sheet polymeric membrane (PAN350) purchased from Sepro Company (America) was used in the UF system. This membrane

Table 2
Characterization of real produced water

Parameter	Unit	Value
Oil and grease	mg/L	12
TDS	mg/L	58,536
COD	mg/L as O_2	525
TSS	mg/L	115
Turbidity	NTU	140
Fe	mg/L	0.42
TOC	mg/L	165
pH	–	9

has a high hydrophilic feature with contact angle = 44° and is formed from polyacrylonitrile. Its molecular weight cut-off is 20 kDa. Recommended operating limits by company for PAN350 are as follows: pH range (3–10), pH range for cleaning (3–10), temperature range (0–100 °C), pressure range (1–10 bar), and pure water flux (1,000 L/m^2 h bar). PAN350 is formed from two layers called top layer with 1 μm thickness, and sub layer as support. The effective surface area of PAN350 during experiments was 66.15 cm^2.

2.4. Filtration

Fig. 1 illustrates a schematic diagram of UF system in this study. Using a centrifuge pump, the feed was pumped to the module. The flow was regulated using valves V1 and V2 as the pressure on the membrane was adjusted by valve V3.

The feed stream was split into two streams, first the concentrate which contained non-passing components was returned to the feed tank. The other one, the permeate flow containing components passed through the membrane was measured by a balance.

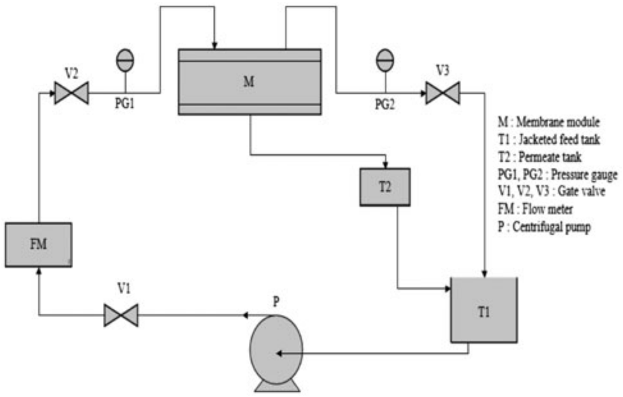

Fig. 1. Diagram of UF experimental setup.

The permeate flow having been measured, was returned to the feed tank in order to have a feed with constant concentration. As the temperature was one of the controlling factors, a cooling/heating system was employed to detect the required temperature. All experiments conducted in a cross-flow operation were carried out in a concentration mode of filtration for 60 min.

2.5. Experimental design based on Taguchi method

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, ANOVA, selecting the optimum levels of factors, and verifying the optimum process parameters through the verification step of the confidence interval [9,11,17,18]. 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 [17]. In this study, three factors with three levels (low, medium, and high) were chosen based on literatures as follows [11,17–19]:

- Temperature: 30, 45, and 60 °C
- TMP: 2, 4, and 6 bar
- CFV: 0.75, 1.5, and 2.25 m/s

Since the feed tank was open, the maximum temperature was not chosen more than 60 °C to eliminate feed evaporation. It should be mentioned that we had to maintain the characteristics of the produced water, accordingly, the pH value and solutes concentrations should be kept stable during the experiments.

Taguchi method employs fractional factorial experimental designs and OAs to decrease the number of experiments based on the number of control factors and their levels [11]. Using L_9 (3^3) OA of Taguchi design, the number of experiments required to investigate the important effects can be reduced to 9; whereas full factorial experimentation requires $3^3 = 27$ experiments [9,11]. Our experiments were carried out based on L_9OAin two repetitions (total runs = 18). Here, each parameter has two degrees of freedom (DOF), and also total DOF is 17 [9].

In Taguchi method "signal" and "noise" introduce the desirable and adverse values for outputs, respectively, and their ratio (S/N) is used to transmute the permeation flux, TOC rejection, and fouling resistance to find the optimum conditions. The larger-the-better, the smaller-the-better, and nominal-the-better are three basic S/N ratios. The equation of the S/N ratio depends on the scale for the quality characteristics to be optimized [12,17]. For high permeation flux and

TOC rejection the "larger-the-better" criteria and for low fouling resistance the "smaller-the-better" criteria were chosen. The performance characteristics were calculated using the following Eqs. (1) and (2) [11,15]:

$$\text{The larger-the-better S/N} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right) \tag{1}$$

$$\text{The smaller-the-better S/N} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}Y_i^2\right) \tag{2}$$

where n is the number of iteration for an experimental combinations (here $n = 2$) and Y_i is the response (here permeate flux, TOC rejection, and fouling resistance). Actually the most motivating factor so as to select Taguchi method to optimize the conditions is S/N ratio because this ratio minimizes the errors happened during the experiments.

ANOVA was applied to determine the significance of the factors. ANOVA's results including: the sum of squares (SS), DOF, mean of square (MS), and error as well as two statistical parameters called F and P are gathered in Table 8. These values are calculated using some equations which have been introduced in previous studies [14,20].

2.6. Hermia models and blocking mechanisms

Hermia defined some rules for filtration process which are helpful in explaining the blocking mechanisms. The governing rule of constant pressure filtration process is expressed by the following equation [13]:

$$\frac{\mathrm{d}^2t}{\mathrm{d}v^2} = k\left(\frac{\mathrm{d}t}{\mathrm{d}v}\right)^n \tag{3}$$

where v, k, and t are permeated volume (output of membrane), the proportionality constant, and filtration time. n depends on the mechanism of action: $n = 2$ for the "Complete blocking" if fouling occurs by complete pore sealing; $n = 1.5$ for the "Standard blocking" if foulants are deposited on the inner surface of the pore and constrict its radius; $n = 1$ for the "Intermediate blocking" if particles settle on one other; and $n = 0$ for the so-called "Cake formation" model when fouling occurs through formation of a layer of particles on the surface of the membrane [13]. By integrating from Eq. (3) and combining various developments on the filtration models, a different correlation for each mechanism can be reformulated. The equations of mentioned models after reformulation are presented in Table 3.

Table 3
Summary of characteristic equations for constant pressure filtration laws [13]

Fouling mechanism	Model
Standard pore blocking	$\frac{1}{J^{\frac{1}{2}}} = \frac{1}{J_0^{\frac{1}{2}}} + K_s t$
Intermediate pore blocking	$\frac{1}{J} = \frac{1}{J_0} + K_i A t$
Complete pore blocking	$Ln(J) = Ln(J_0) - K_b t$
Cake formation	$\frac{1}{J^2} = \frac{1}{J_0^2} + K_c t$

where J, J_0, k_s, k_i, k_b, and k_c are permeate flux, initial permeate flux, standard pore blocking, intermediate pore blocking, complete pore blocking, and cake formation models constant, respectively. The filtration constants can be calculated by drawing the mathematical equations reported in Table 3, then, the constant coefficients obtained from lines lead to calculate the filtration constants. The four different types of membrane fouling mechanisms are clearly illustrated in Fig. 2.

3. Results and discussions

3.1. Experimental results

As mentioned, our experiments were conducted for two times repeatedly. Fig. 3 shows the variations of permeate flux vs. the time of UF process for all nine experiments in repetition 1. As it is illustrated in Fig. 3 and Table 4, the highest point of permeation flux (390 $\mathrm{L/m^2\,h}$) occurred in trial 9, while the lowest one (159$\mathrm{L/m^2\,h}$) did in trial 1.

After one hour of the UF process, values of permeation flux (J_f), TOC rejection, turbidity rejection, and fouling resistance were measured in the two repetitions which are listed in Table 4. As reported, the values of turbidity rejection are constant in all experiments; therefore, the values of turbidity rejection were not considered in the procedure of finding optimum conditions using Taguchi approach. Comparing the pores size of membrane (=20 kDa), and the range of particles size of feed, quite expectedly, the values of turbidity rejection would be constant in all experiments. As the turbidity value is related to TSS as well as the amount of TSS is correlated to particle size distribution, it could be realized that more suspended solids were stuck at the gel layer side due to the fact that the pores size are smaller than size of particles. Therefore, as for the all experiments, turbidity rejections were approximately 99%.

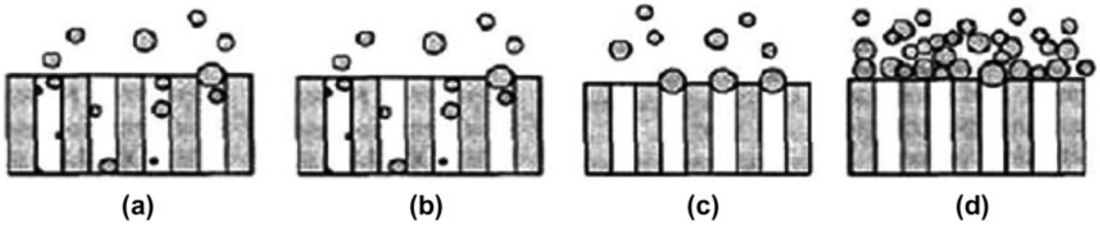

Fig. 2. Schematic views of fouling mechanisms, (a) standard pore blocking, (b) intermediate pore blocking, (c) complete pore blocking, and (d) cake layer formation.

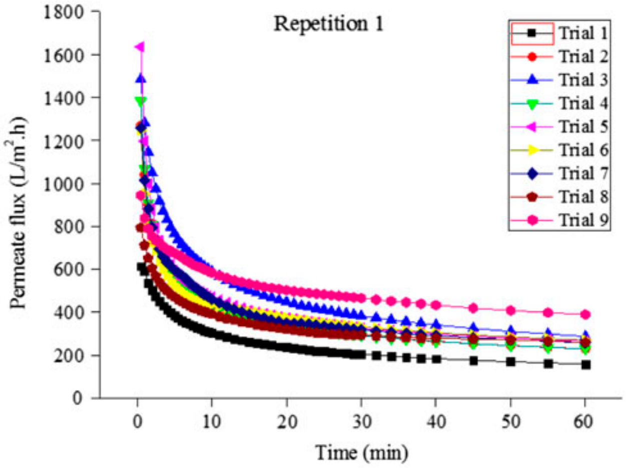

Fig. 3. Permeate flux variation vs. time throughout UF process for all experiments in repetition 1.

3.2. Optimum conditions

Using S/N ratios of experimental results reported in Table 5 and considering the effects of controlling parameters, i.e. temperature, TMP, and CFV on the response parameters, the optimum conditions were found out. The optimal operating conditions were specified based on the criteria that both permeate flux and TOC rejection must have desirable values and fouling resistance amount should be minimized. The aforementioned conditions are TMP = 4 bar (second level), temperature = 45˚C (second level), and CFV = 2.25 m/s (third level). Since these points were employed in the carried out experiments, consequently, the confident experiment was not necessary [15].

3.3. ANOVA results

At this point, the results of ANOVA for permeate flux, TOC rejection, and fouling resistance are discussed. The results of ANOVA for the above-mentioned response parameters are listed in Table 6. The values reported as error arose from the uncontrollable factors (noises), which should be less than 50%; otherwise the results would not be reliable [11,15]. As for the permeate flux reported in Table 6, the value of estimated errors is 2.83%. As shown in this table for TOC rejection and fouling resistance, the values of error are 6.39 and 2.92%, respectively. The values of errors are sufficiently far from the limit. This means that errors only had insignificant effects on the results.

Statistically, there is a tool called an *F* test to see which design parameters can have a significant effect on the quality characteristic. F-ratio values were calculated based on the results of the experiments. F-ratio has been employed in ANOVA only to facilitate qualitative measurement of the contributing factorial effects [15].

For quantitative calculations, the percentage of contribution (%P) was used [11]. The percentage contributions of all factors on permeate flux, TOC rejection, and fouling resistance are reported in Table 6. TMP has the greatest effect on permeation flux; whereas in case of other characteristics, i.e. TOC rejection and fouling resistance; the temperature was the most influential factor. It is easy to understand that variances of CFV do not have much of an effect on the quality characteristics investigated here. Conversely, Salahi and Mohammadi [19] found CFV the most effective controlling parameters followed by TMP, temperature, pH, and salt concentration in the treatment of real oily wastewater using polymeric membrane. Accordingly, the percentage influences of controlling parameters in the membrane filtration processes depends on different agents such as solutes concentrations, membrane type, membrane pores size, size distribution of particles, the range of TMP, temperature, flow velocity, etc.

3.4. Prolonged experiment

After studying the effects of different conditions on PAN350 membrane, its performance under optimum conditions were studied for 8 h. The variations of the permeate flux vs. time from membrane are

Table 4
Experimental results in repetition 1 and repetition 2

Trial no.	J_f (L/m^2 h)	TOC of Permeate (mg/L)	TOC rejection (%)	Turbidity of permeate (NTU)	Turbidity rejection (%)	Fouling resistance×10^{11} (1/m)
Repetition 1						
1	159	38	77	0.38	99	28
2	230	40	76	0.15	99	29
3	288	41	75	0.25	99	30
4	230	45	73	0.25	99	24
5	266	43	74	0.27	99	28
6	270	51	69	0.27	99	33
7	258	46	72	0.50	99	15
8	260	53	68	0.18	99	22
9	390	54	67	0.12	99	24
Repetition 2						
1	157	37	78	0.40	99	27
2	231	41	75	0.19	99	30
3	286	42	75	0.21	99	31
4	232	44	73	0.28	99	23
5	268	42	75	0.24	99	27
6	269	52	68	0.26	99	34
7	259	45	73	0.45	99	17
8	261	54	67	0.19	99	23
9	389	52	68	0.14	99	24

Table 5
Experimental results and corresponding S/N ratios

	J_f (L/m^2 h)			TOC rejection (%)			Fouling resistance×10^{11}(1/m)		
Trial no.	Run 1	Run 2	S/N ratio	Run 1	Run 2	S/N ratio	Run 1	Run 2	S/N ratio
1	159	157	43.97	77	78	37.79	28	27	−28.79
2	230	231	47.25	76	75	37.56	29	30	−29.39
3	288	286	49.16	75	75	37.50	30	31	−29.69
4	230	232	47.27	73	73	37.27	24	23	−27.42
5	266	268	48.53	74	75	37.44	28	27	−28.79
6	270	269	48.61	69	68	36.71	33	34	−30.50
7	258	259	48.25	72	73	37.21	15	17	−24.08
8	260	261	48.31	68	67	36.59	22	23	−27.04
9	390	389	51.81	67	68	36.59	24	24	−27.60

shown in Fig. 4(a). The flux decline is a result of pore blocking, concentration polarization, and cake layer formation [21,22], which mostly occurred in the first one hour of the process; then, permeate flux from membrane decreased gradually to the point that the system reached a steady state. During the first one hour of filtration, the flux decreased by 81%, and then permeation flux declined gradually until the system approached the steady state and in the last hours of the process, the flux was almost constant by reduction of 10%. The main objective of desalination unit was to remove undesirable solutes from feed. Although the flux decline was 91% after 8hours, PAN350 was selected owing to its high hydrophile property, thus its high rejection efficiency. The final amount of flux during 8-h time was finally 125 L/m^2 h. The variations of the permeate flux with higher resolution in the first hour of the process are discussed. As shown in Fig. 4(b) the rapid decrease which was due to pore blocking and concentration polarization followed by cake layer formation occurred during the first 20 min of the process.

Table 6
ANOVA results for permeate flux, TOC rejection, and fouling resistance

Factors	DOF	SS	MS	%P	F-ratio
Permeate flux					
Temperature	2	18363.111	9181.556	30.53	93
TMP	2	30368.111	15184.056	50.71	154
CFV	2	9678.111	4839.056	15.93	49
Error	11	1084.278	98.570	2.83	
Total	17	59493.611		100	
TOC rejection					
Temperature	2	141.444	70.722	62.31	84
TMP	2	48.111	24.056	20.70	29
CFV	2	25.444	12.722	10.60	15
Error	11	9.278	0.843	6.39	
Total	17	224.277		100	
Fouling resistance					
Temperature	2	248.444	124.222	56.52	165
TMP	2	148.778	74.389	33.71	99
CFV	2	31.444	15.722	6.85	21
Error	11	8.278	0.752	2.92	
Total	17	436.944		100	

Fig. 4(b) shows the descending behavior of permeate flux more clearly. The flux decreased by 73, 20, and 11% in the first, second, and third 20 min, respectively. The above experiment confirms the occurrence of membrane fouling and shows that in these specific conditions, it takes place with a higher rate in the first 30 min and slower rate when the system approaches a steady state. SEM micrographs of the surface and cross-sections of fouled membrane are shown in Fig. 5. Part a, is the cross-section image (50 μm) of fresh membrane before UF process, and part b is the side view of formed cake layer. Parts c and d show cross-section micrograph of fresh membrane's pores and membrane's pores blocked by sediments, respectively. Finally, parts e and f are a top view of PAN350 membrane before and after UF process. In Fig. 5(f), the formed cake layer at the end of the process can be observed.

3.5. Membrane fouling mechanism

To determine the fouling mechanism of the PAN350 membrane during 8-h experiment in an experimental manner, the UF resistance of the membrane pore size of 20 kDa was analyzed. The typical methods were represented in the previous studies [23]. Total fouling resistance (R_t) was $13.3 \times 10^{12}\,\mathrm{m}^{-1}$ which is formed from: the natural resistance of fresh membrane ($R_m = 0.4 \times 10^{12}\,\mathrm{m}^{-1}$), the pore blocking resistance of the fouled membrane ($R_p = 4.92 \times 10^{12}\,\mathrm{m}^{-1}$), and the cake filtration resistance of the fouled membrane ($R_c = 7.98 \times 10^{12}\,\mathrm{m}^{-1}$).

The R_m, R_p, and R_c accounted for 3, 37, and 60%, respectively, of the R_t. 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.

Theoretically, Hermia's models [13,24] helped us to find out the dominant mechanism of membrane fouling during the long-term experiment. Like experimental measurements, Hermia's models proved both R_c and R_p had important effects on the performance of the currently UF process. Cake formation and intermediate pore blocking models of Hermia's models (see

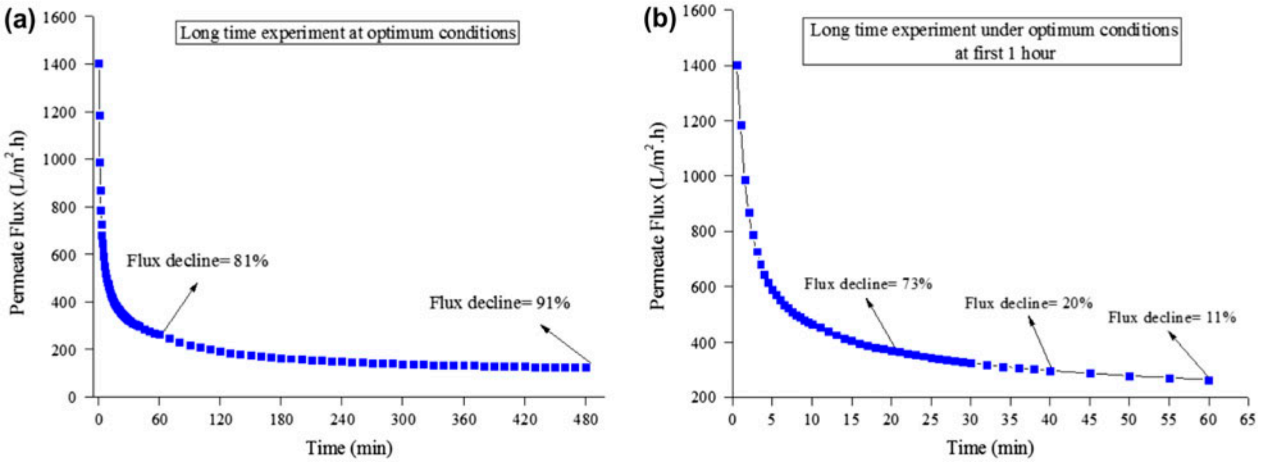

Fig. 4. Permeate flux variation vs. time under optimum conditions ($T = 45\,^\circ\mathrm{C}$, TMP = 4 bar, CFV = 2.25 m/s) for PAN350 membrane, (a) At 8-h long-time experiment, (b) At the first 1-h of long time experiment.

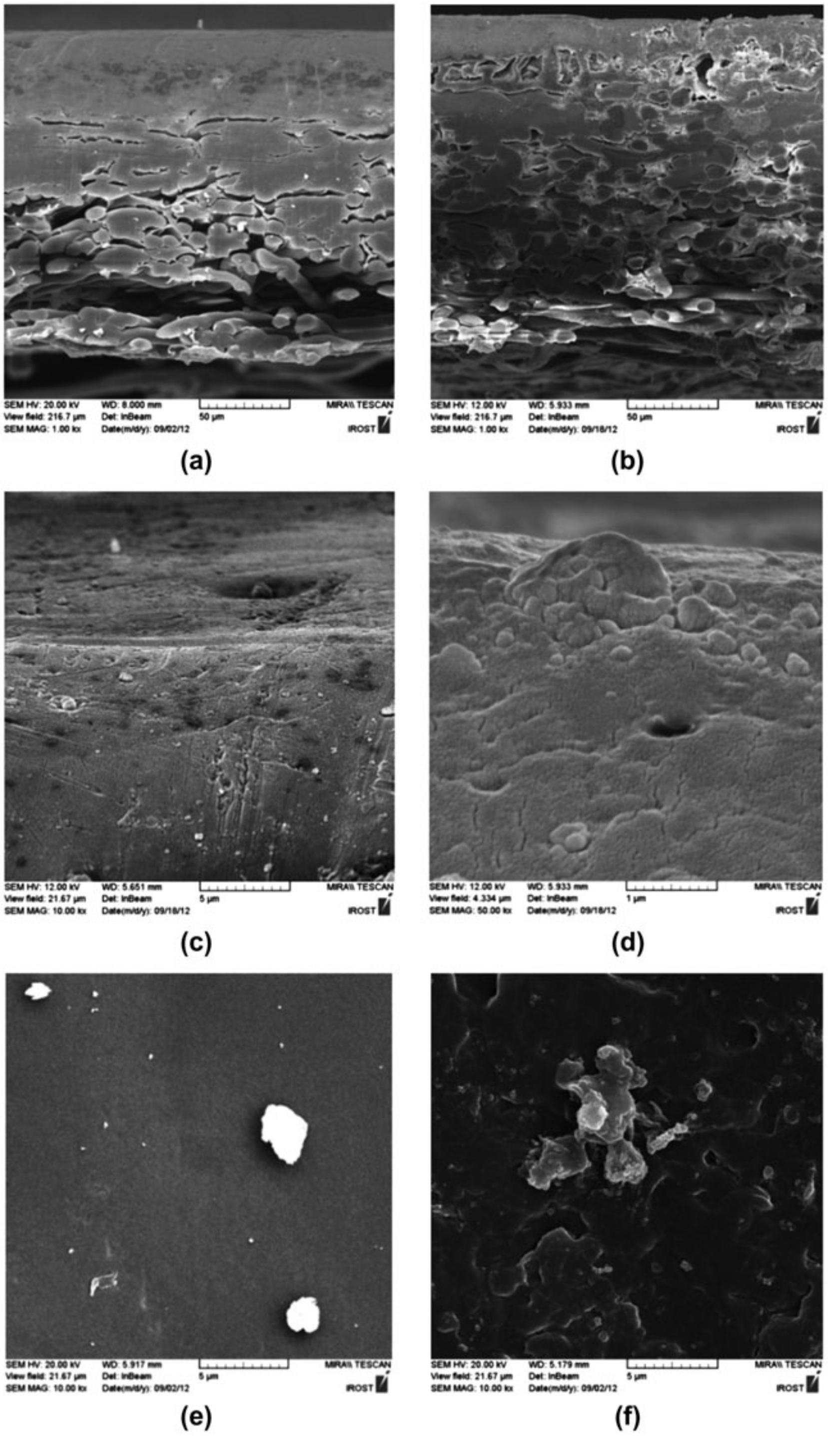

Fig. 5. SEM image of PAN350 before and after UF process, ((a) and (b)) Cross-sections- 50 μm before and after UF process, ((c) and (d)) Cross-section- 5 μm before, and sediments in the pores of membrane after UF process, ((e) and (f)) Membrane surface without any layer before, and compacted sediments and cake layer on the membrane surface after UF process.

Table 3) was well in accordance with the experimental data during the long-term experiment. Accordingly, the flux decline of the process was attributed to the intermediate pore blocking and the cake formation under optimum operating conditions. It is clearly shown that the results obtained from the experimental and mathematical calculations approved the observations from SEM micrographs of Fig. 5. Therefore, it can surely be asserted that the nature and amount of sediments depend on several factors, 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.

3.6. Performance of PAN350 membrane

The performance of the PAN350 membrane in the UF system under the optimal operating conditions is given in Table 7. In addition, all rejections were calculated according to the feed and permeate concentrations so as to evaluate the overall performance of the system. It was demonstrated that the final permeation flux after 8 h was utterly free of oil and TSS; however, TOC could not be entirely removed. Also, the size of particles in the feed decreased from the range of 51–712 nm to 1.2–3.5 nm.

Fig. 6 illustrates the variations of rejection for oil and grease, TSS, turbidity, and TOC during the prolonged experiment in the permeate flow. As permeation flux declined vs. time, the values of removal 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 cause the values of rejections to increase. Oil and grease rejection varied from 84 up to 100% in 8 h. TSS, turbidity, and TOC rejections changed from 98.5 up to

Table 7
Process performance of PAN350 membrane at optimum conditions

Parameter	Produced water quality	Permeate quality	Percent removal-[standard deviation]
Oil and Grease	12	Trace	100-[5.8]
TSS	115	Trace	100-[0.51]
Turbidity	140	0.3	99.78-[0.26]
TOC	165	35	79-[2.15]

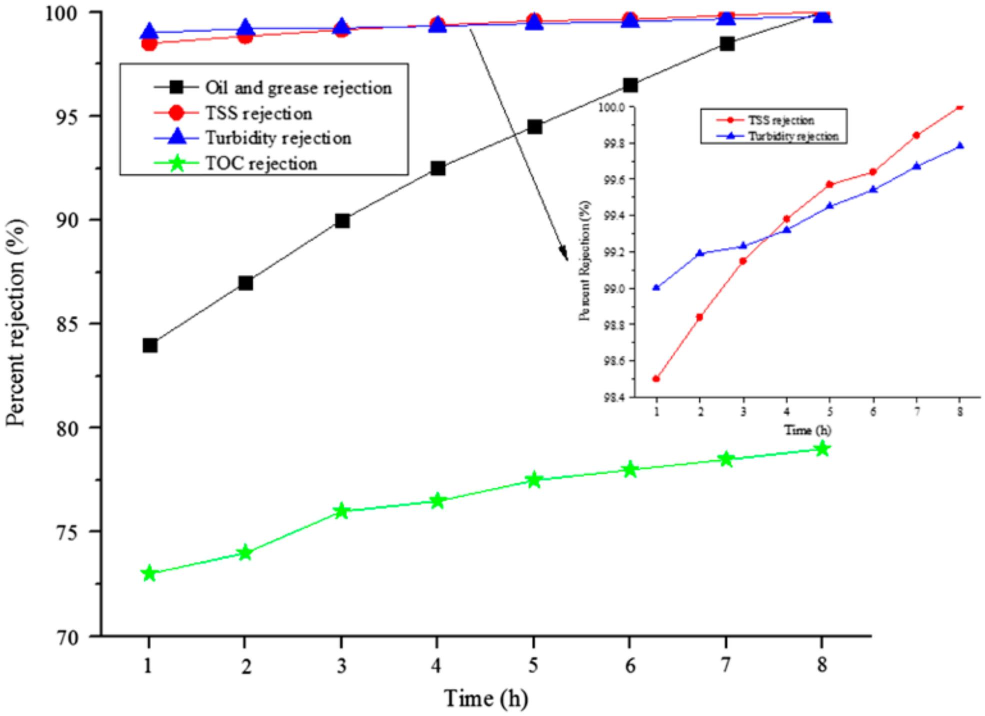

Fig. 6. Variations of Oil and grease, TSS, turbidity, and TOC removal vs. time under optimum conditions ($T = 40^\circ$C, TMP = 3 bar, and CFV = 1.5 m/s) for PAN350 membrane during 8-h experiment.

Table 8
Characteristics of the purified produced water in this study and the standard limits of these values in other applications

Parameters	Unit	Feed quality	Outlet of UF (PAN350) system	Feed water of Tehran refinery's cooling Towers	Standard feed water for cooling towers [25]	Feed water of Tehran refinery's boilers	Standard feed water for boilers [26]	Water characteristic discharged into irrigation systems [27]	Water characteristic discharged into deep wells [27]
Oil and grease	mg/L	12	Trace	–	0	0	–	5	5
TSS	mg/L	114	Trace	0	50	0	5–300[b]	30	–
TDS	mg/L	58,536	–	541.1	2000	1,256	500–3,500[b]	1,300	2000
TOC	mg/L as C	165	35	–	0	–	–	–	–
COD	mg/L as O_2	525	–	100	0	–	–	–	–
Conductivity (20°C)	µs/cm	–	–	650	1,200	3,730	100–7,000[b]	2000	–
Turbidity	NTU	140	0.3	1	–	1.5	–	–	50
Max. size of particles	nm	530	2.5	–	10^5[a]	–	–	–	–
pH	–	9	9	8.9	8.3	9–10	10–10.5	6.5–8.5	5–9.2

[a] The water must not contain solid particles which may deposit in the cooling water system.

[b] Low limit for high pressure drum and high limit for low pressure drum (0–136 bar).

100%, 99 up to 99.78%, and 73 up to 79% during 8-h long experiment, correspondingly.

It is established that PAN350 membrane is suitable to be injected in an oil well in Iran. Likewise, this study determined whether this membrane is a right choice to treat the produced water to be reused in other applications or not. Table 8 introduces a standard maximum limits for feed water of cooling towers and boilers in Tehran refinery, of cooling towers in Australia, and of irrigation systems and deep wells in Thailand. As currently most of treated produced waters are being reused worldwide in many essential applications, it was probed whether existing treated produced water could effectively be reused in the centers and industries requiring this. Table 8 demonstrates that stock treated sample interestingly have the proper qualification of applying in the necessary mentioned table applications. However, the amount of TOC obtained from the UF system is much more than the standard values; therefore, it is strongly suggested that a hybrid UF/RO system should be used. Moreover, a hybrid MF/UF system can also improve adverse membrane fouling during the UF process which was approximately 90% under the optimum conditions quite effectively.

4. Conclusions

In this paper, so as to investigate the merits of refined produced water to be injected into an oil well in Iran, a two-stage UF was conducted in an attempt to meet the requirements of a desalination unit in Iran. Moreover, this purified sample was compared to the standard maximal limits for feed water of cooling towers and boilers in Tehran refinery, of cooling towers in Australia, and of irrigation systems and deep wells in Thailand. In the first stage, Taguchi method was used in order to optimize and analyze the effects of the significant factors on permeation flux, fouling resistance, and TOC rejection. In the second stage, the performance of PAN350 membrane under the optimum conditions was studied. As a result, the optimum conditions were specified as follows: the second level of the temperature (45°C), second level of TMP (4 bar), and third level of CFV (2.25 m/s). In terms of percentage of each factor shown in the ANOVA table, the most effective parameter for minimizing fouling resistance was found to be the temperature. Furthermore, the temperature proves to have the greatest effect on maximizing TOC rejection. TMP was the most influential factor for maximizing the permeation flux. CFV was the least effective parameter as for all three response factors. At the optimum conditions, under an 8-h experiment, a result of 100% oil and grease, 100% TSS, 99.78% turbidity, and 79% TOC rejection was obtained. Eventually, the size of particles in the feed decreased from the range of 51–712 to 1.2–3.5 nm. Our results demonstrate the fact that PAN350 membrane meets the desalination unit requirements which requires the size distribution to be less than 100 nm, the concentration of oil and grease should be less than 5 ppm, TSS = nil, turbidity should be less than 5, and TOC removal should be greater than 65%. Our results indicated that treated produced water had the acceptable quality of applying in the other important mentioned applications. Both pore blocking and cake layer formation mechanisms of fouling affected the flux decline during the UF process. It is strongly suggested that a hybrid MF/UF should be used to improve the membrane fouling during the UF process, and also a hybrid UF/RO system is suggested to be employed so as to reduce the values of TOC.

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