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# Purification of biologically treated Tehran refinery oily wastewater using reverse osmosis

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ABSTRACT

In this paper, results of an experimental study on separation of oil from industrial oily wastewaters with combined biologically method/reverse osmosis (RO) process for purification of Tehran refinery oily wastewater is presented. The effects of different operating parameters on permeation flux and TDS rejection were investigated. Taguchi method ($L_9$ orthogonal array (OA)) was used initially to plan a minimum number of experiments. Analysis of variance (ANOVA) was applied to calculate sum of square, variance, ratio of factor variance to error variance and contribution percentage of each factor on response. The results showed that TMP and temperature have significant effects on the response. Permeation flux was found to increase with increasing transmembrane pressure (TMP), cross flow velocity (CFV) and feed temperature at constant feed concentration but rejection slightly decreases. The pH effects were found to be complex. By increasing acidic and basic nature of the feed, permeation flux was found to increase but rejection decrease. At original oily wastewater composition, high rejection of TDS (87%), COD (95%), $BOD_5$ (95%), TOC (90%), turbidity (82%) and oil and grease content (87%) along with complete rejection of color, free oil and TSS were achieved with a reasonably high permeation flux of 50 $L/m^2$ h. Also, the results show that cake filtration model can well predict the flux decline.

*Keywords:* Reverse osmosis; Composite membrane; Oily wastewater; Water treatment; Permeation flux; Rejection

## 1. Introduction

Treatment (recycling) of oily wastewaters for injecting to cooling tower systems in oil refineries is one of the most economical approaches that can be cost effective in meeting or supplementing the plant water requirements. Feasibility study of recycling the industrial wastewaters as make-up for cooling towers has to be considered as a multitude of factors such as: wastewater quality and quantity, make-up water quantity requirements and cost analysis. Oily wastewater of oil refineries requires proper treatment to meet stringent environmental regulations before disposal or recycling. The general approach for oily wastewater treatment is gravity separation, skimming, dissolved air flotation, de-emulsion coagulation and flocculation. Left over

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minerals may cause problems in production and refining processes when they precipitate to form scale on heaters, exchangers, etc. This can also cause accelerated corrosion in piping and equipment.

Conversion of oily wastewater into irrigation or fresh recyclable water provides an economical tool to handle excessive amounts of this wastewater. Oily wastewater of oil refineries can be used as a source of fresh and industrial water after its oil content and other impurities are removed according to cooling tower water make-up standards [1,2].

Quality requirements for cooling tower water make-up refer to established limits for substances that can promote scaling, corrosion, fouling and biological growth, thus decreasing the performance of cooling tower. Scaling is attributed to the presence of calcium, magnesium carbonates and sulphates, which can precipitate as scales on heat exchangers. Corrosion is related to the presence of high amounts of dissolved solids, including chloride and ammonia, while biological growth is due to the presence of high nutrient concentrations or organic substances. Fouling is mainly due to the presence of high levels of suspended solids [3].

Previously, oily wastewater of Tehran oil refinery was used to be discharged directly into soil or ground water. But according to research and development (R&D) of Tehran oil refinery to treat the oily wastewater due to water shortage and environmental problems, this investigation was carried out in advance. The scarcity of water is also another incentive for recovering fresh water from wastewater. For treatment of an effluent by conventional methods like aerobic or anaerobic digestion, the ratio of biological oxygen demand ($BOD_5$) to chemical oxygen demand (COD) should be >0.6 [6]. Other methods like multiple effect evaporation or incineration are highly energy intensive, and hence, very expensive. This disadvantage emphasizes the need for further research using novel separation methods [3–9].

Biological method include API separator, gravity separation and skimming, dissolved air flotation, de-emulsion coagulation and flocculation, aeration zone and settler. Fig. 1 shows the biologically method used in Tehran refinery. Gravity separation followed by skimming is effective in removing free oil from wastewater. API separator have found widespread acceptance as an effective, low cost, primary treatment step. These, however, are not effective in removing smaller oil droplets and emulsions. Oil that adheres to the surface of solid particles can be effectively removed sedimentationally in a primary clarifier. Dissolved air flotation uses air to increase the buoyancy of smaller oil droplets and this enhances separation. Emulsified oil in influent of dissolved air flotation is removed by de-emulsification with chemicals, thermal energy or both. Dissolved air flotation units typically employ chemicals to promote coagulation and increase flock size to facilitate separation. Biological methods are not qualified to achieve the water quality that is necessary for purification of oily wastewater in refinery processes and that is why a combined advanced treatment process is required. Additional unit operations may be used to improve the effluent quality as dictated by the nature of wastewater and the effluent standard.

Conventional treatment is not sufficient to achieve the water quality requirement needed for recycling wastewaters and that is why combined of at least two advanced treatment processes are usually required.

Membrane separation technology such as RO is efficient when appropriate arrangements are used in such cases [10,11]. RO has been applied for treating wide variety of industrial wastewaters [12,13].

In this study, performance of laboratory scale RO for Purification of biologically treated Tehran refinery oily wastewater (combined biologically method/RO) was evaluated using a thin film composite (TFC) polyamide membrane. The interaction effects of process variables such as TMP, CFV, temperature and pH on the membrane performance (permeation flux and rejection of TDS) were extensively studied.

## 2. Material and methods

### 2.1. Membrane

In all the experiments, polyamide (PA, type UTC-70UB) from Toray membrane produced in Japan was

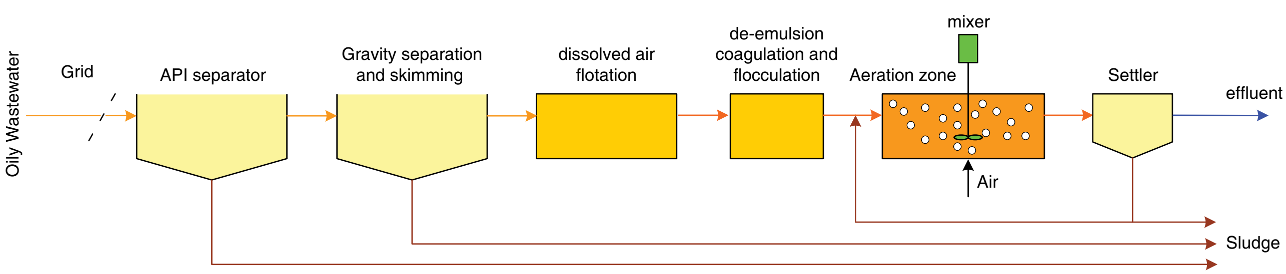


Fig.1. Schematic of the biologically method.

used as RO membrane. Characteristics of the membrane are presented in Table 1. Fig. 2 shows structure of the membrane.

### 2.2. Feed process

Wastewater disposal of sand filter (biologically method outlet) in Tehran oil refinery treatment unit was used as feed. Contaminates of the feed can be categorized into two parts: (1) Organic compounds such as oil and grease, soap, colored compounds and detergents. (2) Mineral compounds such as sodium polyphosphate, sodium silicate, sulphonate, calcium, magnesium, sodium carbonate and chlorides. An analysis result of the feed is shown in Table 2. The feed was collected and used immediately.

Table 1
Characteristics of the RO membrane

| Membrane | | | | Recommended operating limits | | |
|---|---|---|---|---|---|---|
| Series | Name | Material | NaCl rejection | pH range | Pressure range (bar) | Temperature range (°C) |
| UTC-70UB | PA | Polyamide | 99% | 2–11 | 8–30 | 0–60 |

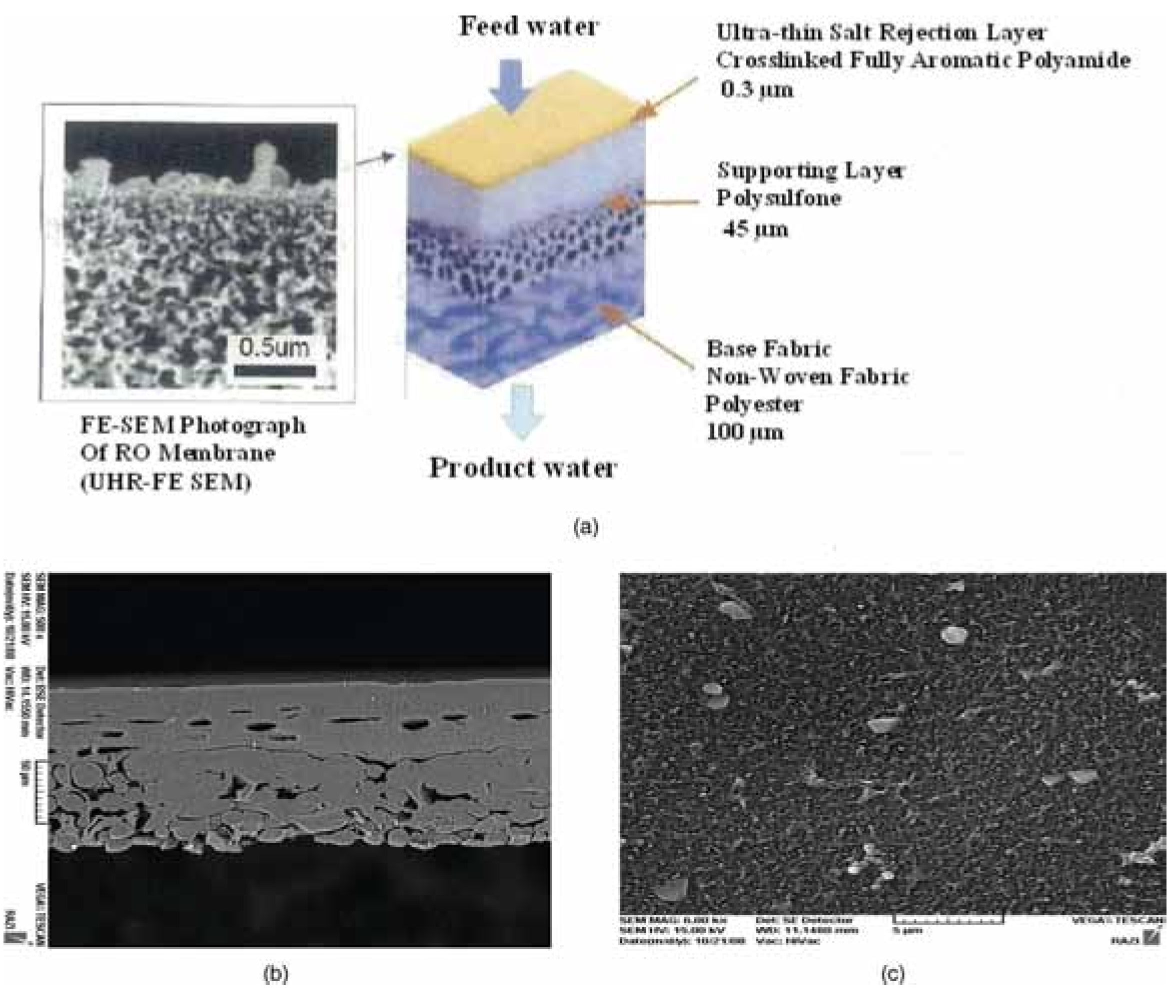


Fig. 2. (a) Different layer of the RO membrane, SEM of the RO membrane. (b) Cross section and (c) surface.

Table 2
Characteristics of Tehran refinery oily wastewater outlet (feed biologically method), biologically method outlet (feed RO), permeate RO and standard cooling tower water

| Parameter | Unit | Standard cooling water | Treatment Feed biologically | Feed RO | Permeate RO | Rejection RO (%) |
|---|---|---|---|---|---|---|
| TSS | mg/L | 0 | 60 | 4 | 0 | 100 |
| TDS | mg/L | 541.4 | 2028 | 1953 | 253 | 87.0 |
| Oil and grease content | mg/L | – | 78 | 7.2 | 1 | 86.1 |
| COD | mg/L | 100 | 124 | 160 | 8 | 95.0 |
| $BOD_5$ | mg/L | 15 | 52 | 86 | 4 | 95.3 |
| TOC | mg/L | – | 81 | 48 | 4.9 | 90.0 |
| Turbidity | NTU | 1 | 53 | 1.1 | 0.2 | 81.8 |

### 2.3. Experimental method

Fig. 3 shows experimental set up used in all the experiments. RO cell was made of two part pieces of stainless steel (Fig. 4). These two parts were sealed by an O-ring and the membrane (34 $cm^2$) was placed between them. It must be mentioned that for each experiment a fresh piece of membrane was used to have the same experimental conditions for all runs. Maximum applied TMP for the RO membrane was 25 bar. During the experiments, CFV, TMP, temperature and pH were controlled precisely. Using permeated volume for 3 h and membrane area, permeation flux was calculated and reported according to its conventional unit (L/($m^2$h)). All of the adjustments and measurements for the RO experiments were the same.

### 2.4. Processing parameters

In the experiments, four process variables at three different levels were studied as follows:

- Temperature ($T$): 27.5, 37.5 and 50 °C.
- TMP: 8, 15 and 20 bar.
- CFV: 0.5, 1 and 1.5 m/s.
- pH: 4, 7 and 10.

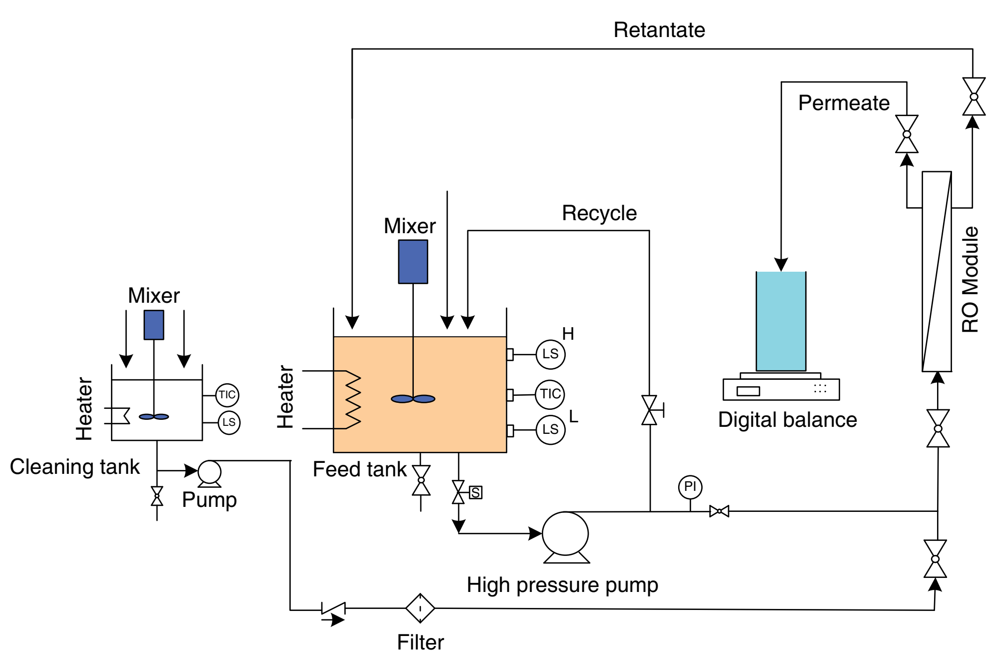


Fig. 3. Schematic of the RO system.

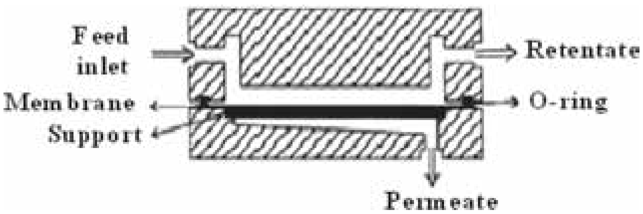


Fig. 4. Schematic view of the module.

### 2.5. Wastewater analysis methods

Samples for measurements of the feed and the permeate total suspended solids (TSS), biological oxygen demand ($BOD_5$), chemical oxygen demand (COD), oil and grease content, turbidity, total organic carbon (TOC) and total dissolved solids (TDS) were taken as necessary and analyzed by the procedure outlined somewhere else [14]. TOC and turbidity were determined using TOC Analyzer (Model DC-190) and Turbidimeter (Model 2100A HACH), respectively.

### 2.6. Percent rejection and permeation flux

In RO membrane process, the separation performance of the membrane is denoted in terms of % rejection of TDS, COD, or any other feed components which is calculated as:

$$R(\%) = \left(1 - C_p / C_f\right) \times 100 \quad (1)$$

where $C_p$ represents the concentration of the particular components in permeate, while $C_f$ represents its feed concentration.

The permeation flux is the volume of permeate collected ($V$) per membrane area ($A$) and time ($t$):

$$J = V / At \quad (2)$$

## 3. Results and discussion

Experiments were conducted using the Taguchi experimental design. Taguchi approach developed rules to carry out experiments, which further simplify and standardize the experiment design. In Taguchi method, the result of experiments are analyzed to achieve the following objectives: (1) to find the best or optimal condition for the product or process, (2) to identify the contribution of individual factors and (3) to estimate the response under optimal conditions. A commonly applied statistical treatment, analysis of variance ANOVA, was also used to analyze the results of experiments and to determine how much variation each factor contributes. By studying the main effects of each factor, the general trends of the influencing factors were characterized.

Based on what has been studied and reported in the literature, the performance of RO membranes is affected by operating parameters including feed temperature, TMP, CFV and pH [2,4,5,15–18].

According to Taguchi parameter design methodology, one experimental design should be selected for the controllable factors. Table 3 shows an $L_9$ orthogonal array, a table of integers whose column elements represent the low, medium and high levels of the column factors. Each row of the orthogonal array represents a

Table 3
Experimental conditions: Taguchi $L_9$ design of experiments

| Experiment number | $T$ (°C)[a] | TMP (bar)[b] | CFV (m/s)[c] | pH (–) |
|---|---|---|---|---|
| 1 | 27.5 | 8 | 0.5 | 4 |
| 2 | 27.5 | 15 | 1 | 7 |
| 3 | 27.5 | 20 | 1.5 | 10 |
| 4 | 37.5 | 8 | 1 | 10 |
| 5 | 37.5 | 15 | 1. 5 | 4 |
| 6 | 37.5 | 20 | 0.5 | 7 |
| 7 | 50 | 8 | 1. 5 | 7 |
| 8 | 50 | 15 | 0. 5 | 10 |
| 9 | 50 | 20 | 1 | 4 |

[a]Feed temperature.
[b]Transmembrane pressure.
[c]Cross flow velocity.

run, that is, a specific set of factor levels to be tested. The $L_9$ orthogonal array accommodates four factors at three levels each in nine runs [19]. The three levels $L_9$ ($3^4$) orthogonal array was used for the optimization process and the corresponding permeation flux and rejection with two replications (response 1 and 2) were obtained under the nine candidate condition for each run.

The data obtained from the experiments may now been analyzed. Taguchi recommends analyzing the mean response for each run and also suggests analyzing variation using an appropriately chosen signal-to-noise ratio (SN). For the larger the better responses, the following relation is used for the SN calculation:

$$\mathrm{SN}_L = -10 \times \log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right) \quad (3)$$

Notice that the SN ratio is expressed in a decibel scale.

Noise factors are those parameters which are either uncontrollable or too expensive to control such as variation of environmental operating conditions. Noise factors may have a negative impact on system performance or may not. The other noise factors of this study were room temperature, variation of pH, concentration polarization, etc.

In these experiments the system is optimized when the response is as large as possible, so we deal with the $\mathrm{SN_L}$ and factor levels that maximizing the $\mathrm{SN_L}$ ratio are optimal.

Taguchi oriented practitioners often use analysis of variance (ANOVA) to determine the factors that influence the average response and the factors that influence the SN ratio.

ANOVA procedure results in calculation of sum of squares (SS), degree of freedom, mean square (variance) and associated *F*-ratio of significance [9,19]. Sum of squares of factors is calculated as follows:

$$\boldsymbol{S}_A = \sum_{i=1}^{K_A}\left(\frac{A_i^2}{n_{Ai}}\right) - \frac{t^2}{N} \quad (4)$$

where, $K_A$ is the number of levels of factor *A* (in this work $K_A = 3$ for all factors), $nA_i$ the number of all observations at level *i* of factor *A* ($nA_i$ = 6 in this work), $A_i$ the sum of all observations of level *i* of factor *A* and *t* is the sum of all observations. Sum of squares of error is computed using the following equation:

$$SS_A = \sum_{i=1}^{K_A}\left(\frac{A_i^2}{n_{Ai}}\right) - \frac{t^2}{N} \quad (4)$$

where $\mathrm{SS}_t$ is the total SS:

$$\mathrm{SS}_t = \sum y_j^2 - \frac{t^2}{N} \quad (6)$$

where, *N* is the number of all observations and *y* is the response (permeation flux). Variance is calculated by dividing the sum of squares by the degree of freedom

$$V_A = \mathrm{SS}_A / \nu_A \quad (7)$$

$\nu_A$ is estimated by

$$\nu_A = \mathrm{K}_A - 1 \quad (8)$$

*F*-ratio is calculated as follows:

$$F_A = \frac{V_A}{V_e} \quad (9)$$

where, $V_e$ is the error variance ($V_e = \mathrm{SS}_e/\nu_e$), and $\nu_e$ is the error degree of freedom, estimated by $\nu_e = \nu_t - (\nu_A + \nu_B + \cdots)$. The total degree of freedom ($\nu_t$) is calculated by subtracting *N* from 1 ($N - 1$). Using $\nu_A$ and $\nu_e$, *F*-ratios are initially extracted from statistical tables at various risks ($\alpha$). If the extracted *F*-ratio is smaller than the calculated one, the statistical significance of effect is concluded. *P*-ratio in the below equatione is the percent of contribution of each factor on the response:

$$P_A = \frac{\mathrm{SS}_A}{\mathrm{SS}_t} \times 100 \quad (10)$$

Table 4 presents SS, variance, the ratio of factor variance on error variance (*F*) and percent of contribution of each factor on response (*P*) for RO membrane. According to these results, TMP has the greatest effect on mean response. The *F* value of all factors is greater than the extracted *F* value of the table for $\alpha$ (risk) = 0.05 ($F$ = 4.26) and $\alpha$ = 0.01 ($F$ = 8.02). This means that the variance of all factors is significant compared with the variance of error and all of them have a significant effect on the response. *P* values of CFV and pH are almost the same and are smaller than that of TMP (79.74%), which means that TMP is the most influential factor on the response. Table 5 shows the mean responses (permeation flux and TDS rejection with two replications) and the SNL at all levels of factors.

Finally, using these findings and modeling significant effects by Taguchi method, results for all combination of levels could be predicated. Then these predictions should be confirmed by some experiments. So spending

Table 4
Statistical results based on $\hat{y}$ for the permeation flux

| Factor | SS[a] | DOF[b] | Variance[c] | $F$[c] | $P$[d] |
|---|---|---|---|---|---|
| $T$ (°C) | 1663.2 | 2 | 831.6 | 60.04 | 12.97 |
| TMP (bar) | 9845.1 | 2 | 4922.5 | 355.38 | 79.74 |
| CFV (m/s) | 317.8 | 2 | 158.9 | 11.47 | 2.3 |
| pH (–) | 655.8 | 2 | 327.9 | 23.67 | 4.98 |
| Error | 124.6 | 9 | 13.8 | – | – |

[a]Sum of squares.
[b]Degree of freedom.
[c]Mean square.
[d]Factor variance to error variance ratio.
[e]Contribution percent of each factor on response.

Table 5
$\hat{y}$ and $SN_L$ values for permeation flux and TDS rejection

| | | Permeation flux | | TDS rejection (%) | |
|---|---|---|---|---|---|
| Factor | Level | $\hat{y}^1$ | $SN_L{}^2$ | $\hat{y}$ | $SN_L$ |
| $T$ (°C) | 27.5 | 37.9 | 21.2 | 87.9 | 38.8 |
| | 37.5 | 48.7 | 30.8 | 83.1 | 38.4 |
| | 50 | 61.5 | 32.2 | 80.3 | 37.9 |
| TMP (bar) | 8 | 18.6 | 20.7 | 87.2 | 38.8 |
| | 15 | 54.3 | 33.7 | 82.3 | 38.2 |
| | 20 | 75.2 | 37.1 | 81.8 | 38.2 |
| CFV (m/s) | 0.5 | 43.6 | 21.2 | 84.8 | 38.5 |
| | 1.0 | 51.1 | 30.3 | 83.9 | 38.3 |
| | 1.5 | 53.4 | 31.9 | 83.1 | 38.4 |
| pH (–) | 4 | 54.7 | 21.3 | 82.1 | 38.1 |
| | 7 | 40.9 | 30.8 | 85.7 | 38.6 |
| | 10 | 52.4 | 30.9 | 83.5 | 38.4 |

[a]Mean response.
[b]Signal to noise ratio.

less time and cost, acceptable results could be derived. Some of these results are presented in Figs. 5 and 6.

### *3.1. Effects of operating conditions on permeation flux and rejection*

#### *3.1.1. Effect of TMP*

Fig. 5a shows that permeation flux of the oily wastewater increases almost linearly from 15 (L/m$^2$ h) at 8 bar to 80 (L/m$^2$ h) at 20 bar. According to Darcy's Law, as TMP increases, while other operating parameters remain constant, permeation flux increases. As well known, permeation flux increases with increasing TMP, but higher TMP causes the cake layer formed on more membrane surface to compress and the membrane is fouled faster [7,8]. Thus, at optimum TMP, permeation flux is high and tendency to cake layer formation is low. To study the effect of TMP on permeation flux and rejection, some experiments were carried out with TMP of 8–20 bar. The results showed that permeation flux linearly increases with increasing TMP.

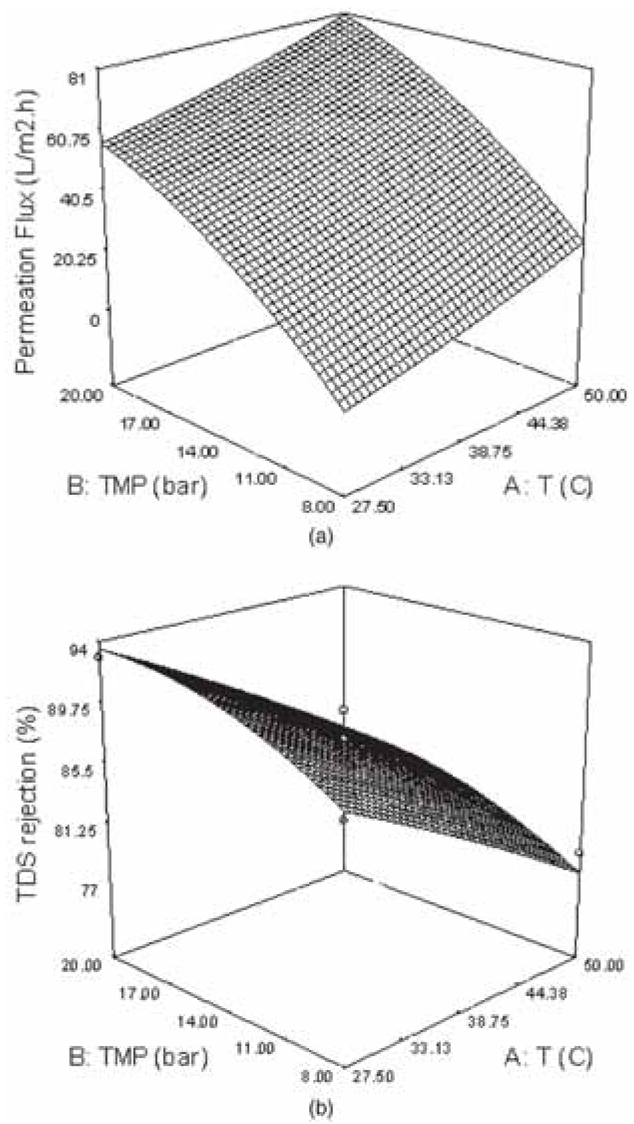


Fig. 5. (a) Effect of TMP and temperature on permeation flux. (b) Effect of TMP and temperature on TDS rejection (CVF: 1 m/s and pH: 7).

Fig. 5b shows the effect of TMP on TDS rejection. The driving force for TDS is influenced by salt concentration which is constant in both low and high TMP. Since permeation flux is affected by TMP so that at high TMP the amount of driving force for permeation flux is high, but the driving force for TDS is constant. As a result, the TDS rejection increases by increasing TMP.

### 3.1.2. *Effect of CFV*

It is well known that increasing CFV increases both the mass transfer coefficient across the concentration polarization boundary layer and the degree of mixing near the membrane surface, thereby reduces both the accumulation of a gel/cake layer on the membrane surface and the fouled membrane resistance [8,18–20]. The main reason is reduction of concentration polarization effect. Turbulency on membrane surface increases by increasing velocity. Therefore, the accumulated compounds on the membrane surface return into the bulk of feed and the concentration polarization effect diminishes. Thus, this causes osmotic pressure to decrease and permeation flux to increase [7].

To study the effect CFV on permeation flux and rejection, some experiments were carried out within a CFV range of 0.5–1.5 m/s. As shown in Fig. 6a the results show that permeation flux increases slightly with increasing CFV. Reynolds numbers at cross flow velocity of 0.5, 1.0 and 1.5 m/s are 2150, 4300 and 6450, respectively (Laminar if $Re < 2300$, transient for $2300 < Re < 4000$ and turbulent if $Re > 4000$). This trend in Reynolds number shows that the flow was passed from laminar to turbulent.

Effects of CFV on TDS rejection were also investigated (Fig. 6b). As shown rejection decreases with increasing CFV. Increasing CFV which results in increasing shear rate enhances mass transfer over the membrane surface and this decreases the rejection. This is due to more diffusion of solutes from the membrane surface to the bulk feed.

To achieve an optimum design, obtaining the maximum permeation flux and considering the minimum investments and operating costs are needed and this means that it is very important to have a membrane with the most effective service time. Primarily, the membrane service time and its permeation flux are affected by concentration polarization (caused by accumulation of solutes) and fouling (formation of a sticky cake/gel layer and/or an irreversible cake/gel layer). Considering that higher CFV leads to more power consumption for pumping, so the choice of very high CFV is not economically feasible. Therefore, the optimum CFV can be considered as 1. 5 m/s ($Re = 6450$).

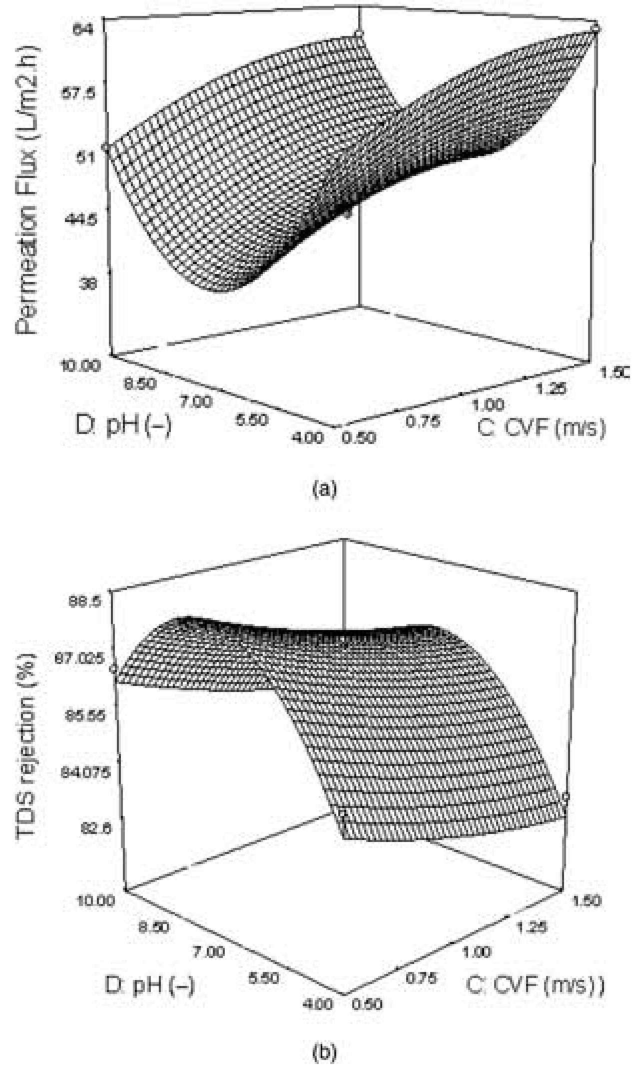


Fig. 6 (a) Effect of pH and CVF on permeation flux. (b) Effect of pH and CVF on TDS rejection % (T: 37.75 °C and TMP: 15 bar).

### 3.1.3. *Effect of temperature*

Temperature also has a serious effect on permeation flux and this can be represented by Arrhenius equation [7]

$$J = A_p \cdot \exp\left(-\frac{E_p}{RT}\right) \tag{11}$$

where $A_p$ is a coefficient and $E_p$ is the nominal activation energy of permeation flux. According to Eq. (11), increasing temperature increases permeation flux, and experimental data confirm this expectation (Fig. 5a). This is because viscosity decreases and diffusivity increases at elevated temperatures [7,8]. From another point of view, increasing temperature increases osmotic pressure and this may decrease permeation flux. At this stage, it must be mentioned that Darcy's Law may be written as follows:

$$J = \frac{\Delta P - \sigma_k \Pi}{\mu\left(R_m + R_f\right)} \quad (12)$$

where $R_m$, $R_f$, $\sigma_k$ and $\Pi$ are the primary membrane resistance, fouling resistance, reflection factor and osmotic pressure, respectively. The experimental data showed that the overall effect of temperature on permeation flux is positive. To study the effect temperature on permeation flux and rejection, some experiments were carried out within a temperature range of 27.5–50 °C. As shown in Fig. 5a the results show that permeation flux is almost linearly increases as temperature increases. It can be due to the fact that viscosity decreases and diffusivity increases at elevated temperatures.

The effect of temperature on TDS rejection is shown in Fig. 5b. According to these results, increasing temperature decreases the rejection. This can also be due to the fact that viscosity reduction increases permeability of the solutes.

#### 3.1.4. Effect of pH

Some experiments were carried out within a pH range of 4–10 to study the effect of pH on permeation flux and rejection. In Fig. 6a, an effect of pH on permeation flux is presented. As observed, with acidic and basic solutions, permeation flux is maximum. The results show that the minimum value of permeation flux is at a pH value of about 6. The pH experiments were performed in a range 4–10. In order to adjust pH, $H_2SO_4$ and NaOH were used. The pH effects on permeation flux and rejection are complex. These effects are shown in Fig. 6b. As observed, the trend for permeation flux variation is a typical behavior. Around isoelectric point the solutes (such as emulsions, fine particles and salts) lose their charge and form larger particles, which settle on the membrane surface resulting in lower permeation flux. Far from the isoelectric point, the particles are dispersed in the bulk media. Fig. 6b indicates that decreasing and increasing of pH cause lower rejection. Thus, the operating pH depends on the permeate requirements. If high amount of permeation flux is needed, the feed should be acidic or basic.

### 3.2. RO membrane performance

The effect of filtration time on permeation flux under the operating parameters: TMP of 15 bar, CFV of 1.5 m/s and feed temperature of 40 °C is presented in Fig. 7. The results show that permeation flux slightly declines with time. According to the results, permeation flux decreases with different rates, i.e. during the first 2 h and the last 2 h; it shows 5% and 0.5% reduction, respectively. The final steady permeation flux shows that fouling does not occur significantly.

Table 2 represents the characterization of the Tehran refinery oily wastewater outlet, biologically method outlet (Feed RO), permeate RO and standard cooling tower water. From the results presented in this table, it can be observed that the treatment efficiency is high. According to the high rejection of effluent components such as TDS (87%), COD (95%), $BOD_5$ (95%), TOC (90%), turbidity (82%) and oil and grease content (87%) along with the complete rejection of color, free oil and TSS, the membrane material is quite appropriate. Also, reasonably high permeation flux (50 L/m$^2$ h) is achievable.

### 3.3. Combination of biological/RO method

Biological methods are proven technology for removal of oil and grease content, suspended solids and colloids, thus providing a good protection for RO. Organic compounds attached to suspended solids can also be removed by biological methods. The results show that biologically pretreated effluents are suitable (oil content and TSS less than 5 mg/L) to be feed to RO plants in order to be further treated and dissolved inorganic compounds are removed. As mentioned, the permeate characteristics of the combined biological/RO method satisfy standards and there is no need for further treatment in order to remove suspended solids or organic compounds.

Table 2 presents the results of treatment methods (biological/RO method). As observed, the oil and grease

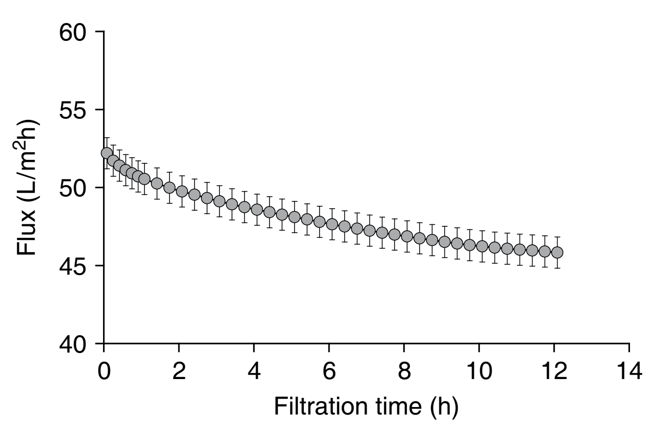


Fig. 7. Permeation flux decline of the RO membrane (TMP = 15 bar, CFV = 1.5 m/s, $T$ = 40 °C).

content is reduced using biological method to 7.2 ppm. However, TOC content removal using biological method is low and this is due to the existence of volatile organic compounds (such as methane, ethane, propane and butane) in the wastewater. More residence time in the API unit is necessary for all of these components to be removed due to their volatility. The values do not change significantly during workdays. A high quality RO membrane is suitable and needed to remove dissolved organic and inorganic compounds and to recycle the wastewater as cooling water make-up. As can be observed in Table 2, there is no need for further treatment in order to remove more inorganic compounds (TSS, TDS, turbidity, calcium, magnesium, etc.) or organic compounds (oil and grease content, COD, BOD5 and TOC). The permeate characteristics of the combined biological/RO method showed 100%, 87.5%, 98.7%, 93.5%, 92.3%, 93.9% and 99.6% reductions in TSS, TDS, in oil and grease content, COD, $BOD_5$, TOC and turbidity, respectively. Comparison of the permeate characteristics of the combined biological/RO method with the standards of cooling water systems shows that quality of the finally treated outlet water is high and even better than that is currently introduced to the cooling towers.

### 3.4. Prediction of permeation flux by the Hermia's models

As shown by Hermia [21], the filtration laws can be written into one characteristic form as presented in Eq. (13). This equation relates the resistance (inverse of flux, $dt/dV$) with variation of the resistance ($d^2t/dV^2$).

$$\frac{d^2t}{dV^2}=k\left(\frac{dt}{dV}\right)^{\xi} \tag{13}$$

where $t$ is the operation time, $k$ is the fluid characterization constant, and $\xi$ is the constant indicating the fouling mechanism. When Eq. (13) is drawn in a log-scale graph, the slope of the curve is equal to the $\xi$ value.

$$Ln\left(\frac{d^2t}{dV^2}\right)=Ln(k)+\xi.Ln\left(\frac{dt}{dV}\right) \tag{14}$$

It can be applied as a criterion identifying different mechanisms of pore blocking in a membrane, after investigation studies on volume of permeation flux in time at constant pressure. Assuming that parameter $\xi$ can have four discrete values: $\xi = 2$ (complete pore blocking), $\xi = 1.5$ (standard pore blocking), $\xi = 1$ (intermediate pore blocking) and $\xi = 0$ (cake layer formation), the fluid characterization constant, $k$, has in each case a different value, to insure that the physical interpretation of the phenomena presented in the model is preserved [21].

The ability of a simple cake filtration analysis to predict the variation of permeation flux with time during cross flow filtration leads various fouling mechanisms to be proposed to better characterize the permeation flux performance. The various fouling mechanisms that have been widely used are cake formation, intermediate law, standard pore blocking and complete pore blocking [22,23]. The cake formation correlation can be reformulated in term of permeation flux per unit time as follows [24]:

$$\frac{t}{V}=\frac{K_c}{2}V+\frac{1}{Q_0} \tag{15}$$

where $Q_0$, $V$, $t$ and $K_c$ are the initial volumetric permeate rate, the total filtrate volume, the filtration time and the constant of the cake filtration model, respectively. Also, permeate flux can be obtained by:

$$\frac{1}{J^2}=\frac{1}{J_0^2}+K_c t \tag{16}$$

where $J_0$ is the initial permeation flux.

In this section, the Hermia's models were used to interpret the fouling phenomenon occurring in RO of Tehran oil refinery oily wastewater. The fitting of the experimental data to these models permits to distinguish whether permeation flux decline is controlled by the cake layer formation or not. After comparison of the experimental data with the Hermia's model, it can be observed that fouling of the polyamide membrane completely follows the cake layer formation model. Fig. 8 shows agreement of the experimental data with this

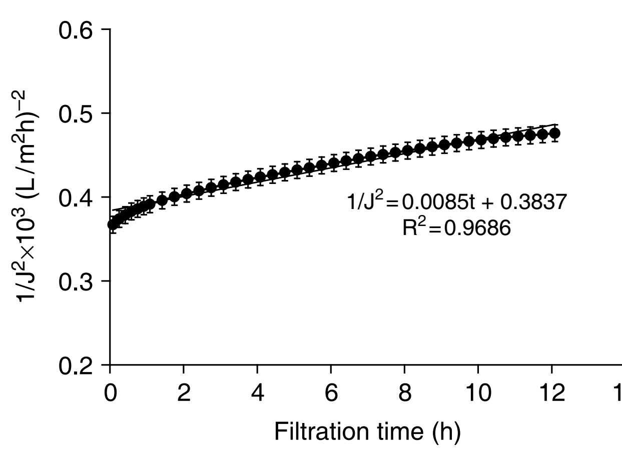


Fig. 8. Permeation flux predicted by the cake formation model for the RO process (lines: predicted data; symbols: experimental results).

model. Deviation of the experimental data from the cake layer formation model is less than 4%. According to the cake layer formation model, permeation flux decreases with increasing the resistance in proximity of the membrane surface (where solutes accumulate).

## 4. Conclusion

In this study, the effects of operating conditions (temperature, TMP, CFV and pH) on performance of RO membrane were studied. Taguchi data analysis method was utilized to study four parameters in three levels ($L_9$ OA). Effect of TMP (8, 15, 20 bar), temperature (27.5, 37.5, 50 °C), CFV (0.5, 1, 1.5 m/s) and pH (4, 7, 10) on permeation flux and rejection was scrutinized. Due to the results, higher TMP, CFV and temperature and acidic and basic solutions were recommended to modify performance of RO membrane. ANOVA analysis was applied to evaluate the relative importance of the effects of variance factors. It was realized that TMP and CFV have significant effects on the response and TMP has the largest contribution to the total sum of squares (SS) and correspondingly as a major effect on permeation flux.

RO was found very promising separation process for treatment of oily wastewaters in oil refineries and water recovery due to its high permeation flux and efficient decrease in TDS, COD, $BOD_5$ and color.

The results showed high efficiency of biological/RO system to decrease turbidity, TSS, $BOD_5$, COD from Tehran refinery oily wastewater. Also, low values of COD (8 ppm) and $BOD_5$ (4 ppm) and no indication of fecal contamination are the main characteristics of the treated water. Generally, combined biological/RO method was found to be very effective for purification of the oily wastewater. Long-term analysis is needed to analyze the membrane fouling and determine ultimate feasibility.

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