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Integrated membrane pilot plant for refinery wastewater treatment in order to produce boiler feedwater

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ABSTRACT

Treatment of Tehran refinery effluent, high in oil and grease (O&G), total organic carbon (TOC), and total dissolved solids (TDS), as boiler feedwater was proposed by a treatment scheme comprising microfiltration (MF), ultrafiltration (UF), and reverse osmosis (RO). To find optimum conditions for each membrane operation, effects of operating parameters such as transmembrane pressure (TMP), flow rate (*Q*), and temperature on permeation flux and TOC or TDS removal efficiencies were investigated. A tubular ceramic MF (α-Al_2O_3) membrane module was employed for treatment of oily wastewater before UF. The optimum operating condition was found as TMP of 1.25 bar, *Q* of 32.5 L min^{-1}, and temperature of 32.5℃. MF reduced turbidity and solid particles content of the wastewater for UF. UF was investigated in this study to reduce turbidity and O&G of the wastewater prior to RO, which was necessary to reduce salinity to an acceptable level for using as boiler feedwater. The optimum UF experiments were found at TMP of 2 bar, temperature of 25℃, and *Q* of 12 L min^{-1}; using a spiral wound polyacrylonitrile membrane module. UF reduced O&G and turbidity almost completely. Another spiral wound Polyamide RO membrane module was used to finally treat the wastewater. The optimum condition was found as TMP of 15 bar, temperature of 30℃, and *Q* of 10 L min^{-1}. Analysis of the oily wastewater treated by the MF–UF–RO integrated membrane system exhibited 100% reduction in total suspended solids (TSS), 99.43% reduction in turbidity, 99.87% reduction in O&G, 97.43% reduction in TOC, and 97.93% reduction in TDS. As a result, the effluent of MF–UF–RO integrated membrane system could be recommended as boiler feedwater.

Keywords: Oily wastewater; MF–UF–RO integrated membrane system; Boiler feedwater

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1. Introduction

Refineries consume large volumes of water and chemicals for processing crude oil. The discharge of their wastewaters into the environment without proper treatment causes serious and long-lasting consequences to human, planet, and animal life [1,2]. Conventional processes such as coagulation, flocculation, biological, and carbon adsorption can be employed for treatment of refinery oily wastewaters. However, due to dwindling supply and increasing demand of water in the refineries, their future in many countries like Iran depends on treatment processes for recovery of the wastewaters to be reused [3,4]. Membrane processes have been the technology-of-choice to provide recyclable waters via treatment of lower quality resources. Applications of membrane separation processes for wastewater treatment in the petrochemical industry allow reusing water, achieving high water quality, and have been proved to be effective processes in concentrating the bulk of pollutants into small liquid volumes for further disposal [5–8]. In industrial processing, water is used in numerous applications requiring likewise different qualities of water. Examples of different applications are cooling water, water for rinsing and chemical production, boiler feedwater, purified water, water for injection, etc. [9]. Most factories require large volumes of steam continuously in their production lines. The most pressing issue for boiler operation is that it must be fed with water of excellent quality in order to maintain highly efficient operation. Typically, the boiler feed is supplied with fresh water, potentially resulting in high operation costs in countries where the fresh water tariff is high. The alternative of reusing oily wastewater that has been treated and purified by membranes would eventually help to reduce the total water consumption and the quantity of discharged wastewater [10]. The reuse of water in production often requires a higher standard of treatment than is required in order to satisfy discharge norms [11,12]. In steam generation systems, ensuring the quality of boiler feedwater is essential for successful unit operation. This reduces the use of boiler chemicals because of less frequent blow down requirements [11]. Demands for the boiler water quality are different for various types and working pressures of boilers. Here is also a question of usage of water in boiler circuits: water can be used as circulation water or feedwater to cover sludge blow-off and surface blow-down losses. Generally, clear and colorless water must be assured, without suspended solids, oils, and aggressive chemicals. Other parameters of product water are low content of hardness, alkalinity, carbon dioxide, oxygen and SiO_2, and pH value above 8.5 [13].

Membrane technology has also been extended to agricultural- and food-processing industrial wastewater treatment for providing process quality water to sugar refinery and boiler feedwater [11]. The feasibility of membrane technology in treating and recycling wastewater has been demonstrated by a number of researchers. Miller and Potts [14] conducted a study to identify the most feasible source of water for producing boiler feed for sugar-refining processes using UF and RO membranes. The investigated sources of water included municipal water, canal water, and groundwater. They found that groundwater with membrane treatment offers the most economical solution. Manth et al. [15] developed a scheme for reusing treated secondary effluent. Under their scheme, treated secondary effluent from sewage treatment plants was treated by membrane filtration coupled with chemical treatment; with the aim of producing boiler feedwater for a power station in Australia. The use of RO membranes was shown to largely reduce the chemical consumption due to the capability of RO membranes to remove dissolved solids. Maragliano and Moss [16] utilized a demineralized plant in Italy to treat seawater for boiler feedwater. The treated water flux remained relatively stable for the first two years before a significant flux decline was experienced as a result of fouling. The problem, however, was successfully resolved with regular cleaning; little deterioration in quality occurred thereafter. Lei and Liang [17] reported the feasibility of using circulating cooling wastewater to produce boiler feedwater and showed that it has both economical and environmental benefits. Other successful experiences in producing boiler feedwater using MF and RO with industrial wastewater, river water, and sweet wastewater have been demonstrated by Nooijen et al. [18]. Koo et al. [10] designed a RO membrane plant in Malaysia to treat wastewater of a palm oil factory. Prior to the membrane process, the effluent was first treated using biological treatment and UF membrane systems. They monitored the quantity and quality of the permeate stream of RO membrane over 43 days. Their results showed the system functioned effectively. However, the system started to deteriorate after 15 days of operation according to the membrane biofouling. Nevertheless, the fouling problem could be resolved by chemical cleaning of the RO membrane. Shao et al. [19] developed a pilot plant with hollow fiber membranes to remove dissolved oxygen from two water sources (ground water and surface water in local area) for the boiler feedwater. They found that this process was efficient in removing the dissolved oxygen from boiler feedwaters. A pilot plant was also designed and constructed for palm oil mill effluent treatment by Ahmad et al. [20] in Malaysia. Two stages of treatment were conducted whereby coagulation, sedimentation, and adsorption play their roles in the first stage as a membrane pretreatment process, and UF and RO membrane processes are combined for the membrane separation treatment as the second stage. The results from the overall treatment system showed that it has a high potential for producing boiler feedwater that can be recycled back to the plant. Liu et al. [21] investigated performance of a membrane bioreactor in disposing municipal raw sewage for reusing as boiler feedwater. According to their results, application of this process not only meets nowadays demanding of saving energy source and reducing investment in disposing wastewater, but also provides a successful attempt for reusing the treated wastewater in those fields with high quality water demanding. Yejian et al. [22] constructed a two-stage pilot-scale plant for palm oil mill effluent treatment in Malaysia. Anaerobic digestion and aerobic biodegradation constituted the first biological stage, while UF and RO membrane units were combined as the second-membrane separation stage. The results showed that the high quality effluent is crystal clear and can be used as boiler feedwater. To recover milk components and produce water of quality high enough to be reused as boiler feedwater, Balannec et al. [23] studied performances of NF and RO membranes during dead-end concentration filtration. Their results showed that water quality, close to vapor condensates issued from milk and whey drying steps, is needed for reuse as boiler feed; it should be likely reached with an RO + RO cascade or possibly with a single RO using a low-charged feed. Vourch et al. [24] conducted a study to treat dairy process water by NF or RO operations to concentrate dairy matter and to produce purified water for reuse. Accordingly, both TOC and conductivity of water treated by a single RO or NF/RO operations were convenient for reuse as boiler feedwater. With a two-stage RO + RO process, more purified water complying with the TOC drinking water limit was achieved. Nandy et al. [7] reported using a UF/RO plant for recovery of textile units effluents in India as boiler feedwater. The plant consisted of chemical, biological, tertiary, and advanced treatment processes before membrane separation processes. The treatment scheme implemented resulted in conservation of around 55% of fresh water demand for the industry. Additionally, Manth et al. [15] and Clever et al. [8] reported scenarios in which river water was treated using RO technology and UF as a pretreatment system to produce boiler feedwater and process water, respectively. Clever et al. [8] reported that the integration of UF and RO for production of deionized water from surface water is more economically feasible than other conventional processes. Cuda et al. [13] investigated wastewater treatment processes and reported that RO is better in treating larger amounts of water with higher levels of TDS when compared with ion exchange methods. Apachitei et al. [25] reported using a UF/RO plant to treat refinery and petrochemical effluents to acceptable levels for reuse as cooling water and/or boiler feedwater. Furthermore, Manth et al. [15], Cuda et al. [12] and Apachitei et al. [26] agreed that UF as a pretreatment process prior to RO is essential in order to maintain efficiency and protect the functions of treatment plants.

Although applications of membrane technology for wastewater treatment have been widely reported in the past, application of membranes in treating wastewater effluents to meet boiler feedwater standards is still very limited in terms of permeate water flux. The study presented here focuses on efficient treatment processes to treat API oil water separator (gravity separation device) effluent of Tehran refinery as boiler feedwater using an integrated membrane system (MF–UF–RO) in a pilot. The system could produce permeate with characteristic of the boiler feedwater standards. The operating pressure of Tehran refinery boiler is <60 bar. The standard for boiler feedwater is the American Boiler Manufacturers Association (ABMA).

2. Materials and methods

2.1. Process feed

The feed was taken from Tehran refinery. The original temperature of the feed was in the range of 25–30˚C depending on the season. Analysis of the feed is presented in Table 2. Characterization was required to ensure existence of an oil emulsion. The droplet size distribution was below 20 μm, indicating an emulsified oil in water mixture. The result of droplet size distribution is presented in Fig. 1.

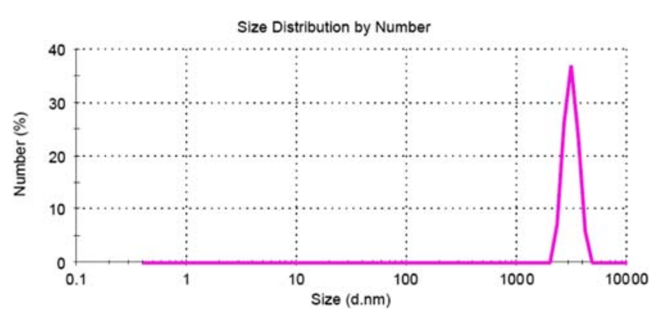

Fig. 1. Oil droplet size distribution of the wastewater.

Table 1
Characteristics of the membranes

	MF membrane	UF membrane	RO membrane
Membrane type	Ceramic (α-Al_2O_3)	Polyacrylonitrile (PAN)	Polyamide (PA)
Inner diameter (mm)	4	–	–
Outer diameter (mm)	30	–	–
Number of channels	19	–	–
Area (m^2)	0.24	1.2	2.6
Length (m)	1	0.5	1
Pore size MWCO (kDa) or (μm)	0.2 μm	100 kDa	–
Max. working pressure (bar)	10–1	9–5	41
Max. working temperature (°C)	1,200	50	45
pH	14–0	10–2	12–2

2.2. Membranes

In this study, MF190, PAN-2521, and BW30-2540 commercial membrane modules were used. The MF membrane module, MF190, supplied by FILTEC™ Membrane Company, was a kind of tubular membrane module. The UF membrane module, PAN-2521, a spiral wound membrane module, was the product of AMFOR Membrane Technology Company. The RO membrane module, BW30-2540, a spiral wound module, was also supplied by FILTEC™ Membrane Company. All these membranes modules have stainless steel housings. Table 1 lists the properties of these membranes.

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

$$R\ (\%) = \left(\frac{C_{\text{feed}} - C_{\text{permeate}}}{C_{\text{feed}}}\right) \times 100 \quad (1)$$

where C_{permeate} represent concentration of each particular component in permeate and C_{feed} is the related feed concentration.

In all experiments, choice of the optimum values (for TMP, temperature, and flow rate) is based on high permeation flux, high TOC removal efficiency, and economic conditions.

2.3. Pilot system

To find the optimum condition for each membrane process, the performance at membrane in different conditions within 90 min was studied. To control temperature, there were a heater and a coil of cooling water. Each tank was equipped with a thermostat to set its temperature. There were two analog flow meters in the way of feed and permeate streams.

PFD of the pilot is shown in Fig. 2. MF was started from TK-101. P-101, a horizontal centrifugal pump, pumped the feed from TK-101 to the bottom of MF module and it was fed to the membrane channels. The experiments were carried out in a total recycle mode of filtration, where retentate and permeate were continuously recirculated into the feed tank using V-01 and V-03. Therefore, the feed concentration in the circulation loop remained constant.

Only MF runs involved the following procedure: forward filtration time of 280 s, backwashing filtration time of 15 s, and rest time of 5 s for 90 min. These time intervals could be set by a control system. Tank (TK-103), a horizontal centrifugal pump, and three valves (V-01, V-02, and V-04) were used for backwashing. Hot distillated water was used to backwash the MF membrane using P-102. In this loop, V-04 was opened to send the hot water into the membrane module from the permeate side and V-02 was opened to send the

Table 2
Characteristics of the Tehran refinery effluent

Parameter	Unit	Tehran refinery effluent
Total suspended solids (TSS)	mg/L	60
Total dissolved solids (TDS)	mg/L	1164
conductivity	μS/cm	2068
Total organic carbon (TOC)	mg/L	78
Chemical oxygen demand (COD)	mg/L	124
biological oxygen demand (BOD)	mg/L	54
Oil and grease (O&G)	mg/L	81
Turbidity	NTU	53
Calcium (Ca^{2+})	mg/L	152
Magnesium (Mg^{2+})	mg/L	35
Silica (SiO_2)	mg/L	11
Chloride (Cl^-)	mg/L	87
pH	–	8

mixture of feed and hot water, out. By supplying the MF permeate in TK-102, this tank could be used as the UF feed tank; so V-05 should be opened instead of V-03.

UF was started from TK-102. P-101 pumped the feed from TK-102 to the bottom of UF module. The experiments were carried out in a total recycle mode of filtration, where retentate and permeate were continuously recirculated into the feed tank. Therefore, the feed concentration in the circulation loop remained virtually constant. No backwashing was used in the UF experiments. To supply the UF permeate for RO runs, TK-103 was used.

P-102 pumped the feed from TK-103 to a vertical multistage centrifugal pump (P-103) to provide high pressure. P-103 pumped the high pressure feed to the bottom of RO module. Retentive and permeate were continuously recirculated into the feed tank. Fig. 3 presents schematic of the pilot.

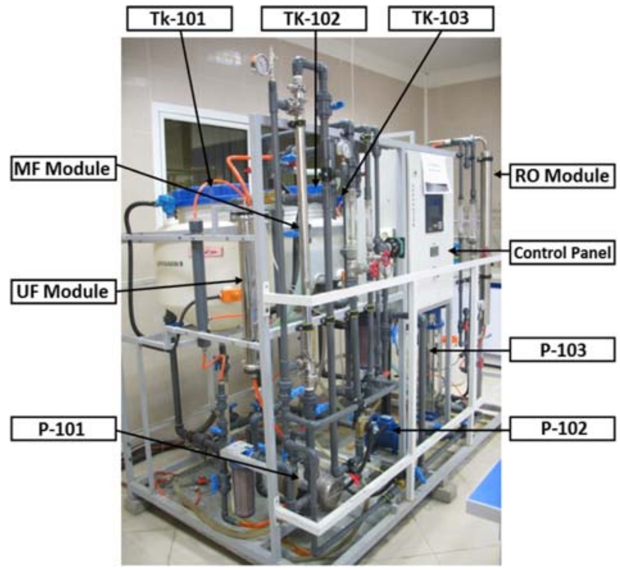

Fig. 3. Picture of the integrated membrane pilot plant.

2.4. Wastewater analysis methods

Samples for measurements of the feed and the permeate total suspended solids (TSS), biological oxygen demand (BOD), chemical oxygen demand (COD), oil and grease content, turbidity, total organic carbon (TOC), oil and grease (O&G), and total dissolved solids (TDS) were taken as necessary and analyzed by the procedure outlined in standard methods [15]. TOC was estimated using TOC Analyzer (Model DC-190). Oil and grease content values were estimated using the FTIR spectrometer set to scan 2930 cm^{-1} using TOG/TPH Analyzer Infracal (USA) Wilks Enterprise. TSS values were analyzed by the procedure outlined in the standard methods (ASTM 2540D) using Whatman 2.5 cm GF/C-Class Microfiber.

To measure TSS, the water sample was filtered through a reweighed filter. The residue retained on the filter was dried in an oven at 103–105˚C until the weight of the filter became constant. TSS was calculated as follows [26]:

$$\text{TSS (mg/L)} = ([A - B] * 1000)/C$$

where A = end weight of the filter, B = initial weight of the filter, and C = volume of water filtered.

Turbidity values were estimated using a Turbidimeter (Model 2100A HACH). Droplet size distribution of the emulsified oil in water was estimated using Laser Light Scattering (LLS) method using LLS instrument (SEMA Tech laboratory—SEM-633).

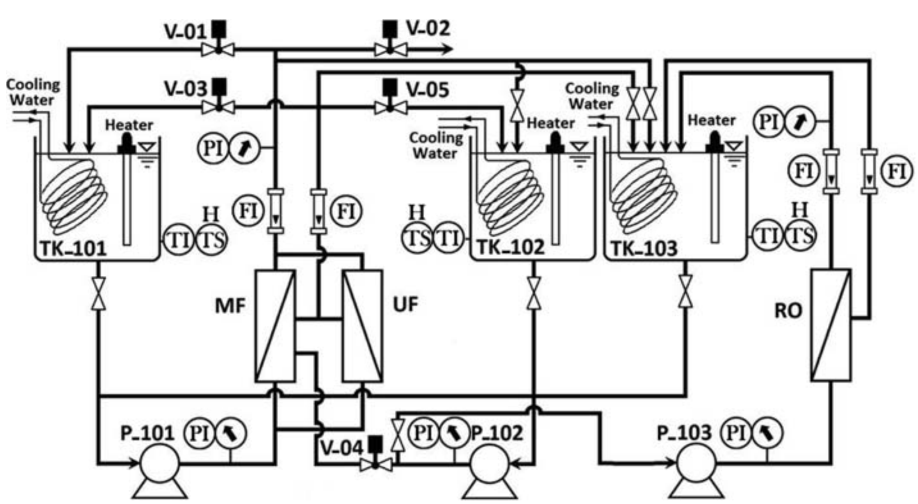

Fig. 2. Process flow diagram (PFD) of the integrated membrane pilot plant.

3. Results and discussion

3.1. Microfiltration process

3.1.1. Effect of TMP

Darcy's law is a phenomenologically derived constitutive equation that describes the flow of a fluid through a porous medium. It is a simple proportional relationship between the permeation flux through a porous medium, the viscosity of the fluid, and the pressure drop over a given thickness. Eq. (2) shows Darcy's law:

$$J = -k\left(\frac{P_b - P_a}{\mu L}\right) \tag{2}$$

the permeation flux, J ($m^3/m^2\,s$) is equal to the product of the k permeability of the medium (m^2), and the pressure drop (Pa), all divided by the viscosity, μ (Pa·s) and the length the pressure drop is taking place over. In Darcy's law, there is a linear relationship between TMP and permeation flux.

Fig. 4 shows effect of TMP on flux and TOC removal efficiency in a range of 0.75–1.75 bar. According to the Darcy's law, increasing pressure increases permeation flux, however, fouling restricts this fundamental law. In fact, it must be noted that in experiments, relationship between TMP and permeation flux is not linear but however Darcy's law can explain this phenomenon almost.

Increasing pressure makes the oil droplets more compact on the membrane surface and blocks the membrane pores. Oil droplets can fill membrane pores and formed cake gel/layer.

Cake/gel formation usually occurs when particles/oil droplets larger than the average pore size accumulate on the membrane surface, forming a "cake/gel." Standard pore block is the most dominant phenomenon when retained particles/oil droplets are dimensionally smaller than the average pore size of the membrane. It is often called adsorptive fouling or pore narrowing. Complete pore blocking occurs when the particles/oil droplets are dimensionally similar to the mean pore size of the membrane. In this model, particles/oil droplets plug individual pores. In intermediate pore blocking, each particle/oil droplet can block some membrane pores or settle on other particles/oil droplets previously blocked some other pores with superposition of particles/oil droplets.

Thus, at a best pressure, permeation flux is high, while tendency to cake/gel layer formation and blocking of membrane pores is low [2].

As shown in Fig. 4, increasing TMP up to 1.25 bar increases permeation flux; however, after that permeation flux is nearly constant.

As observed in Fig. 4, TOC removal efficiency is higher than 95%. At lower TMP, TOC removal efficiency slightly increases from 96 to 97.8% with increasing TMP, however at higher TMP (more than 1.25 bar), TOC removal efficiency decreases from 97.8 to 95%. This can be due to the fact that for TMP above 1.25 bar, O&G droplets can pass through the membrane pores and thus TOC removal efficiency decreases. This also reveals that TMP above 1.25 bar is not appropriate for high effluent quality [1,27].

To achieve the optimum operating pressure, obtaining the maximum permeation flux and the highest effluent qualities are needed. As a result, a TMP of 1.25 bar can be considered as the optimum operating pressure because at higher TMP, TOC removal efficiency decreases as TMP increases, while permeation flux does not change any more.

3.1.2. Effect of flow rate Q

Effects of Q on permeation flux and TOC removal efficiency in a range of 11–32 L min^{-1} are presented in Fig. 5. It is shown that increasing Q increases steady

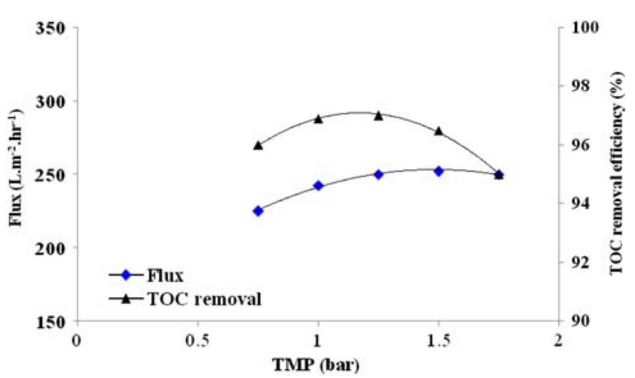

Fig. 4. Effects of TMP on MF permeation flux and TOC removal (Q: 32.5 L min^{-1}, T: 32.5˚C).

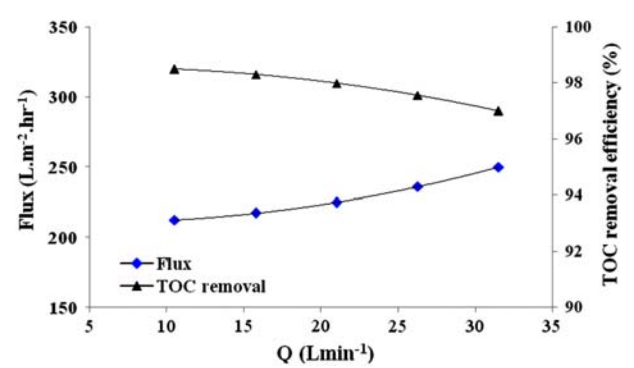

Fig. 5. Effects of Q on MF permeation flux and TOC removal (TMP: 1.25 bar, T: 32.5˚C).

permeation flux [27]. Increasing Q which increases Reynolds number promotes turbulency and increases mass transfer coefficient. This can reduce aggregation of feed components in the cake/gel layer and as a result, the aggregated materials on the membrane surface diffuse back to the bulk feed solution, and this weakens the effect of concentration polarization and increases permeation flux [30,31].

It is also shown that TOC removal efficiency slightly decreases with increasing Q. This phenomenon may be influenced by existence of the cake/gel layer. At lower Q, the cake/gel layer is easily developed and natural organic matter can accumulate on the membrane surface. The cake/gel layer acts as another filter layer and this further restricts passing of natural organic matter through the membrane resulting in higher TOC removal efficiency. At higher Q, higher shear rate and more turbulency sweep the deposited droplets particles away from the membrane surface; therefore, the cake/gel 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 [28,32]. As shown in Fig. 5, at a Q of 32 $L\,min^{-1}$ permeation has its highest value and TOC removal efficiency has an acceptable value so the optimum Q of 32 $L\,min^{-1}$ can be considered for the pilot operation.

3.1.3. Effect of temperature

Effects of feed temperature on permeation flux and TOC removal efficiency are presented within a temperature range of 25–40˚C, as shown in Fig. 6. As observed, increasing operating temperature decreases viscosity and as a result increases permeation flux [6,31]. On the other hand, at higher temperature, O&G can more easily pass through the membrane. Thus, TOC removal efficiency of the membrane decreases. This can also be due to the viscosity effect [29].

It must be also mentioned that by increasing temperature, permeation flux increases, but running the system at higher temperature increases its operational cost. Based on the results, a temperature of 32.5˚C can be recommended to achieve high permeation flux at low-operational cost and with acceptable TOC removal efficiency.

3.2. Ultrafiltration process

3.2.1. Effect of TMP

Increasing pressure increases permeation flux, but higher pressure causes the cake/gel layer formed on the membrane surface to be compressed. This accelerates formation of cake/gel layer on the surface of membrane [33–35]. Thus, at the optimum pressure, permeation flux is high and tendency to cake/gel layer formation is low. Fig. 7 shows steady permeation flux as a function of pressure.

The results show that, at high pressures (2–3 bar), permeation flux is almost constant. The reason for this phenomenon can be filling of membranes pores and formation of cake/gel layer layers on membrane surface [2,3].

As observed in Fig. 7, at lower TMP, TOC removal efficiency increases from 39.5 to 50.7% with increasing TMP; however at higher TMP (more than 2 bar), TOC removal efficiency decreases from 50.7 to 39% with increasing TMP. This can be due to the fact that at higher TMP, O&G droplets can pass through the membrane pores and thus TOC removal efficiency decreases. This also reveals that TMP above 2 bar is not appropriate for a high-quality effluent. To achieve the optimum operating pressure, obtaining the maximum permeation flux and the best effluent quality are needed. As a result, a TMP of 2 bar can be considered as the optimum operating pressure. Because at higher TMP, TOC removal efficiency decreases as TMP

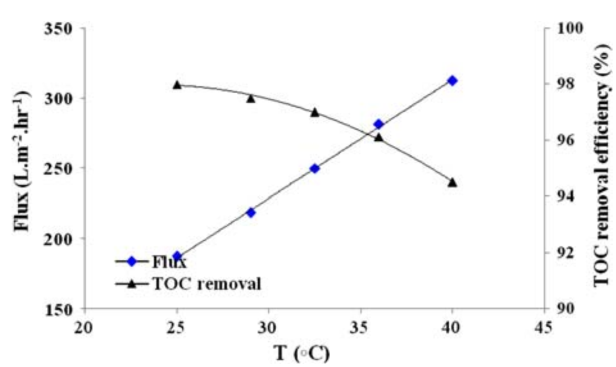

Fig. 6. Effects of temperature on MF permeation flux and TOC removal (TMP: 1.25 bar, Q: 32.5 $L\,min^{-1}$).

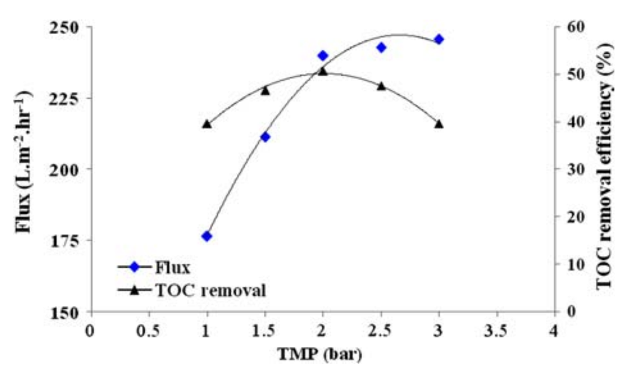

Fig. 7. Effects of TMP on UF permeation flux and TOC removal (Q: 12 $L\,min^{-1}$, T: 25˚C).

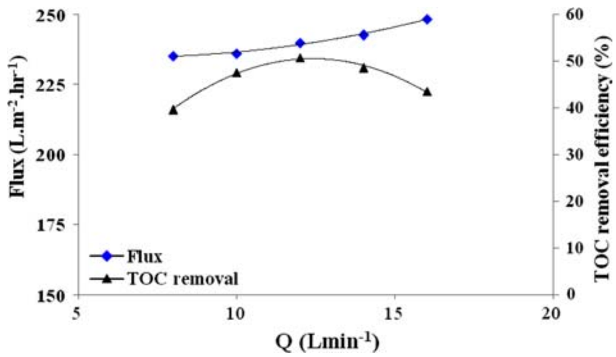

Fig. 8. Effects of Q on UF permeation flux and TOC removal. (TMP: 2 bar, T: 25˚C).

increases, while permeation flux does not change any more.

3.2.2. Effect of flow rate Q

As shown in Fig. 8, increasing Q enhances turbulency and as a result permeation flux increases. The main reason is reduction of concentration polarization effect. The more turbulency and the higher shear stress on the membrane surface are the result of increasing Q. Therefore, the accumulated compounds on the membrane surface return to the bulk of feed and concentration polarization effect diminishes [38,39]. From the results, it can be concluded that, at higher Q, cake/gel layer resistance is lower and subsequently permeation flux is higher. It should also be noticed that increasing Q, increases energy consumption. In this study, experiments were carried out with a maximum flow rate of 16 L min^{-1}; however, results of other researchers showed that at a definite threshold, increasing velocity does not affect permeation flux significantly [38,39].

As also observed, TOC removal efficiency increases at lower Q. This phenomenon may be due to the fact that the feed molecules spend shorter time over the membrane surface at higher Q. As mentioned the UF membrane module, PAN-2521, is hydrophilic. Increasing Q increases turbulency so the molecules have shorter time over the membrane surface and water molecules have more chance to go through the membrane due to the membrane hydrophilic behavior.

At higher Q, some parts of the cake/gel layer are removed from the membrane surface by hydrodynamical forces and returned to the bulk of feed. Thus, at higher Q, the cake/gel layer is thinner and permeation flux is higher [36,37]. As a consequence, more natural organic matter can pass through the membrane and TOC removal efficiency decreases [40,41].

It can be observed that at Q of 12 L min^{-1}, TOC removal efficiency is at high levels and permeation flux is not really differ so it can be considered as the optimum flow rate.

3.2.3. Effect of temperature

Increasing temperature increases permeation flux and experimental data confirm this expectation (Fig. 9). It is because viscosity decreases and diffusivity increases at elevated temperatures [42]. At higher temperatures, since viscosity decreases and diffusivity increases, permeation flux is higher [42]. TOC removal efficiency first decreases because of lower viscosity. However, specific properties of some solutions such as dissolved matters, their interaction, etc. limit this effect. As Fig. 9 shows, increasing temperature decreases the TOC removal efficiency in range of (25–30˚C) and remains almost constant in range of (30–35˚C). It is because viscosity of wastewater decreases and diffusivity increases at elevated temperatures. Therefore, at higher temperatures, oil and grease can more easily permeate through the membrane (according to the Darcy's law) and lead to TOC removal efficiency decreases [2,4]. Therefore, the best-operating temperature is about 25˚C.

3.3. Reverse osmosis process

3.3.1. Effect of TMP

Increasing TMP increases permeation flux, but higher TMP causes the cake/gel layer formed over the membrane surface to compress. To study the effect of TMP on permeation flux and TDS removal efficiency, some experiments were carried out within TMP range of 10–20 bar. Fig. 10 shows that permeation flux increases with increasing TMP.

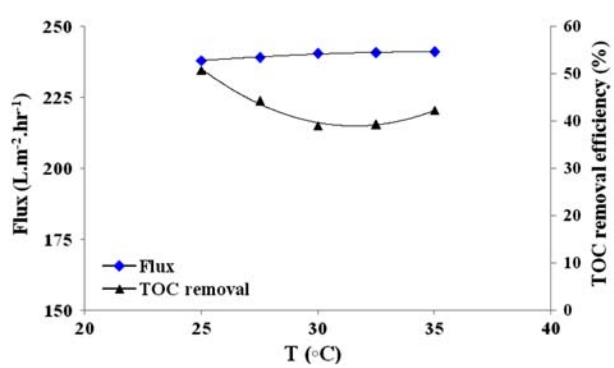

Fig. 9. Effects of temperature on UF permeation flux and TOC removal (TMP: 2 bar, Q: 12 L min^{-1}).

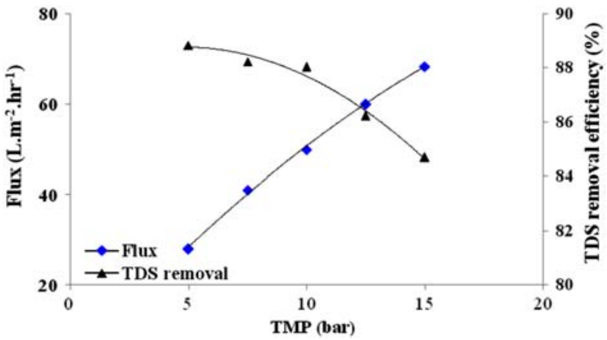

Fig. 10. Effects of TMP on RO permeation flux and TOC removal (Q: 10 L min^{-1}, T: 30°C).

Fig. 10 also shows the effect of TMP on TDS removal efficiency. The results indicate that the TDS removal efficiency decreases slightly with increasing the TMP. This can also be due to the passage of small amount of solute through the membrane at high TMP. As a result, a TMP of 15 bar can be considered as the optimum operating pressure because permeation flux has the highest value and TDS removal efficiency does not change a lot and has an acceptable value.

3.3.2. Effect of flow rate Q

It is well known that increasing Q increases both mass transfer coefficient across the concentration polarization boundary layer and degree of mixing near the membrane surface, thereby reducing both the accumulation of a cake/gel layer on the membrane surface, and the fouled membrane resistance [4,5].

Cake/gel formation usually occurs when particles/oil droplets larger than the average pore size accumulate on the membrane surface, forming a "cake/gel".

Therefore, the accumulated compounds on the membrane surface return to the bulk of feed and concentration polarization effect diminishes. This, thus, causes osmotic pressure to decrease and permeation flux to increase [4–6]. To study the effect of Q on permeation flux and TDS removal efficiency, some experiments were carried out within a Q range of 5–15 L min^{-1}. The results are shown in Fig. 11. The results indicate that permeation flux decreases with increasing Q. Effect of Q on TDS removal efficiency was also investigated. It can be observed with increasing Q, TDS removal efficiency first increases then decreases. Increasing Q which results in increasing shear rate enhances mass transfer coefficient over the membrane surface and this decreases TDS removal efficiency. This is due to increasing diffusion of solutes through the membrane. Considering that higher Q leads to more power consumption for pumping so the choice of very high Q in not economically feasible. Therefore, the optimum Q is 10 L min^{-1}.

3.3.3. Effect of temperature

Temperature has also a serious effect on permeation. Increasing temperature increases permeation flux [6]. To study the effect temperature on permeation flux and rejection, some experiments were carried out within a temperature range of 25–35°C. The results shown in Fig. 12 indicate that permeation flux increases as temperature increases. It is because viscosity decreases and diffusivity increases at elevated temperatures.

Fig. 12 also shows effect of temperature on TDS removal efficiency. According to the results, as observed, increasing temperature decreases TDS removal efficiency. This can also be due to the fact that the viscosity reduction increases permeability of solutes [42]. Based on the results, a temperature of 30°C can be recommended to achieve high permeation flux at low-operational costs and with acceptable TDS removal efficiency.

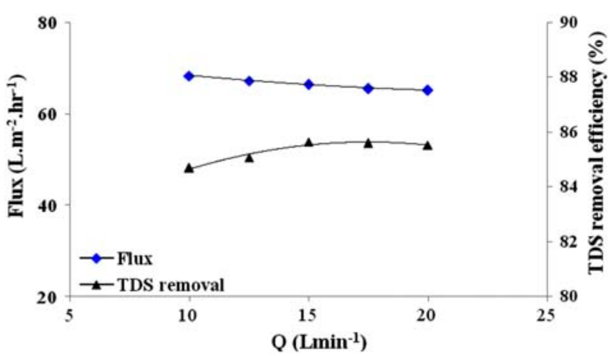

Fig. 11. Effects of Q on RO permeation flux and TDS removal (TMP: 15 bar, T: 30°C).

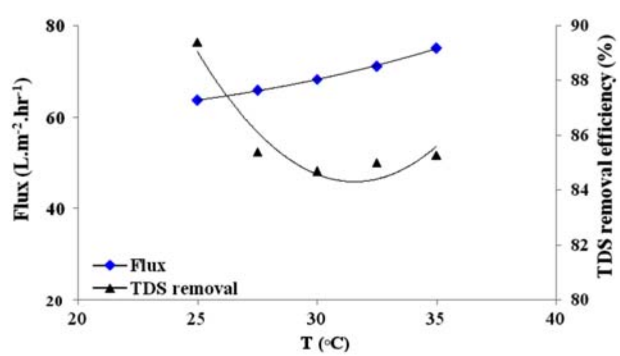

Fig. 12. Effects of temperature on RO permeation flux and TDS removal (TMP: 15 bar, Q: 10 L min^{-1}).

Table 3
Characteristics of the integrated membrane system permeate

Parameter	Unit	Tehran refinery boiler feedwater	Integrated membrane system permeate
Total suspended solids (TSS)	mg/L	0	0
Total dissolved solids (TDS)	mg/L	1265	24
conductivity	μS/cm	3730	37
Total organic carbon (TOC)	mg/L	–	2
Chemical oxygen demand (COD)	mg/L	–	4
Biological oxygen demand (BOD)	mg/L	–	2
Oil and grease (O&G)	mg/L	–	0.1
Turbidity	NTU	–	0.3
Calcium (Ca^{2+})	mg/L	1.4	1
Magnesium (Mg^{2+})	mg/L	0.8	1
Silica (SiO_2)	mg/L	16.5	0.37
Chloride (Cl^-)	mg/L	75	21
Total hardness	mg/L	2.2	2

3.4. Performance of the MF/UF/RO

As can be observed in Table 3, the permeate characterization of the oily wastewater treated by the MF–UF–RO integrated membrane system confirms its very high quality. The results present 100% reduction in TSS, 99.43% reduction in Turbidity, 99.87% reduction in O&G, 97.43% reduction in TOC, and 97.93% reduction in TDS. In ABMA standards, for boiler feedwater, the content of TDS and TSS is 750 and 2 ppm, respectively (Boiler operating pressure <60 bar). As a result, the effluent of the MF–UF–RO integrated membrane system can be recommended as boiler feedwater. The values of the main parameters after treatment can be compared with those of boiler feedwater used in Tehran refinery and ABMA standard, and there is no need for further treatment in order to remove inorganic compounds (suspended solids, total dissolved solids, turbidity, calcium, magnesium, etc.) or organic compounds (O&G content, COD, BOD, and TOC).

4. Conclusion

The results of the present study reveal that the integrated membrane system can be successfully implemented for recovery and reuse of Tehran refinery API wastewater as boiler feedwater. MF and UF operate at low pressures prior to RO and effectively remove suspended solids, turbidity, and O&G. RO operates at a pressure of 15 bar with more than 97% salt rejection. Although it does not reach the standard for one parameter, treated Tehran refinery oily wastewater when compared with Tehran refinery boiler feedwater is almost the best qualified water that can be used as boiler feedwater in Tehran refinery.

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