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Oily wastewater treatment using a hybrid UF/RO system

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ABSTRACT

Oily wastewaters and oil–water emulsions are two of the major pollutants of the environment. Treatment of the oily wastewater using hybrid ultrafiltration/reverse osmosis (UF/RO) system was experimentally studied and the results were presented. Polyacrylonitrile and polyamide membranes were used as the UF and RO membranes, respectively. In this research, Taguchi method was used initially to plan a minimum number of experiments. An L_9 orthogonal array was employed to evaluate effects of temperature (25, 37.5 and 5 °C), TMP (1.5, 3 and 4.5 bar), CFV (0.25, 0.75 and 1.25 m/s) and pH (4, 7 and 10) on permeation flux, rejection and fouling resistance. According to the results, the optimum operating conditions of the UF process were found as following: TMP (3 bar), CFV (1 m/s), operating temperature (40 °C) and pH (9). The results indicated that the treated wastewater has sufficient quality to be introduced to the RO process as a pretreatment feed. Afterwards, the treated outlet water of the hybrid UF/RO system was studied. Analysis of the second step showed 100%, 98%, 98%, 95% and 100% reductions in oil and grease content, TOC, COD, TDS and turbidity, respectively. Comparison of results of this method showed that quality of the finally treated outlet water is high and even better than standard water that are currently introduced to cooling towers.

Keywords: Oily wastewater; Hybrid membrane; Makeup, Cooling water

1. Introduction

Oily wastewaters are one of the major pollutants of the aquatic environment. Large amounts of wastewaters are generated daily by a variety of industrial sources [1,2]. Oily wastewater is produced in oil refining processes. An important fraction of these are oily wastewaters for which current treatment technologies are often costly and ineffective [3–5]. The current trend in industrial wastewater management focuses both on pollution prevention by source trend reduction/clean technology and closed water system, in which wastewater recycling may not be required in all cases, it presents on alternative for industries with high water consumption, when either stringent discharge limits are imposed or limited fresh water resources exist [6].

UF is one of the most effective methods for oily wastewater separation [1,3,5–8] in comparison with the traditional separation methods such as mechanical separation, filtration, and chemical de-emulsification. However, membrane fouling is a main drawback in the practical application of UF in oily wastewater separation [4]. Conventional pretreatment, based on mechanical filtration and chemical dosing systems, can be quite expensive.

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With the development of the new generation of composite RO membranes based on aromatic polyamide polymers, the performance has improved dramatically.

In a typical oily wastewater plant, the various unit operations may include skimming, emulsions breaking, dissolved air flotation, gravity separation, chemical emulsification, etc. Conventional treatment is not sufficient to achieve the water quality requirements need for recycling refinery effluents and that is whey a combination of that least two advanced treatment processes is usually required. Additional unit operations may be used to improve the effluent quality as dictated by the nature of the wastewater and the effluent standard. In recent years, membrane processes such as microfiltration (MF), UF, nanofiltration (NF), and RO are increasingly being applied for treating oily wastewater [1,3,5,7–10].

As mentioned above the oily wastewater contains dissolved solids that can pass through a UF membrane due to their very small particle size, so RO should be applied for total dissolved solids (TDS) removal. One of the factors for selecting RO over other membrane filtration processes such as MF, UF, etc. is that monovalent salt cannot pass through RO membranes. RO can remove salt particles which cannot be removed by MF or UF membranes [11,12].

This paper presents an investigation of the possibilities of using UF as a pretreatment for RO, in a membrane filtration system which can assure the water quality requirements needed for recycling refinery oily wastewater effluent as cooling water make-up. In this system, UF can remove suspended, colloidal materials, bacteria and virus and organic compounds, while RO removes dissolved salts, thus leading to a lower consumption of corrosion inhibitors, anti-scaling agents, biocides and chemical in the cooling tower. In this study, the results from laboratory scale of the oil separation from refinery wastewater using the UF process and further purification of permeate by the RO process.

2. Experimental

2.1. Membrane

In all the experiments, polyacrylonitrile (PAN) and polyamide were used as UF and RO membranes, respectively. Characteristics of the membranes are presented in Tables 1 and 2.

2.2. Feed process

Outlet of the API unit of Tehran refinery was used as the feed. The feed was taken daily and used immediately. Analysis of the feed taken from the wastewater of the API unit is presented in Table 3.

2.3. Experimental method

Fig. 1 shows experimental set-up used in all experiments. UF and RO cell was made of two part pieces of stainless steel (Fig. 2).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 new piece of membrane was employed. During the experiments, exact supervision was done to control CFV, TMP, pH and temperature.

2.4. Experimental design

As previously discussed, many parameters have effects on performance of the UF process. According to previous studies, four parameters were selected [3,10–15]. It is believed that they have the greatest effect on permeate flux, rejection and fouling resistance: feed temperature, TMP, CFV and feed pH. Four factors were adjusted each with three levels (low, medium and high). The matrix experiment was designed by selecting an appropriate OA (L_9 array) [16].

Table 1
Characteristics of the UF membrane

Membrane			Recommended operating limits		
Name	Material	MWCO	pH range	Pressure range (bar)	Temperature range (°C)
PAN	Polyacrylonitrile	20 kDa	1.5–10.5	1–10	0–100

Table 2
Characteristics of the RO membrane

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

Table 3
Characteristics of the wastewater and the treated wastewater (UF and RO) (TMP = 3 bar, CFV = 1 m/s and T = 40 °C)

Parameter	Unit	Feed	Treatment	
			RO	UF
TSS	mg/l		60 Trace	Trace
TDS	mg/l	2028	1424	96
Content of oil and grease	mg/l	78	0.2	0
COD	mg/l	124	41	2
TOC	mg/l	81	17.6	2
Turbidity	NTU	53	0.4	0

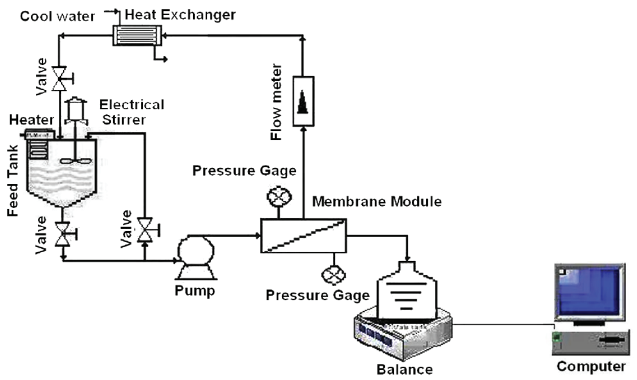

Fig. 1. Schematic of the UF and RO systems.

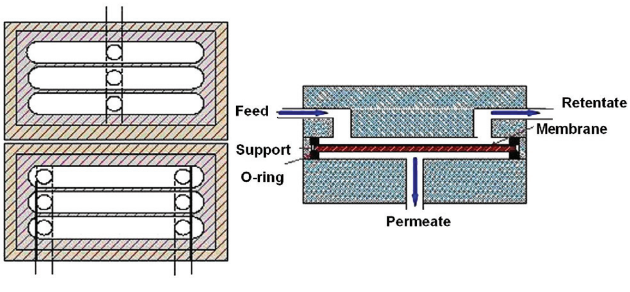

Fig. 2. Schematic view of the UF and RO modules.

The three levels L_9 OA is presented in Table 4. They were used for the optimization process and corresponding permeation flux, rejection and fouling resistance were obtained at the nine candidate conditions for each run.

Four factors with their levels were selected as follows:

- Temperature (T): 25, 37.5 and 50 °C.
- Transmembrane pressure (TMP): 1.5, 3 and 4.5 bar.
- Cross-flow velocity (CFV): 0.25, 0.75 and 1.25 m/s.
- pH: 4, 7 and 10.

Permeation flux and fouling resistance are key factors for UF process evaluation. Flux shows the amount of permeate rate. Fouling resistance shows the significance of cake/gel layer on the membrane surface and its effect on flux decline.

The flux was measured gravimetrically with an electronic balance with weighting the permeation. Fouling resistance (R_f) was calculated as follows:

$$R_f = \left(\frac{\Delta P}{\mu J_{ww}}\right) - \left(\frac{\Delta P}{\mu J_{wi}}\right) \quad (1)$$

where ΔP is the TMP, μ is the solution viscosity, J_{wi} is the initial water flux and J_{ww} is the water flux after fouling.

3. Results and discussion

3.1. UF process

3.1.1. Effects of TMP on permeation flux, fouling resistance and rejection

Effects of TMP on permeation flux, fouling resistance and rejection are presented in Fig. 3. It can be observed that, with increasing TMP up to 3 bar, permeation flux increases linearly, however, at higher TMPs it is nearly constant. This can be due to compression of the cake/gel layer formed on the mem brane surface at high pressures. According to the Darcy's law, increasing TMP increases permeation flux, however, fouling restricts this fundamental law. Increasing TMP makes the sediments more compact on the membrane surface and blocks the membrane pores [3,13,14]. Thus, at an optimum TMP, permeation flux is high, while tendency to cake/gel layer formation is low [14]. As shown in Fig. 3b, until a TMP of 3 bar, fouling resistance increases slightly however, after that it increases severely. This can also be due to low tendency to cake/gel layer formation at TMPs up to 3 bar

Table 4
Experiment condition: Taguchi L_9 design of experiments

Experiment number	T (°C)	TMP (bar)	CFV (m/s)	pH
1	25	1.5	0.25	4
2	25	3	0.75	7
3	25	4.5	1.25	10
4	37.5	1.5	0.75	10
5	37.5	3	1.25	4
6	37.5	4.5	0.25	7
7	50	1.5	1.25	7
8	50	3	0.25	10
9	50	4.5	0.75	4

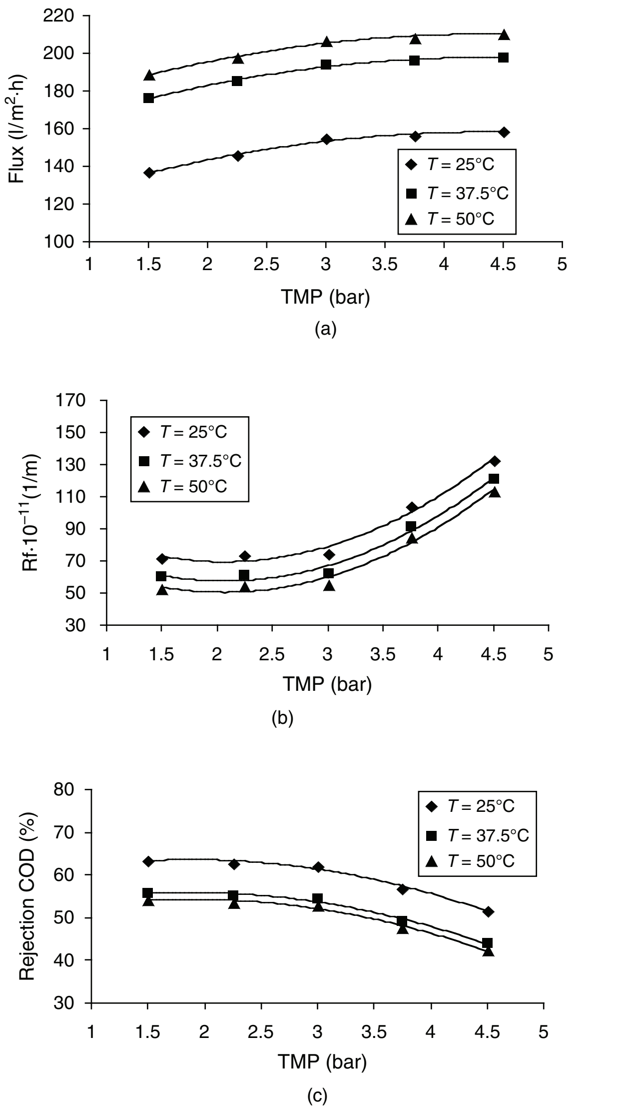

Fig. 3. Effect of TMP on permeation flux (a), and fouling resistance (b) and COD rejection (c); at CFV = 0.75 m/s and pH = 10.

and as a result, the fouling resistance growth is low, however, after that the resistance increases sharply because the cake/gel layer becomes denser. Fig. 3c also presents effect of TMP on COD rejection. The results indicated that the rejection increases slightly with increasing TMP. This can also be due to formation of the thicker cake/gel layer, where this layer traps oil drops among sediment pores and does not let them pass through. Thus, a TMP of 3 bar is the optimum operating pressure.

3.1.2. Effects of CFV on permeation flux, fouling resistance and rejection

Unlike conventional filtration which can be maintenance intensive, costly, and environmentally unfriendly, membrane separation technology employs CFV where captured impurities on the membrane are constantly swept away by the concentrate stream. Thus the membrane surface is continuously cleaned, prolonging the life of the membrane and reducing maintenance costs [12]. Increasing CFV increases mass transfer coefficient in the concentration boundary layer and also increases the extent of mixing over the membrane surface. This can reduce aggregation of the feed components in the gel layer, and as a result, the aggregated materials on the membrane surface diffuse back to the bulk solution, so the concentration polarization effects diminish. This increases the effective pressure difference consequently [14,15,17–19], and thus, permeation flux increases.

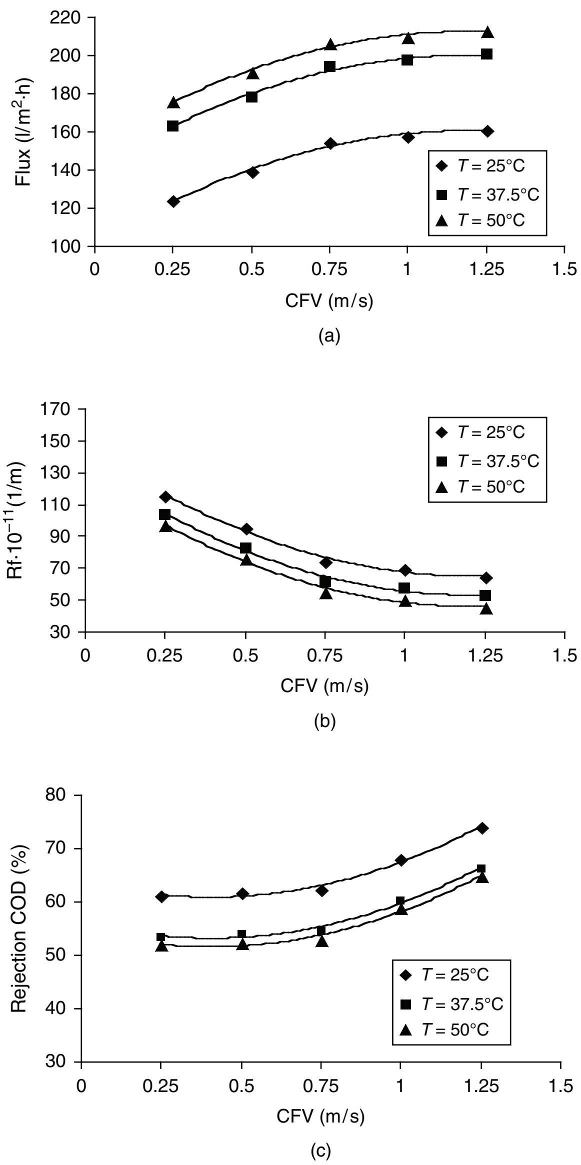

Fig. 4. Effect of CFV on permeation flux (a), fouling resistance (c) and COD rejection (c); at TMP = 3 bar and pH = 10.

In Fig. 4, effects of CFV on permeation flux, fouling resistance and rejection are presented. It can be observed that permeation flux increases sharply until a CFV of 1 m/s and after that it does not change significantly. The influence of two different CFVs on permeation flux was also compared. At low CFV (0.25 m/s), there was a little turbulency so the cake/gel layer could be formed easily. Therefore, maximum fouling was observed and permeation flux reduced consequently. At higher CFVs (up to 1 m/s), more turbulency was made so the aggregated materials on the membrane surface diffused back to the bulk solution and as a result there was no sediment formation. Thus, permeation flux increased. Further increasing CFV more than 1 m/s did not affect fouling resistance and permeation flux (see Fig. 4b). The results indicated that increasing CFV slightly increases the rejection. This can also be due to the fact that increasing turbulency decreases residence time of the components on the membrane surface where there is a challenge between water and oil molecules to pass through the membrane and water molecules have more change to pass through so the rejection increases. Also, less fouling and high hydrophilic nature of the membrane surface increases the rejection (see Fig. 4c). Considering that higher CFVs lead to more power consumption for pumping so the choice of very high CFVs is not economically feasible. Therefore, the optimum CFV is 1 m/s.

3.1.3. Effects of temperature on permeation flux, fouling resistance and rejection

Increasing temperature increases the osmotic pressure slightly [3,8,13], on the other hand, decreases the feed viscosity, and as a result, increases the solvent and the solutes permeabilities (diffusivities) [20–23]. As shown in Fig. 5a, increasing operating temperature increases permeation flux. In other words, temperature has a double effect on permeation flux [15,21–24]. Increasing temperature up to 40 °C increases permeation flux because the viscosity effect is more significant than the osmotic pressure effect, however, further increasing temperature has a negligible effect on permeation flux and it remains almost constant. The osmotic pressure effect enhances and the viscosity effect diminishes at higher temperatures till these two effects are equilibrated finally. As observed in Fig. 5b, increasing temperature decreases the membrane fouling and this is due to increasing the oil solubility. According to the results, increasing temperature decreases the rejection (see Fig. 5c). This can also be due to the viscosity effect. At higher temperatures, oil and grease can more easily permeate through the membranes. The results show that the optimum temperature of 40 °C can be recommended to achieve high permeation flux at low operating costs.

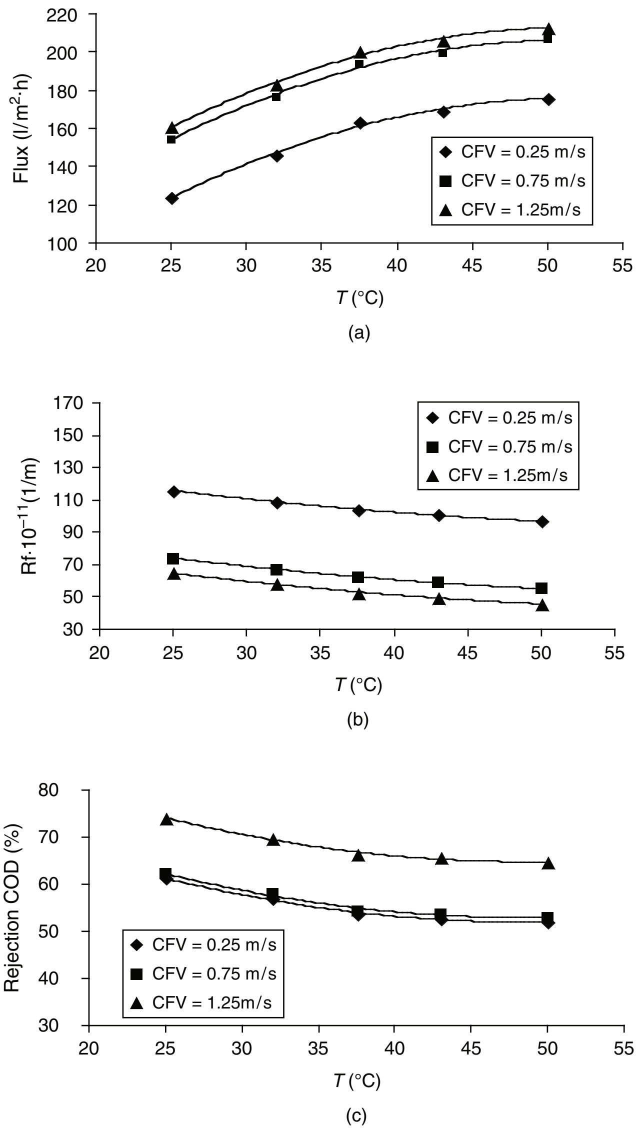

Fig. 5. Effect of CFV on permeation flux (a), fouling resistance (c) and COD rejection (c); at TMP = 3 bar, pH = 10.

3.1.4. Effects of pH on permeation flux, fouling resistance and rejection

Fig. 6 presents effects of pH on permeation flux, fouling resistance and the rejection. As observed, with acidic and basic solutions, permeation flux increases (see Fig. 6b). This means that the feed chemistry is change at higher (to significant extent) and lower pH valves and this causes fouling resistance on the membrane surface to reduce and permeation flux of the membrane to enhance (see Fig. 6b). It can be also observed that the rejection with acidic and basic solutions decreases (see Fig. 6c). This can be due to the fact that acidic and basic solutions can deform oil droplets and facilitate their transfer pass through the membrane. The best pH should be selected

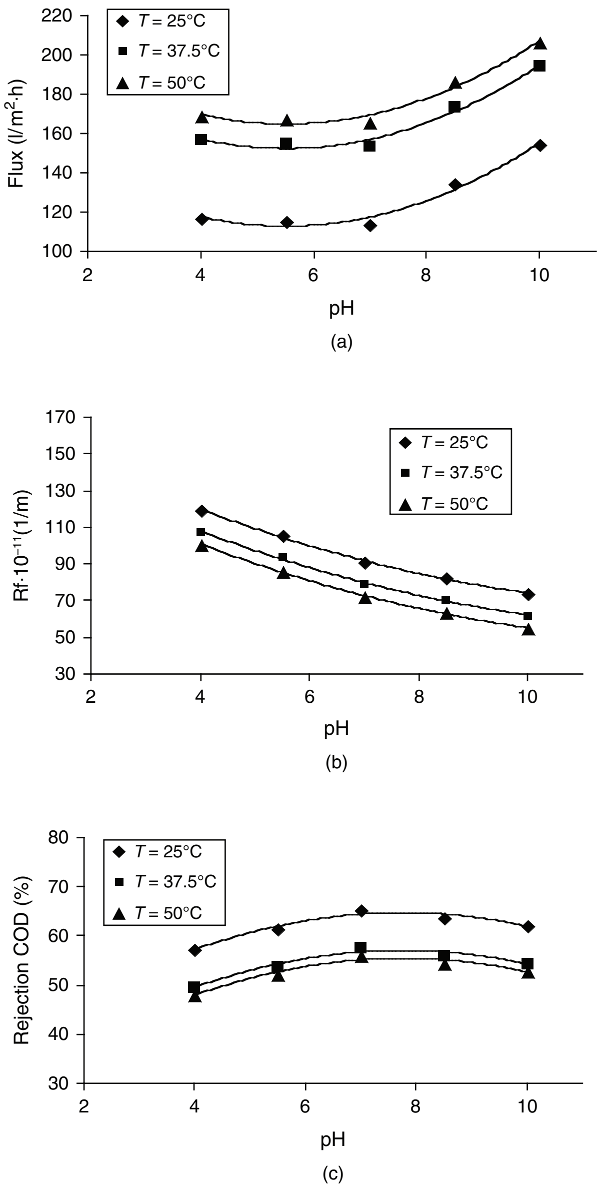

Fig. 6. Effect of pH on permeation flux (a), fouling resistance (b) and COD rejection (c); at TMP = 3 bar and CFV = 0.75 m/s.

according to maximum permeation flux, minimum fouling resistance, suitable rejection and maximum chemical stability. Thus, a pH of 9 can be the optimum value.

3.2. UF process performance

To achieve an optimum design, obtaining the maximum outlet flow 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). The effect of time on permeation flux, porosity and COD rejection is presented in Figs. 7 and 8. The results show that the reduction rate is high in the first 20 min and thereafter decrease gradually with time. To confirm this, corresponding fouling layer porosity is nearly constant with time after initial sharp decline. Because of this porosity reduction, permeation flux decreased progressively (as observed in Fig. 7). In the present case UF was mainly influenced by growing a compressible cake/gel layer (sediments deposition) on the membrane surface. The permeation flux decline rate decreases as time goes on and this due to the fact that the deposition rate is equilibrated with the shear rate induced by cross-flow velocity. COD rejections of the PAN increase a little increased sharply (see Fig. 8). Its can also be attributed to the growing a compressible cake/gel layer on the membrane surface.

The competency of direct UF of the outlet wastewater of direct UF of the outlet wastewater of the API

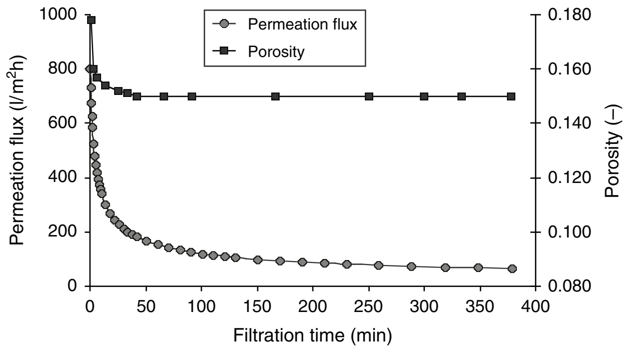

Fig. 7. Effect of time on permeation flux and porosity (TMP = 3 bar, CFV = 1 m/s, T = 40 °C).

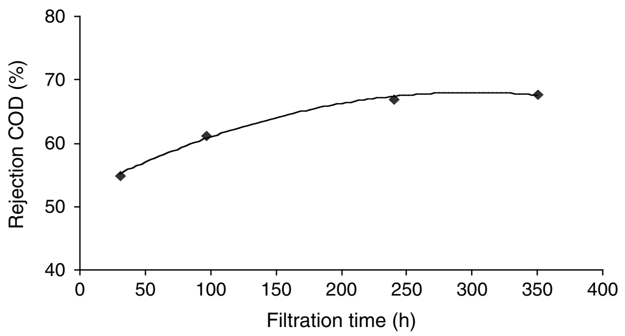

Fig. 8. Effect of time on COD rejection (TMP = 3 bar, CFV = 1 m/s, T = 40 °C).

unit of Tehran refinery can be indicated by the quality of permeate. Table 3 represents characteristics of the outlet wastewater of the API unit of Tehran refinery before and after UF. From the results presents in Table 3, it can be observed that the treatment efficiency is high. In any cases, the quality of permeate appear to be good, as TSS is completely retained (100% removal efficiency), turbidity reduction is greater than 99% and there is also good retention (99%) of oil and grease content. In addition these results COD levels of the effluent were reduced up approximately 65% after UF.

3.3. RO process performance

The effect of time on permeation flux is presented in Fig. 9. The results show that permeation flux is slightly decline with time. The stable permeation flux shows that fouling does not occur in a relatively long time. The completeness of direct of the permeate of the UF process can be indicated by the quality of permeate. Table 3 represents characterization of the permeate of the UF process before and after RO. From the results presented in Table 3, it can be observed that the treatment efficiency is high. This can be attributed to morphology and material of the membrane, resulting in suitable effluent qualities. In any case, the quality of permeate appear to be good, at organic effluent composition, of TDS (93%), COD (95%), and TOC (88%) along with complete rejection of turbidity, oil and grease and TSS were achieved with a reasonably high flux of 50 $l/m^2 h$.

3.4. UF/RO treatment of refinery oily wastewater effluents

UF is a proven technology for the removal oil and grease content, suspended solid and colloids, as well as of bacteria and viruses, thus realizing a good protection for the RO membrane. Organic compounds attached to suspended solids can also be removed by UF. Turbidity, COD and total organic carbon were contained in the study in order to assess the removal efficiencies of suspended solids (expressed as turbidity) and organic content (expressed as TOC and COD). As expected, the removal of suspended solids and colloids by UF was very good, with average removal efficiencies of turbidity of 99%. Organic compounds attached to total suspended solids, have been also removed to certain extent, i.e., 66% expressed as COD removal and 77% as TOC removal. Dissolved organic materials can pass through UF membrane. The quality of the UF membrane is oily wastewater of API unit of Tehran refinery after passing through the UF membrane is suitable to be feed to a RO system in order to remove further dissolved inorganic compounds and to recycle the effluent as cooling water make-up. As can be observed from Tables 3 and 5, where the values of the main parameters that are influenced by UF are compared with the standard for recycling, there is no need for other treatment in order to remove further the suspended solids or the organic compounds.

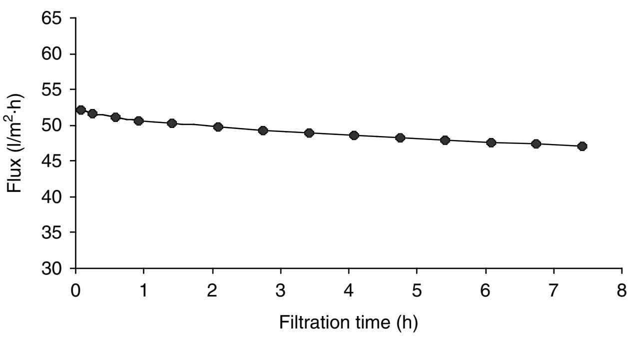

Fig. 9. Effect of time on permeation flux (TMP = 15 bar, CFV = 1.25 m/s, pH= 9, T = 35 °C).

Table 5
Charateristics of the UF/RO and the standard water

Parameter	Unit	Feed	Permeate UF/RO	Standard cooling tower
TSS	mg/l	60	0 (100%)	0
TDS	mg/l	2028	96 (95%)	541.4
Content of oil and grease	mg/l	78	0 (100%)	0
COD	mg/l	124	2 (98%)	100
TOC	mg/l	81	2 (98%)	0
Turbidity	NTU	53	0 (100%)	1

4. Conclusion

An experimental study to treat and reuse oily wastewater generated from the oil distribution and refinery industry was performed. The feasibility of using an UF/RO membrane treatment to reuse oily wastewater was investigated. The results showed that a TMP of 3 bar, a CFV of 1 m/s, a temperature of 40 °C and a pH of 9 are the best operating parameters. The idea application of a hybrid UF/RO system to convert excessive amounts of API wastewater into fresh recyclable water showed to be feasible and technically sound. During the experiments, the UF/RO system ran safely and successfully, without any chemicals required for disinfection, flocculation, enhanced chemical backwash and cleaning. In order to recycle the refinery oily wastewater effluent as cooling water make-up, UF is considered to be good pre-treatment for RO process, which has to remove further dissolved inorganic and organic compounds, in order to achieve the requirement for recycling. Application of RO post-treatment, allows RO permeate back into cooling tower. Rejection of COD is 70% for UF treatment. The rejection of COD after UF/RO treatment increased up to 98% and TDS to 95%. RO treatment will permit reuse of treated water as industrial water (make-up cooling tower).

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