Iran. J. Environ. Health. Sci. Eng., 2010, Vol. 7, No. 5, pp. 413-422

REVERSE OSMOSIS OF REFINERY OILY WASTEWATER EFFLUENTS

[1]A. Salahi,*[1]T. Mohammadi, [2]F. Rekabdar, [3]H. Mahdavi

[1]Research Centre for Membrane Separation Processes (RCMSP), Faculty of Chemical Engineering, Iran University of Science and Technology (IUST), Tehran, Iran
[2]Polymer Science and Technology Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran
[3]School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran

Received 5 March 2010; revised 6 November 2010; accepted 13 November 2010

ABSTRACT
Laboratory-scale reverse osmosis (RO) studies were carried out to determine feasibility of the process for treatment of Tehran refinery oily wastewater. The effects of transmembrane pressure (TMP), cross flow velocity (CFV), temperature and pH on permeation flux and separation performance of the thin film composite (TFC) polyamide (PA, type UTC-70UB) RO membrane were investigated. At original effluent composition, high rejection of TDS (87.0%), COD (95.0%), BOD_5 (95.3%), TOC (90.0%), turbidity (81.8%) and oil and grease content (86.1%) along with complete rejection of color, free oil and TSS were achieved with a reasonably high flux of 50 L/m^2h. Permeation flux was found to improve with increasing TMP, CFV and temperature at constant feed concentration but rejection decreased slightly. The pH effects were found to be complex; by increasing acidic and basic nature of the feed, permeation flux was found to increase and rejection to reduce. The results showed that, RO is very suitable for treating and recycling refinery oily wastewater effluents. Also, fouling of the membrane completely followed Hermia's model (cake filtration mechanism).

Key words: RO; Composite membrane; Oily wastewater; Permeation flux; Rejection

INTRUDUCTION
The current trend in industrial wastewater management focuses both on pollution prevention by source reduction/clean technologies and closed water system, in which wastewater recycling plays a major role. Even if total recycling may not be required in all cases; this presents an alternative for industries with high water consumption, when either stringent discharge limits are imposed or limited fresh water resources exist (Teodosiu *et al.,* 1998).
Quality requirements for cooling water make-up refer to established limits for substances that can promote scaling, corrosion, fouling and biological growth, thus decreasing the performance of cooling towers. Scaling is attributed to the presence of calcium, magnesium carbonates and sulphates, which could 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, mainly due to presence of high levels of suspended is also a problem (Teodosiu *et al.*, 1998).
Previously, oily wastewater effluent from Tehran refinery used to be discharged directly into soil or groundwater. But, due to the emergence of environmental consciousness, the Pollution Control Boards have become stricter and imposed very stringent norms. The scarcity of water also

*Corresponding author: Email: torajmohammadi@iust.ac.ir
Tel:+9821 77 24 04 96, Fax: +9821 77 24 04 95

is another incentive for recovering pure water from effluents.

For the treatment of the effluents 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 (Chian and Dewalle, 1997). 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 (Chian and Dewalle, 1997; Marchese *et al.,* 2000; Madaeni *et al.,* 2001; Izanloo *et al.*, 2006; Naghizadeh *et al.,* 2008; Mohammadi *et al.,* 2005, 2009, 2010).

Conventional treatment is not sufficient to achieve the water quality requirements needed for recycling effluents and that is why a combined of at least two advanced treatment processes is usually required. In order to establish an advanced treatment scheme for oily wastewater refinery effluent, the following aspects ad options have to be considered (Teodosiu *et al.,* 1998):

- The level of suspended solids can be decreased by: coagulation–flocculation, sedimentation/sand filtration, microfiltration and ultrafiltration.
- The level of organic matter in dissolved form can be decreased by active carbon adsorption, chemical oxidation and reverse osmosis (RO); if organic matter is in suspended form, ultrafiltration can also be used.
- The level of dissolved solids can be decreased by applying RO, ion exchange and electrodialysis.
- The possibility of integrating the proposed treatment schemes with existent feasibilities.
- Capital and operating costs.

Membrane separation technology such as RO yields inclement results when applied judiciously in such cases (Rautenbach and Albrecht, 1989; Noble and Stem, 1995). RO has been applied for treating wide variety of industrial effluents (Ragutenble *et al.*, 2000; Lee and Lueptow, 2001).In this study, the performance of an original laboratory scale RO unit for the treatment of sand filtration effluent in Tehran refinery wastewater effluents has been evaluated using thin film composite (TFC) polyamide (PA, type UTC-70UB) membrane. The effects of process variables such as transemembrane pressure (TMP), cross flow velocity (CFV), temperature and pH on membrane performance with permeation flux and respect to present rejection of total dissolved solids (TDS) were extensively studied.

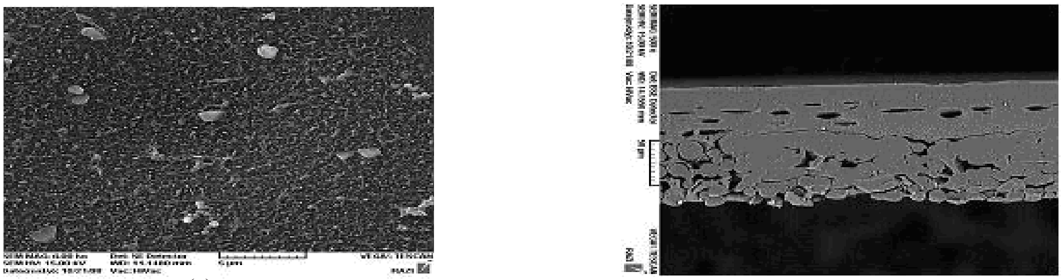
MATERIALS AND METHODS

Membrane

In all experiments, TFC polyamide membrane from Toray membrane of Japan was used as RO membrane. Characteristics of the membranes are presented in Table 1. Fig. 1 shows the structure of the employed membrane.

Table 1: Characteristics of the PA 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



(a) (b)

Fig.1: (a) Surface SEM of the PA membrane and (b) cross sectional SEM of the PA membrane

Feed process

The effluent of sand filter in Tehran Refinery wastewater treatment unit was employed 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. The approximate analysis of the feed is shown in Table 2.

Experimental methods

Fig. 2 shows the experimental set up used in all the experiments. RO cell was made of two part pieces of stainless steel (Fig. 3). These two parts were sealed by O-rings 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.

Table 2: Characteristics of the RO process and the cooling water

Parameter	Unit	Feed	Treatment	
			Permeate RO	Standard cooling tower
Total suspended solids (TSS)	mg/L	4.0	0 (100%)	0
Total dissolved solids (TDS)	mg/L	1953	253 (87.0%)	541.4
Content of oil & grease	mg/L	7.2	1 (86.1%)	-
Chemical oxygen demand (COD)	mg/L	160.0	8 (95.0%)	100
Biological oxygen demand (BOD_5)	mg/L	86.0	4 (95.3%)	15
Total organic carbon (TOC)	mg/L	48.0	4.9 (90.0%)	-
Turbidity	NTU	1.1	0.2 (81.8 %)	1
Color	Pt/Co units	51.0 (yellowish)	Nil (100%)	Nil

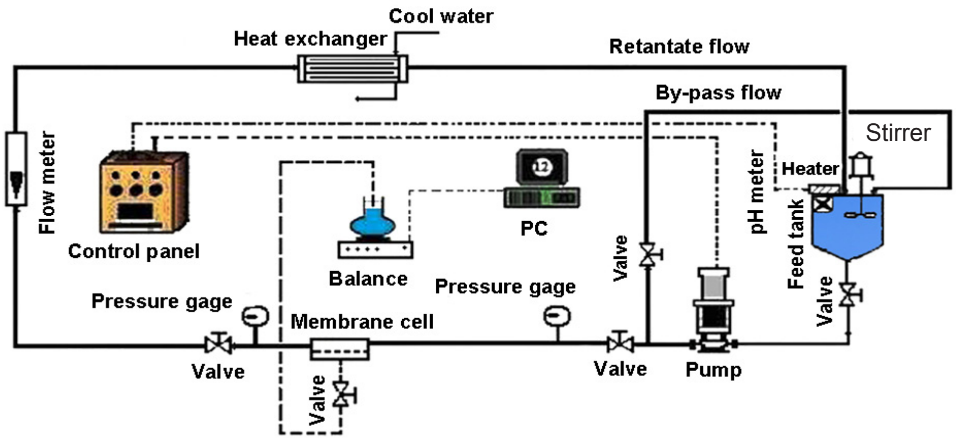


Fig.2: Schematic of the RO system

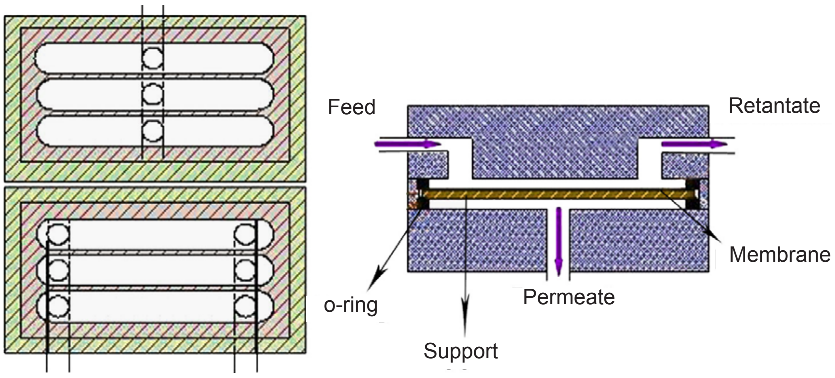


Fig.3: Schematic view of the RO module

Since membranes were not completely homogenous, each piece of membrane was initially evaluated by pure water. During the experiments, exact supervision was done to control CFV, TMP, temperature and pH. 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 RO experiments were the same.

Wastewater analysis methods

Samples for measurements of the feed and the permeate total suspended solids (TSS), BOD_5, COD, oil and grease content, turbidity, total organic carbon (TOC), color (platinum-cobalt procedure) and TDS were taken as necessary and analyzed by the procedures outlined in standard methods (APHA, 2001). TOC and turbidity were estimated using TOC Analyzer (Model DC-190) and Turbidimeter (Model 2100A HACH), respectively.

Percent rejection and permeation flux

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

$$R\,(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (1)$$

Where: C_p represent concentration of each particular component in the permeate and C_f is the related feed concentration.

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

$$J = \left(\frac{V}{At}\right) \quad (2)$$

Experimental design

As previously discussed, many parameters have effects on performance of the RO process. According to previous studies, four parameters were selected (Karakulski *et al.,* 1995; Abdessemed *et al.*, 1999; Tomaszewska *et al.*, 2005; Mohammadi *et al.,* 2009 and 2010). It is believed that they have the greatest effect on permeation flux: temperature, TMP, CFV and pH.

The levels of the four factors were as follows:

- Temperature (T): 27.5, 37.5 and 50 °C
- Transmembrane pressure: 8, 15 and 20 bar
- cross flow velocity: 0.5, 1 and 1.5 m/s
- pH: 4, 7 and 10

Four factors were adjusted each with three levels (low, medium and high). The matrix experiment was designed by selecting an appropriate orthogonal array (L_9 array) for control parameters (Fillho *et al.,* 1999) (Table 3).

The three levels L_9 orthogonal table 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 conditions for each run. So with spending less time and cost, acceptable results following can be derived.

Table 3: Experiment conditions: Taguchi L_9 design of experiments

Experiment number	T (°C)	TMP (bar)	CFV (m/s)	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

RESULTS

Effects of operational conditions on permeation flux and rejection

Effect of TMP

Increasing TMP increased permeation flux, but higher TMPs caused the cake layer formed on membrane surface to compress. This accelerates membrane fouling (Mohammadi *et al.*, 2005, 2009, 2010). 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 where carried out within TMP range of 8–20 bar. The results shown in Fig. 4a show that permeation flux is linearly increased as TMP increases. The permeation flux for oily wastewater effluent feed increased almost linearly from 15-30 (L/m^{2}h) at 8 bar to 70-90 (L/m^{2}h) at 20 bar. According to Darcy's Law, as TMP increases, while other operating parameters remain constant, permeation flux increases.

Fig. 4b shows the effect of TMP on TDS rejection. The results indicate that the rejection was decreased slightly with increased the TMP. This can also be due to the passage of small amount of solute through the membrane at high TMP.

Effect of CFV

It is well know that increasing CFV increased both the mass transfer coefficient across the concentration polarization boundary layer and the degree of mixing near the membrane surface, there by reducing both the accumulation of a gel layer on the membrane surface, and the fouled membrane

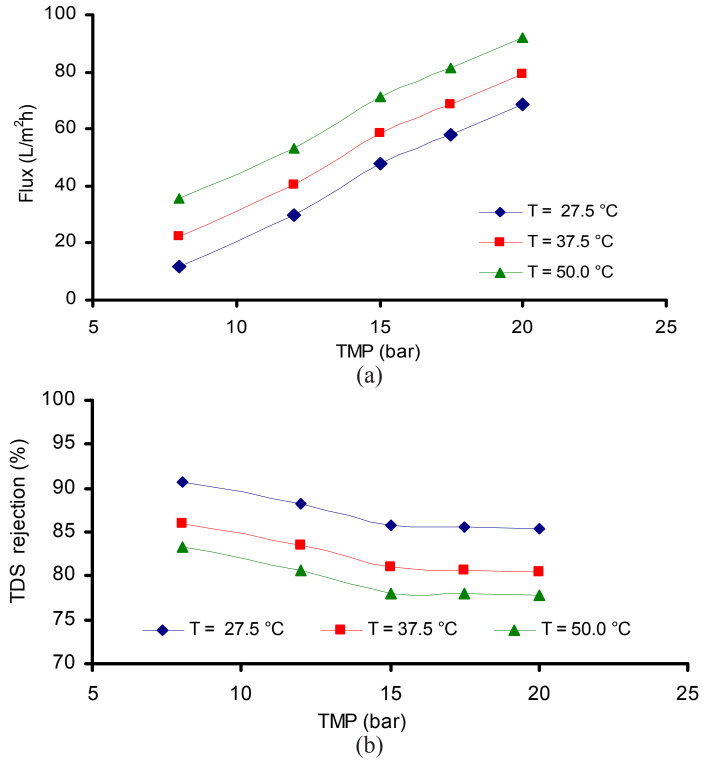


Fig. 4: Effect of TMP on permeation flux (a) and TDS rejection (b)

resistance (Madaeni *et al.*, 2001; Marchese *et al.,* 2000). Therefore, the accumulated compounds on membrane surface return into the bulk of fluid and concentration polarization effect diminishes. This, thus, causes osmotic pressure to decrease and permeation flux to increase (Mohammadi *et al.*, 2005, 2009, 2010).

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. The results are shown in Fig. 5. In Fig. 5a, effects of CFV on permeation flux is presented. The results indicate that the permeation flux was increased with increasing the CFV. Effects of CFV on rejection TDS were also investigated, as shown in Fig. 5b. As can be observed rejection decreases with increasing CFV. Increasing CFV which results in increasing shear rate enhances mass transfer of the membrane surface and this decreases the rejection. This is due to increasing diffusivity solute from the membrane.

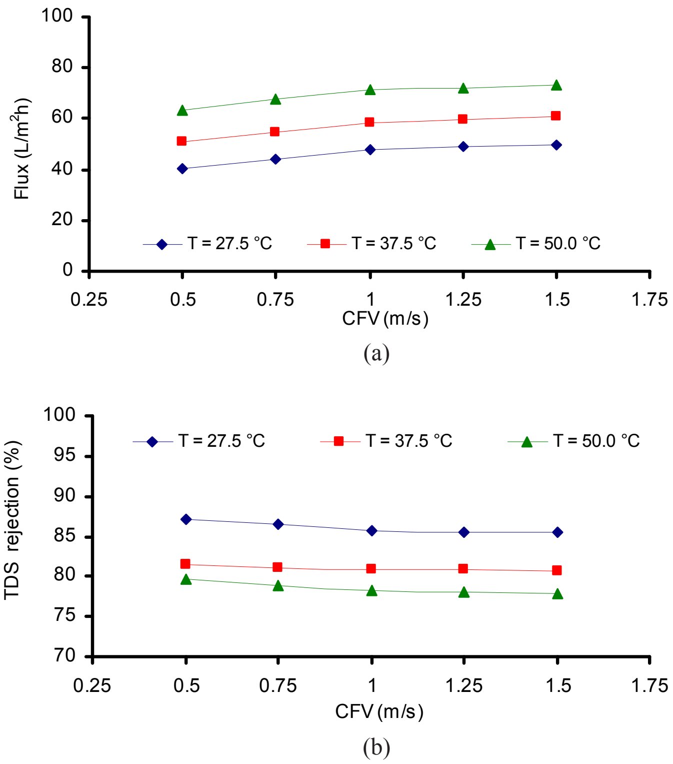


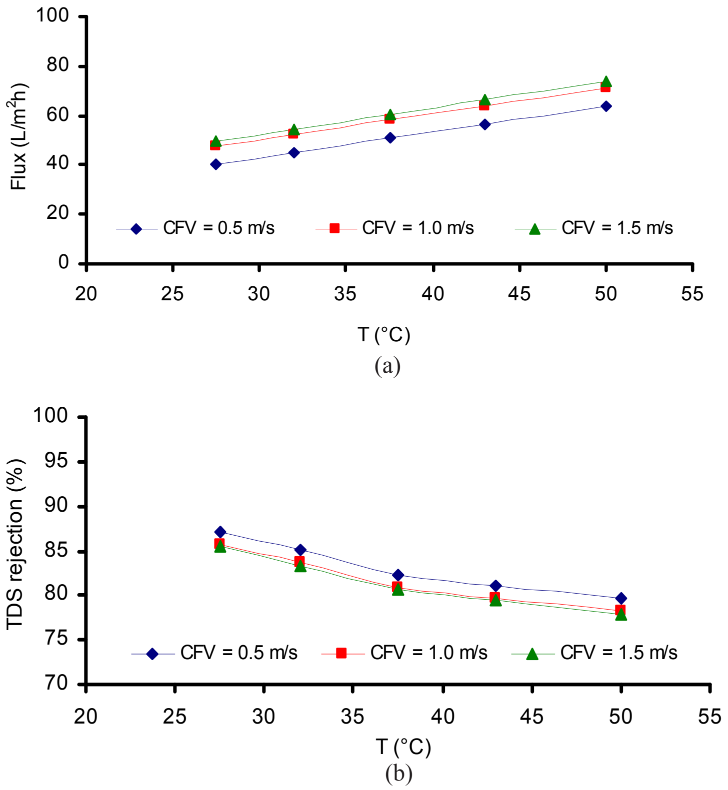
Fig.5: Effect of CFV on permeation flux (a) and TDS rejection (b)

Considering that higher CFVs leads to more power consumption for pumping so the choice of very high CFVs in not economically feasible. Therefore, the optimum CFV is 1.25 m/s.

Effect of temperature

Temperature has also a serious effect on permeation flux and this can be represented by Arenius equation (Mohammadi *et al.*, 2005, 2009, 2010). Also, according to Darcy's Law, increasing temperature increases permeation flux. To study the effect temperature on permeation flux and rejection, some experiments were carried out within a CFV range of 25–50 ^{o}C. The results shown in Fig. 6a show that permeation flux is almost linearly increased as temperature increases. It is because viscosity decreases and diffusivity increases at elevated temperatures.

In Fig. 6b the effect of temperature on TDS rejection is shown. According to these results, increasing temperature decreased the rejection. This can also be due to that viscosity reduction that increased solutes permeability.



(a)

(b)

Fig.6: Effect of temperature on permeation flux (a) and TDS rejection (b)

Effect of pH

To study the effect pH on permeation flux and rejection, some experiments were carried out within a pH range of 4 -10. In Fig. 7a, effects of pH on permeation flux is presented. As observed, with acidic and basic solutions, permeation flux increases. The results show that the minimum values of permeation flux are at a pH value of about 7. It can be said that the net electrostatic forces between solutes and membrane surface are attractive. Also, In Fig. 7b the effects of pH on rejection are presented. It can be observed that rejection with acidic and basic solutions decreases. The result showed that the TDS rejection of RO process is almost stable and their characteristics change within a tolerance of 3%. While the, permeation flux is major specification of RO membrane. Thus, it is the recommended to adjust the feed pH to acidic (less 5) or basic (greater 8).

RO membrane performance

The effect of time on permeation flux under the same operational conditions is presented in Fig. 8. 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 completely of direct of the outlet wastewater of the sand filtration unit of Tehran refinery can be indicated by the quality of permeate. Table 2 represents characterizations of the outlet wastewater of the sand filtration unit of Tehran refinery before and after RO. From the results presented in Table 2, it can be observed that the treatment efficiency of RO is high. This can be attributed to the PA membrane material, resulting in a very high quality. Analysis of the permeate revealed very high rejection for TDS (87.0%), COD (95.0%), BOD_5 (95.3%), TOC (90.0%), turbidity (81.8%) and oil and grease content (86.1%) along with complete rejection of color, free oil and TSS with a reasonably high flux of 50 $L/m^2.h$.

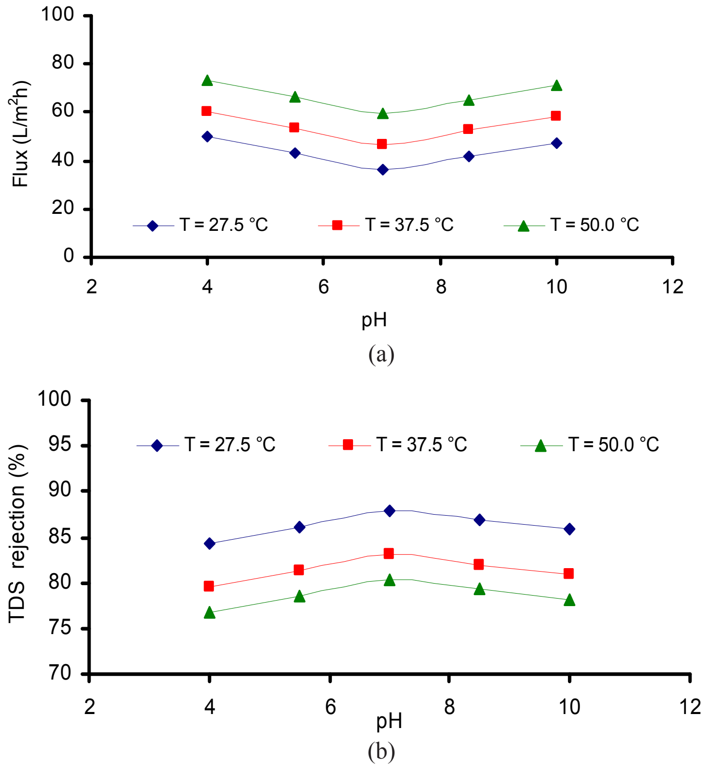


Fig.7: Effect of pH on permeation flux (a) and TDS rejection (b)

Prediction of permeation flux by the Hermia's models (Hermia's, 1982)

In this section, Hermia's models were used to interpret the fouling phenomenon occurring in RO of Tehran refinery oily wastewaters. The fitting of the experimental data to these models permits to distinguish weather permeate 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 PA membrane completely follows the cake layer formation model. Fig. 9 shows

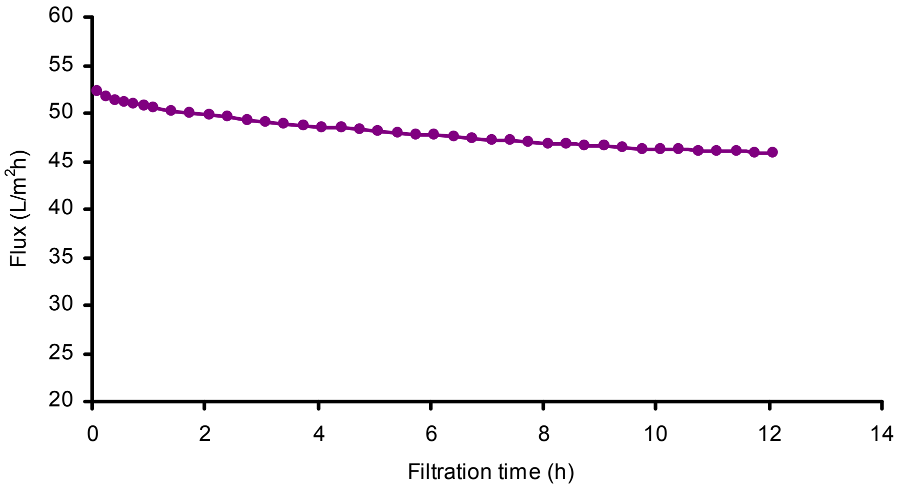


Fig 8: Effect of time on permeation flux for PA membrane for RO process (TMP=15 bar, CFV=1.25 m/s, T=40 °C)

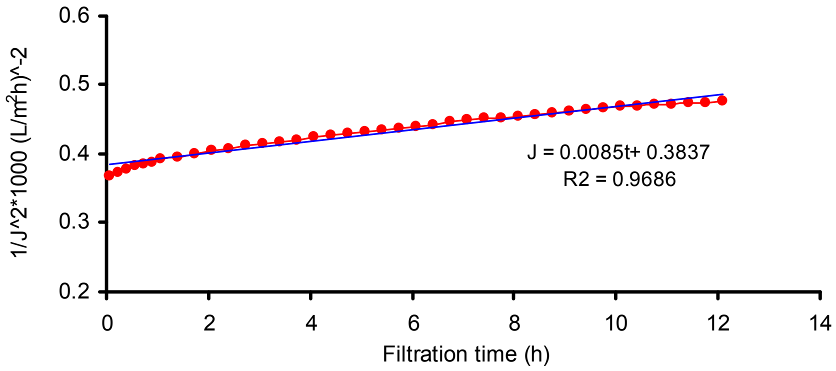


Fig 9: Permeate flux predicted by the cake formation model for RO process (lines: predicted data; symbols: experimental results)

agreement of the experimental data with this 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).

Evaluation of removal efficiencies

As can be observed in Table 2, the permeate characterization of the RO membrane shows that it has very high quality, and as a result, it is suitable to be recycled as cooling water make–up. Also, the values of the main parameters after treatment by RO can be compared with the standard values for recycling, and as observed, there is no need for further treatment in order to remove inorganic compounds (suspended solids, total dissolved solids, turbidity, calcium, magnesium, …) or organic compounds (oil and grease content, COD, BOD_5 and TOC).

DISCUSSION

During the last few years there has been a continuous and important growth in water consumption and consequently a strong increase of the domestic and industrial wastewater potential sources of environmental problems. Reclamation of wastewater in thus becoming a major goal in several countries where is water scarcity. Such a process might be very useful for solving the problems of increasing wastewater flow rates extending the capacity of the existing treatment plant. RO has been found to be a very promising separation process for treatment of refinery oily wastewater effluents and water recovery due to the high fluxes obtained along side significant rejection of TDS, COD, BOD_5 and color.

The obtained results show a very good efficiency of the process combining a sand filtration and an RO membrane for removing TSS, turbidity, BOD5, COD from oily wastewater. The pollutant levels in permeate were an acceptable under standard for recycling. As mentioned, characteristics of the permeate of the RO process the related standards and there is no need for further treatment in order to remove suspended solids or organic compounds.

The removal efficiency of organic and inorganic was very good: (1) law values of COD (8 ppm), BOD_5 (4 ppm) and absence of indicators of fecal contamination is the main characteristics of the treated water: (2) it can be concluded from these that the RO process is efficient and that a thin film composite (TFC) is a good choice.

ACKNOWLEDGEMENTS

This work was supported by Research Institute of Petroleum Industry (RIPI) of Iran. The authors also appreciate the cooperation of Polymer Science and Technology Division of RIPI, Industrial and Environmental Protection Division of RIPI and Tehran Oil Refining Company. In addition, authors wish to thank Mr. Nikbakht and Mrs. Joda (Research and Development Division of Tehran Oil Refining Company), and Mr. Gheshlaghi (Membrane Research Center of Razi University) for their

assistance during experiments.

REFERENCES

Abdessemed, D., Nazzel, G., Ben Aim, R., (1999). Treatment of wastewater by ultrafiltration, Desalination., **126**: 1–5.

APHA, Standard methods for the examination of water and wastewater (2001). 20th ed. American Public Health Association (APHA), Washington, DC.

Chian, E.S.K.,and Dewalle, F.B., (1997). Treatment of high strength acidic wastewater with completely mixed anaerobic filter, Water Res. **11:** 295-304.

Fillho, A.P., Giacomo, B.D., Zirondi, R.B., (1999). Application of Taguchi Design of experiments techniques to estimate coordinate measuring machine uncertainty, 15th Brazilin congress of mechanical engineering.

Hermia, J. (1982) Constant pressure blocking filtration laws-application to power law Non-Newtonian fluids. Trans. Inst. Chem. Eng., **60**: 183–187.

Izanloo, H., Mesdaghinia, A.R., Nabizadeh, R., Nasseri, S., (2006). Effect of organic loading on the performance of aerated submerged fixed-film reactor (asffr) for crude oil-containing wastewater treatment, Iran. J. Environ. Health. Sci. Eng., **3**(2): 85-90.

Karakulski, K., Koztowski, A., Morawski, A. W., (1995). Purification of oily wastewater by ultrafiltration, Sep. Technol., **5**: 197–205.

Lee, S., and Lueptow, R.M., (2001). Reverse osmosis filtration for space conditions wastewater: membrane properties and operating conditions, J. Membr. Sci., **182**: 77-90.

Madaeni, S.S., (2001). The Effect of Large Particles on Microfiltration of Small Particales, J. Porous Mater., **18**: 143-148.

Marchese ,J., Ocheoa, N.A., Pagliero, C., Almandoz, C., 2000. Pilot-Scale Ultrafiltration of an Emulisified Oil Wastewater, Sci. Technol. **34**: 2990-2996.

Mohammadi, T., and Esmaeelifar, A., (2005). Wastewater of a vegetable oil factory by a hybrid ultrafiltration-activated carbon process, J. Membr. Sci., **254**: 129 – 137.

Mohammadi, T., Abbasi, M., Salahi, A., Mirfendereski, M., Pak, A., (2010). Dimensional analysis of permeation flux for microfiltration of oily wastewaters using mullite ceramic membranes, Desalination **252**: 113–119.

Mohammadi, T., Salahi, A., Rahmatpour, A., Rekabdar, F., (2009). Oily wastewater treatment using ultrafiltration, Desalin. Water Treat. **6**: 289–298.

Mohammadi, T., Salahi, A., Abbasi, M., (2010). Permeate flux decline during UF of oily wastewater: Experimental and modeling, Desalination **251**: 153–160.

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

Naghizadeh, A., Mahvi, A.H., Vaezi, F. Naddafi, K., (2008). Evaluation of hollow fiber membrane bioreactor efficiency for municipal wastewater treatment, Iran. J. Environ. Health. Sci. Eng., **5**(4): 257-268.

Noble, R.D., Stem, S.A, (1995). Membrane Separation Technology: Participle and Application, Elsevier, Amsterdam,

Teodosiu, C.C., Kennedy, M.D., Vanstraten, H.A., (1998). Evaluation of secondary refinery effluent treatment using ultragiltration membranes, PII: S00**43** –1354: 00433 – 3.

Ragutenble, R., Linn, T., Eilers, L., (2000). Treatment of severely pressure reverse osmosis and nanofiltration potential and limits of the process, J. Membr. Sci., **174**: 231 –241.

Rautenbach, R., Albrecht, R, Membrane Processes, (1989). John *Wiley* & Sons Ltd., cheichester,

Tomaszewska, M., Orecki, A., Karakulski, K., (2005). Treatment of bilge water using a combination of ultrafiltration and reverse osmosis, Desalination **185**: 203–212.