Reuse of Refinery Treated Wastewater in Cooling Towers

Nikazar, Manouchehr[*+]***; Jamshidi, Mishana***
Faculty of Chemical Engineering, Amirkabir University of Technology, Tehran, I.R. IRAN

ABSTRACT: *In this report, experimental investigation of waste water treatment by reverse osmosis to enable its reuse in cooling tower is presented. A polyamide spiral wound RO membrane followed by three filters as RO pretreatment (two activated carbon and one cartridge filter) and samples of Tehran refinery treated waste water have been used. The effect of operating conditions such as pressure difference, temperature and feed concentration on permeation flux, permeate concentration and fouling have been studied. The results show that continuous operation with a pressure difference of 6 bar and a temperature of 30 °C are the best operating conditions. Analysis of the water treated by RO represents 95 %, 100 %, 93 % and 97 % reduction in TDS, TH, Cl^- and SiO_2, respectively. Comparison between the treated wastewater analysis and city water used in cooling tower as make up water shows the suitability of reverse osmosis method for the above mentioned purpose.*

KEY WORDS: *Reverse osmosis, Wastewater, Fouling.*

INTRODUCTION

The current trend in industrial wastewater management focuses both on pollution prevention by source reduction (clean technologies) and closed water systems, in which wastewater recycling plays a major role. Even if total recycling may not be required in all cases, it represents an alternative for industries with high-water consumption, when either stringent discharge limits are imposed or limited fresh water resources exist.

Recycling of refinery effluent for cooling water systems is one of the options that can be cost-effective in meeting or supplementing the plant water requirements. An analysis of the possibility of recycling industrial effluents as make-up for cooling towers has to consider a multitude of factors such as effluent quality and quantity, make-up water quality, requirement, evaluation or different treatment schemes and cost analysis.

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 is mainly due to presence of high levels of suspended solids, but organic fouling via adsorption of dissolved organic compounds is also problem [1]. The treatment process of Tehran refinery wastewater is shown in Fig. 1.

According to data given in table 1 there is no

* *To whom correspondence should be addressed.*
+ *E-mail:nikazar@aut.ac.ir*
1021-9986/08/4/1 7/$/2.70

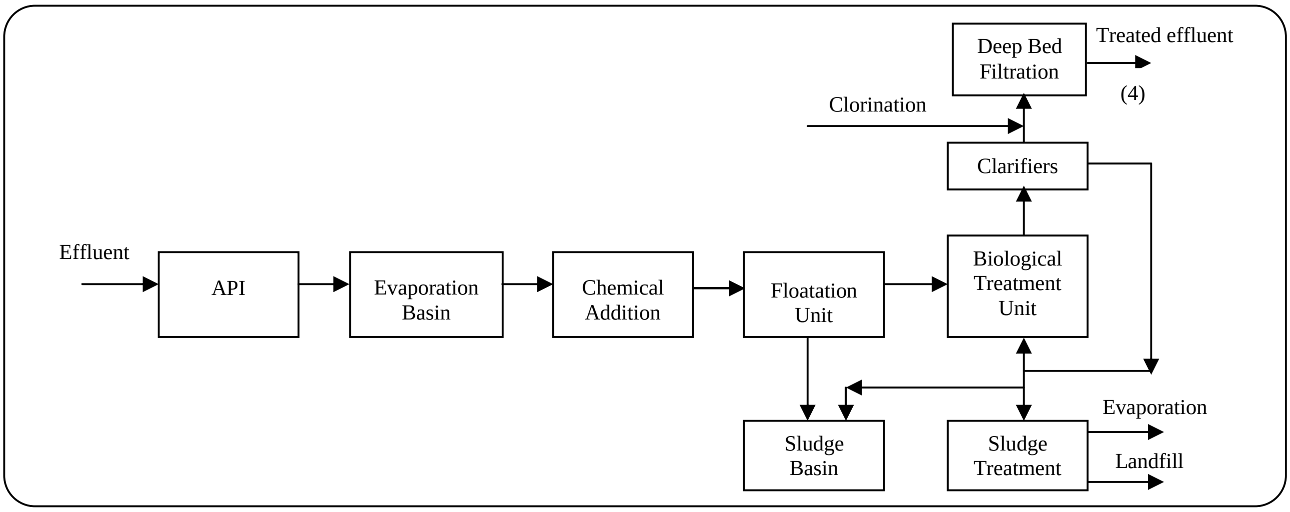

Fig. 1: Diagram of Tehran refinery wastewater treatment plant.

Table 1: Analysis of Tehran refinery wastewater treatment plant (numbers refer to stages of waste treatment illustrated in Fig. 1).

	1	2	3	4
pH	7.5-8.5	7.5-8.5	7.5-8.5	7
Free Oil (ppm)	76	10	-	-
BOD (ppm)	300	245	15	0
COD (ppm)	700	300	100	0
SS (ppm)	-	-	6000	0
TH (ppm)	450	450	450	450
Cl^- (ppm)	600	600	600	600
SiO_2 (ppm)	30	30	30	30
TDS (ppm)	1800	1800	1800	1800

changes in TDS but there are changes in BOD, COD and TSS as a result of the treatment process.

There are many methods to reduce TDS such as electrodialysis, ion exchange, distillation and reverse osmosis. Taking into condition factors such as feed quality, the treated wastewater quality and costs, reverse osmosis was selected for this study [2].

THEORETICAL BACKGROUND OF REVERSE OSMOSIS

Reverse osmosis is the finest level of filtration available. The RO membrane acts as a barrier to all dissolved salts and inorganic molecules, as well as organic molecules with a molecular weight greater than approximately 100. Water molecules, on the other hand, pass freely through the membrane creating a purified product stream. Rejection of dissolved salts is typically 95 % to greater than 99 %. The applications for RO are numerous and varied, and include desalination of seawater or brackish water for drinking purposes, wastewater recovery, food and beverage processing, biomedical separations, purification of home drinking water and industrial process water. Also, RO is often used in the production of ultra pure water for use in the semiconductor industry, power industry (boiler feed water), and medical/laboratory applications [3].

The main parameters in reverse osmosis are as follows [4]:

$$Posm = 1.19\,(T + 273) \times \Sigma\,(mi) \qquad (1)$$

Posm : osmotic pressure (psi)

T: temperature (°C)

Sum (mi) : sum of molar concentration of all solution ions

$$J_w = A \times (NDP) \qquad (2)$$

J_w: flux of water passes through membra

A: water transport coefficient f (T)

NDP: Net Driving Pressure = ΔP-Δ Posm

$$\Delta P\text{: transmembrane pressure} = \frac{P_{feed} + P_{reject}}{۲} - P_{permeate}$$

$$J_S = B \times (C_m - C_p) \qquad (3)$$

J_S: flux of salt passes through membrane

C_m- C_p : driving force for the mass transfer of salts

B: salt transport parameter coefficient f(T)

$$C_p = \frac{Q_S}{Q_W}$$

Q_S: flow rate of salt through the membrane (independent of pressure)
Q_W: flow rate of water through the membrane (dependent of pressure)
C_P: salinity of permeate

Concentration polarization [4]

As water flows through the membrane and salts are rejected by the membrane, a boundary layer is formed near the membrane surface in which the salt concentration exceeds the salt concentration in the bulk solution. This increase of salt concentration is called concentration polarization. The effect of concentration polarization is to reduce actual product water flow rate and salt rejection versus theoretical estimates. The Concentration Polarization Factor (CPF) or Beta can be defined as a ratio of salt concentration at the membrane surface (C_s) to bulk concentration (C_b):

$$CPF = C_s / C_b \qquad (4)$$

Pretreatment [3,5]

The feed water, depending on its source, may contain various concentrations of suspended solids and dissolved matter. Suspended solids may consist of inorganic particles, colloids and biological debris such as microorganisms and algae. Dissolved matter may consist of highly soluble salts, such as chlorides, and sparingly soluble salts, such as carbonates, sulfates, and silica. During the RO process, the volume of feed water decreases, and the concentration of suspended particles and dissolved ions increases. Suspended particles may settle on the membrane surface, thus blocking feed channels and increasing friction losses (pressure drop) across the system. Sparingly soluble salts may precipitate from the concentrate stream, create scale on the membrane surface, and result in lower water permeability through the RO membranes (flux decline). This process of formation of a deposited layer on a membrane surface is called membrane fouling and results in performance decline of the RO system. The objective of the feed water pretreatment process is to improve the quality of the feed water to the level which would result in reliable operation of the RO membranes. Depending on the raw water quality, the pretreatment process may consist of all or some of the following treatment steps:

- Water disinfection with chlorine.
- Clarification with or without flocculation.

.Clarification and hardness reduction using lime treatment.

- Media filtration.
- Reduction of alkalinity by pH adjustment.
- Addition of scale inhibitor.
- Reduction of free chlorine using sodium bisulfite or activated carbon filters.
- Water sterilization using UV radiation.
- Final removal of suspended particles using cartridge filters.

Control of fouling is of utmost importance. Although several techniques are involved, pretreatment of feed, chemical cleaning and optimization of operational conditions such as temperature and transmembrane pressure can be considered to reduce fouling. The most common way to study fouling is to measure permeate flux reduction with time.

Cleaning [3,5]

Over time, membrane systems can become fouled with any of a number of foulants such as colloids, organic matter, metallic scales, and biological constituents. These materials can build up on the membrane surface and in the feed brine channel which can cause a severe loss of performance in the system: pressure requirements increase to maintain flow, pressure drops increase, and salt rejection can suffer. If the system is not cleaned and the system continues to build up foulants, the elements may "telescope" causing the integrity of the membrane surface to be compromised and rendering the membrane irreversibly damaged.

For study the cleaning effect following equation are used :

$$J = \frac{\Delta P}{\mu \sum R} \qquad (5)$$

$$\sum R = R_m + R_f + R_c \qquad (6)$$

$$R_m = \frac{\Delta P}{\mu J_{wi}} \qquad (7)$$

$$R_f = \left(\frac{\Delta P}{\mu J_{ww}} \right) - R_m \qquad (8)$$

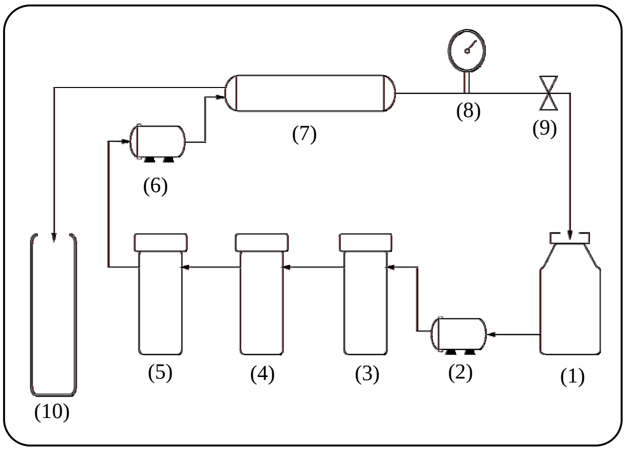

Fig. 2: Schematic diagram of experimental set up.

$$R_c = \left(\frac{\Delta P}{\mu J_{wc}}\right) - R_m \quad (9)$$

$$R_R = \left(\frac{R_f - R_c}{R_c}\right) \times 100 \quad (10)$$

J: flux of water passes through membrane
μ:fluid viscosity
J_{wi}: initial flux of water
J_{ww}: flux of water after fouling
J_{wc}: flux of water after cleaning
R_m: resistance of clean membrane, (L^{-1})
R_f: fouling resistance, (L^{-1})
R_c: resistance of membrane after cleaning, (L^{-1})
$R_{R:}$ cleaning efficiency, (%)

Factors Affecting Reverse Osmosis Performance [3]

Permeate flux and salt rejection are the key performance parameters of a reverse osmosis process. Under specific reference conditions, flux and rejection are intrinsic properties of membrane performance. The flux and rejection of a membrane system are mainly influenced by variable parameters including:

- Pressure
- Temperature
- Feed water salt concentration

In this study, it has been tried to determine the influence of temperature, transmembrane pressure on permeate flux and fouling.

Table 2: Analysis of Samples.

	Sample 1	Sample 2
pH	7.4	6.4
TDS (ppm)	1850	2410
TH (ppm)	452	530
Ca^{2+} (ppm)	348	382
Mg^{2+} (ppm)	104	148
Cl^- (ppm)	612	700
Cl_2 (ppm)	0	0.5
SiO_2 (ppm)	23.1	25

EXPERIMENTAL SET UP

The experimental set up is presented in Fig. 2. It consists of the following main parts:

1- Storage tank
2- Feed pump
3- Sedimentation pre filter
4- Granual activated carbon filter (GAC)
5- Carbon black filter
6- RO feed pump
7- RO membrane
8- Pressure gauge
9- Pressure regulating relief valve
10-Reject storage tank

The membrane used in the research was a polyamide membrane provided by Filmtec(1) Company. It was fitted in a spiral wound module with 0.5 m^2 effective area.

The feed was pumped by means of a diaphragm pump (max. pressure 90 psi) in to the RO module. The trans-membrane pressure was adjusted by throttling the valve 9.

Samples of Tehran refinery treated waste water have been used in these experiments. The analysis of the samples is presented in table 2.

RESULTS AND DISCUSSION

Eeffect of transmembrane pressure

The effect of transmembrane pressure on permeation flux at a temperature of 25 °C and a concentration of 1850 ppm TDS is presented in Fig. 3.

(1) Filmtech RO membrane elements for potable and industries are the most reliable. These elements are NSF/ANSI standard 58 listed. These elements are rated at 50 psi and will purify 20 % more than competitive elements rated at 60 psi.

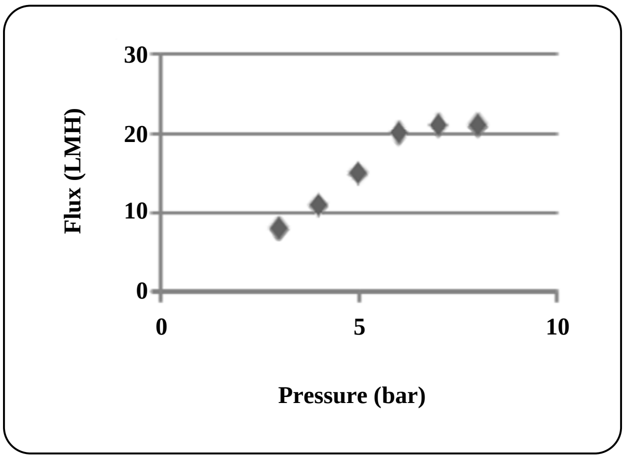

Fig. 3: Effect of transmembrane pressure on permeation flux (sample 1).

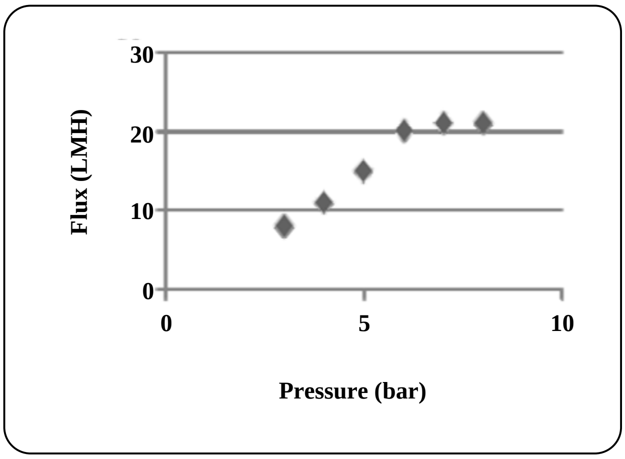

Fig. 4: Effect of Transmembrane pressure on permeate concentration.

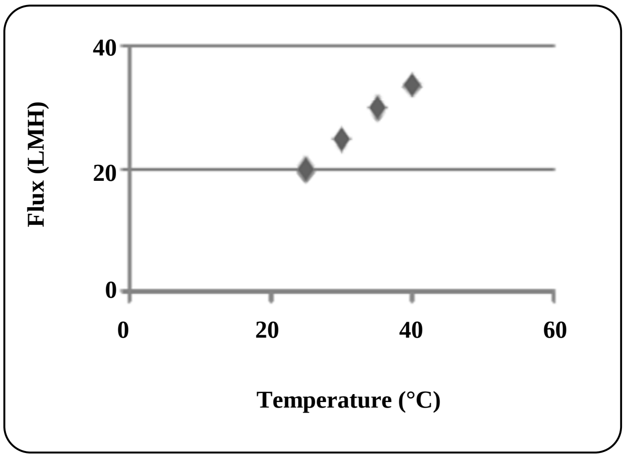

Fig. 5: Effect of temperature on permeation flux (sample 1).

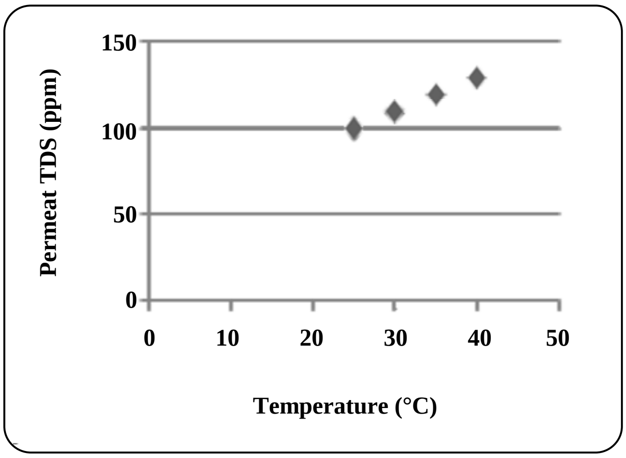

Fig. 6: Effect of temperature on permeate salinity (sample 1).

Flux is calculated as volume of permeat (lit) in area of membrane (m^2) in a period of time (hour) which can be shown as LMH. It can be observed that the permeation flux increases with increasing transmembrane pressure up to pressure of 6 bar. The high transmembrane pressure result in a restrictive (limiting) factor namely concentration polarization.

The effects of transmembrane pressure on permeate concentration at a temperature of 25 °C and a pressure of 6 bar is presented in Fig. 4.

As can be observed permeate concentration decreases with increasing transmembrane pressure.

It can be explained that the reduced pressure decreases permeate flow rate and hence dilution of salts (the salt flows at a constant rate through the membranes as its rate of flow is independent of pressure).

Effect of temperature

As shown in Fig. 5, permeation flux increases with rise in temperature and the corresponding reduction in viscosity. It must be mentioned that all experiments have been carried out at a concentration of 1850 ppm TDS and a pressure of 6 bar. Temperature affects the diffusion rate of water and dissolved ions across membrane. Figs. 6 and 7 show the effect of temperature on permeate concentration and fouling rate, respectively.

Effect of feed concentration

To study the effect of feed concentration, experiments were carried out with another sample. Effect of feed concentration on permeation flux is shown in Fig. 8.

Osmotic pressure of the feed water is directly proportional to feed water salinity. Permeate flux is

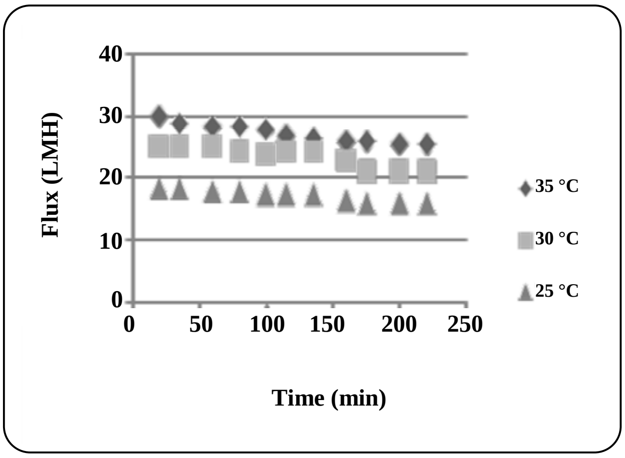

Fig. 7: Effect of temperature on fouling rate (sample 1).

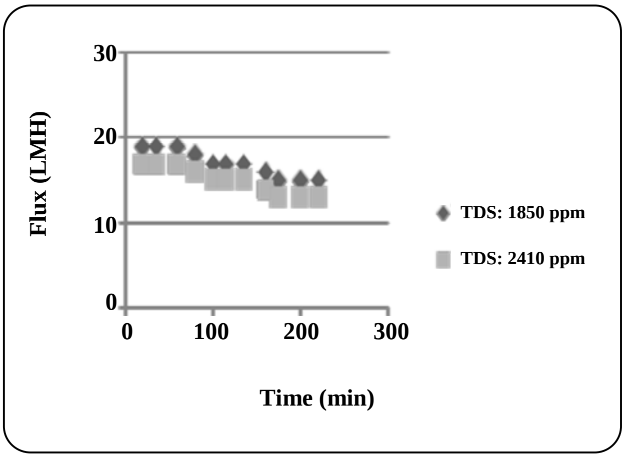

Fig. 9: Effect of feed concentration on fouling rate.

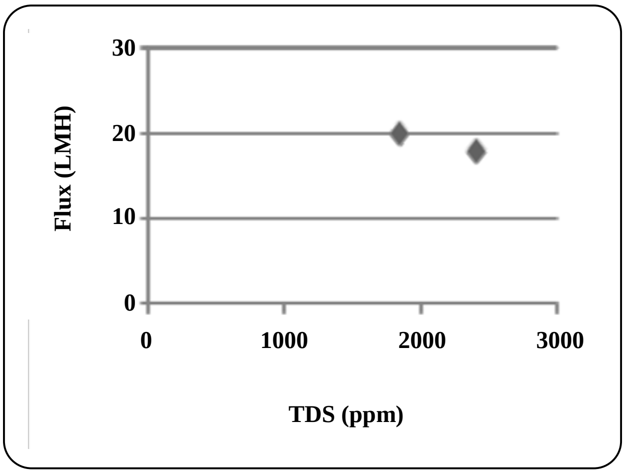

Fig. 8: Effect of concentration on permeation flux.

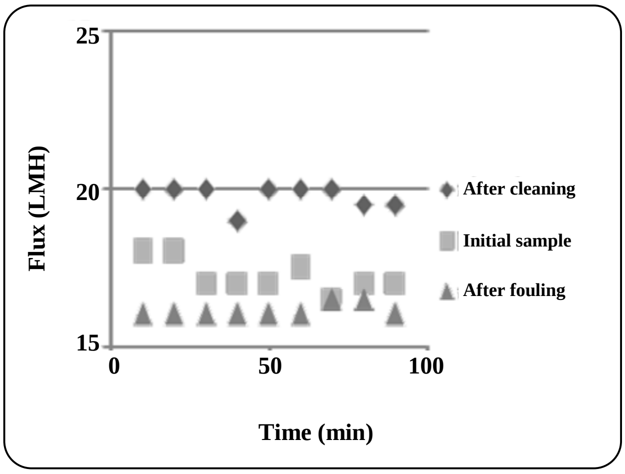

Fig. 10: Effect of cleaning on fouling rate.

proportional to the available net driving pressure (NDP). NDP is the difference between the applied feed pressure and the average osmotic pressure at the membrane surface. Therefore, higher feed salinity will require higher feed pressure to produce a given permeate flow. Permeate salinity is proportional to the average feed salinity at the membrane surface. Therefore, an increase in feed salinity will result in a correspondingly higher permeate salinity.

Fouling studies

Effect of temperature and feed concentration (salinity) on fouling rate are shown in Figs. 8 and 9 respectively.

The effect of cleaning is shown in Fig. 10. The results are as follows:

$R_m = 7.4 \times 10^{13}$ (m^{-1})

$R_f = 1.2 \times 10^{13}$ (m^{-1})

$R_c = 0.7 \times 10^{13}$ (m^{-1})

$R_R = 80$ %

Product analysis

Product analysis and reduction percent for two samples are shown in tables 3 and 4 and the comparison between the product analysis and the raw water that is used in cooling towers is shown in table 5.

CONCLUSIONS

- 95 %, 100 %, 93 % and 97 % reduction in TDS, TH, Cl^- and SiO_2, respectively, show desirability of reverse osmosis method for the mentioned purpose.

- The optimum operating temperature and pressure for our experiments are 30 °C and 6 bar, respectively.

- Cleaning efficiency of 80 % shows the effectiveness of cleaning solution.

Table 3: Analysis of sample1.

Flow	TDS	TH	Cl^-	SiO_2
Sample 1 (ppm)	1850	452	612	23.1
Product 1 (ppm)	95	0	44	0.7
Reduction (%)	95	100	93	97

Table 4: Analysis of sample 2.

Flow	TDS	TH	Cl^-	SiO_2
Sample 2 (ppm)	2410	530	700	25
Product 2 (ppm)	200	17.1	50	0.8
Reduction (%)	92	97	93	97

Table 5: Comparison between products of treatment of sample 1 and 2 and city water.

Flow	TDS	TH	Cl^-	SiO_2
Product 1 (ppm)	95	0	44	0.7
Product 2 (ppm)	200	17.1	50	0.8
City Water	200-400	200-300	80-120	5-20

Acknowledgements

The authors express their thanks to Dr. B. Bonakdarpour for editing the manuscript.

Received : 20th November 2005 ; Accepted : 26th May 2008

REFERENCES

[1] Carmen, C., Teodosiu, M., Evaluation of Secondary Refinery Effluent Treatment Using Ultrafiltration Membrane, *Journal of Water Research*, 33(1999).

[2] Cheran, M., Rajagopalan, N., Membraine Processing of Oily Streams Wastewater Treatment, *J. Membrane Science*, **151**, 13 (1998).

[3] Buhrman, F., Vander, M., Treatment of Industrial Wastewater for Reuse, Elsevier, *Desalination,* **1124**, 263 (1999).

[4] Bodalo, S. J., Gomez, C. L., Spiral Wound Membrane RO and the Treatment of Industrial Effluent, Elsevier, *Desalination*, **160**, 151 (2004).

[5] Moghadam, M. K., Saadabadi, M., Modeling of Membrane Fouling and Flux Decline in Reverse Osmosis During Separation of Oil in Water Emulsion, Elsevier, *Desalination,* **157**, 369 (2003).