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COD removal from industrial wastewater plants using reverse osmosis membrane

S.S. Madaeni* and S. Samieirad

Membrane Research Center, Department of Chemical Engineering, Razi University, Kermanshah, Iran

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Abstract. Treatment and reuse of industrial wastewater is becoming a major goal due to water scarcity. This may be carried out using membrane separation technology in general and reverse osmosis (RO) in particular. In the current study, polyamide (FT-30) membrane was employed for treatment of wastewater obtained from Faraman industrial zone based in Kermanshah (Iran). The effects of operating conditions such as transmembrane pressure, cross flow velocity, temperature and time on water flux and rejection of impurities including COD by the membrane were elucidated. The aim was an improvement in membrane performance. The results indicate that most of the chemical substances are removed from the wastewater. In particular COD removal was increased from 64 to around 100% as temperature increased from 15 to 45°C. The complete COD removal was obtained at transmembrane pressure of 20 bars and cross flow velocity of 1.5 m/s. The treated wastewater may be reused for various applications including makeup water for cooling towers.

Keywords: membrane; reverse osmosis; COD; wastewater; industrial water.

1. Introduction

Membrane processes have been considered a promising technology for wastewater recycling and reuse (Lee *et al*. 2005). Membrane processes offer a number of advantages over conventional wastewater treatment processes including resistance against the fluctuations (shocks) in the feed, higher product quality, lower land requirements and the possibility to use mobile units (Sostar-Turk *et al*. 2005). Moreover membrane technology reduces the energy consumption (Saffaj *et al*. 2004). Membrane processes such as nanofiltration (NF), ultrafiltration (UF) and reverse osmosis (RO) have been applied for treating a wide variety of industrial effluents (Nataraj *et al*. 2006a).

Treatment by reverse osmosis (RO) reduces high levels of dissolved solids but has limitations when used for the removal of organic compounds from effluents of the chemical industry (Bodalo-Santoyo *et al*. 2004). The process has been applied in chemical, textile, petrochemical, electrochemical, food, paper and the treatment of municipal wastewater (Ghabris *et al*. 1989). An appropriate index for showing the amount of organics in water is chemical oxygen demand (COD). This is a test for assessing the quality of effluents and wastewaters prior to discharge. Reverse osmosis may be employed for COD polishing (Madaeni and Mansourpanah 2003). If the treated water is drained into natural water, the COD has to be below 125 mg/L, if it is released into sewer the limit is 800 mg/L (Galambos *et al*. 2004). Reverse osmosis membranes may decrease the COD of the effluent as high

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* Corresponding author, Professor, E-mail: smadaeni@yahoo.com

as 90 to 99% (Cowan *et al.* 1992). The quality of water or wastewater plays an important role in industrial processes and local ecology (Bes-Pia *et al.* 2002). Some special cases including boilers require high quality water due to the higher temperature and pressure conditions (Stephenson *et al.* 2000).

Lynch *et al.* (1984) compared the performances of cellulose acetate with FT30 composite membranes. The FT30 membrane showed greater rejection (>90%) for most organic compounds compared to the cellulose acetate membranes. In another study (Madaeni *et al.* 2004) the rejection of sugar by FT30 membrane was demonstrated as 55%. Siler and Bhattacharyya (1985) studied the concentration of wastewater using FT30 membrane. The raw wastewater had high concentration of organic (aliphatic acid, phenol), inorganic (NH_3, Cl^-) and color. Rejections by the membrane were 60–94% for conductivity, 15-90% for NH_3, and 75% to 88% for TOC (with phenol rejections ranging from 75-94%).

Williams *et al.* (1990) showed that TOC rejections of FT30 membrane were in the range of 80 to 96%. Pusch and Zheng (1989) studied rejections of four composite membranes (HR-95, HR-98, FT30, PEC 1000) and two asymmetric membranes (Solrox SC-200 and SC-1000). The feed contained a variety of organic compounds, including methanol, ethanol, acetonitrile, formamide, benzylalcohol, phenol, benzenaldehyde, benzoic acid, and aniline in single and multi-component system. Rejections ranged from 25 to 99.9% depending on the membrane and solute type. The reverse osmosis FT30 membrane was screened for COD removal from biologically treated wastewater from an alcohol manufacturing plant. The COD in permeate decreased from 30000 ppm to around 10000 ppm (Madaeni and Mansourpanah 2003).

A hybrid nanofiltration and reverse osmosis pilot plant was used to remove the contaminants of the distillery spent wash. Removal of 99.90% of chemical oxygen demand (COD) was achieved (Nataraj *et al.* 2006a). Electrodialysis pilot plant was used for the removal of nitrates and hardness from simulated brackish water to produce good quality drinking water (Nataraj *et al.* 2006b).

The membrane-based electrodialysis is capable to produce good quality drinking water from wastes contained chromium ions (Nataraj *et al.* 2007a). The pilot plant of a hybrid microfiltration and electrodialysis system was employed to remove contaminants from industrial wastewater with the recovery of more than 90% (Nataraj *et al.* 2007b).

Charge density and pore size are important parameters in predicting the separation effects in NF membranes using neutral and charged solutes (Hussain *et al.* 2008).

The aim of this study was elucidating the optimum operating conditions for maximum removal of impurities in treatment of industrial wastewater using an appropriate reverse osmosis membrane. In particular the complete removal of COD was of interest. Finding a potential industrial application of the produced water was the second major aim of the current research.

2. Materials and methods

2.1 Apparatus

In the experimental trials, a cross-flow batch concentration process was employed. Fig. 1 shows the schematic of the experimental set-up. Characteristics of the pump includes: $Q_{Max} = 480$ L/h, $P_{Max} = 80$ bars and $T_{Max} = 50^{o}C$. The cell consists of two cubic parts and was made of a specific alloy. The membrane with an area of 0.002 m^2 was sandwiched between the two parts. The membrane

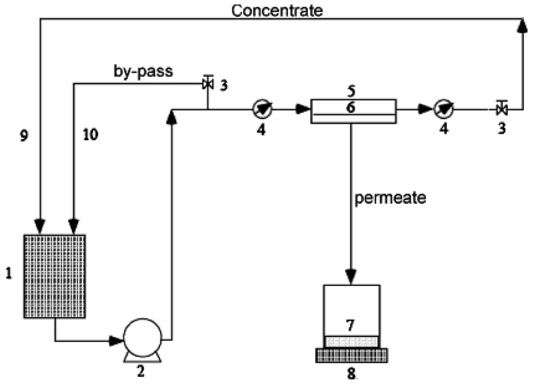

Fig. 1 Schematic of reverse osmosis system (1: feed tank; 2: pump; 3: valve; 4: pressure gauge; 5: cross-flow cell; 6: membrane; 7: permeate; 8: balance; 9: concentrate; 10: bypass)

settled on a resistant compact foam layer to protect it against deformation and displacement. There were two oil pressure gauges (0-60 bar) on the flow line to show the pressure of the liquid before and after the cell. There was a by-pass before the cell to recycle a part of feed to the tank. There were two valves one on the by-pass stream and the other on the retentate stream to adjust the main flow rate and desired operating pressure.

2.2 Membrane

Thin-film composite polyamide reverse osmosis membrane, FT-30, (Filmtec Company, USA), was used for this study. Maximum operating pressure for the membrane is 1,000 psi (6.9 MPa), maximum operating temperature is 45°C. pH range in continuous operation is 2 to 11. For short-term cleaning pH range is 1 to 13. The characteristics of the membrane are presented in Table 1.

2.3 Feed

In the experiments, the wastewater was sampled from Faraman wastewater treatment plant (Kermanshah, Iran). The treated sewage through the biological process was used as feed in all experiments. Batch feed samples were collected and tested. This was repeated for each run. Although the details of the feed characteristics were changed for each sample, the overall propertied were remained constant. Each time the characteristics of the feed and permeates were elucidated and the real numbers were reported as the membrane performance. The COD of the feed varied between 1500 and 3500 mg/lit. Composition of raw and treated waste water are shown in Table 2. The pH of the solution was in the range of 7–8.

Table 1 Membrane characteristic

Membrane	Skin material	Support material	Surface characteristic	Membrane structure	Thickness (μm)
FT30	Polyamide	Polyester and polysoulfone	Smooth	Two layer	160

Table 2 Composition of raw and treated waste water

Component	Input wastewater (ppm)	Treated wastewater (ppm)
Fluoride	1.71	0.01
Chloride	246	25
Nitrite	128	11
Nitrate	140	22
Sulfate	120	10
Phosphate	87	8
Carbonate	50	5
Bromide	1.32	0.04
Nickel	16.3	0.4
Cobalt	3.21	0.07
Cadmium	0.17	0.11
Lead	1.41	0.41
Copper	2.35	0.02
Iron	39.4	1.1
Manganese	1.35	0.17
Zinc	17	1.22
COD	3500	20
BOD	2000	10
T.S.S	800	75
T.D.S	2400	180
Sodium	300	40
Potassium	279	0
Calcium	641	40
Magnesium	194	10
Total hardness	2500	60

2.4 Pre-treatment

The first step in the pre-treatment process was screening. In this step, suspended particles were removed and the contamination of the sewage reduced to approximately 20%. This was followed by stabilization and neutralization steps. Sewage was collected in the stabilizing tank for homogenization. In the biological step the microorganisms were applied to remove the organic material dissolved in the sewage. The sewage passed through the anaerobic reactor. The biological refinement was carried out in the aerating basins by the aerobic bacteria, where the bacteria feed on the organic matters by consuming oxygen. This process causes the contamination to be decreased. Finally, the sludge of the aerating basin entered the sedimentation stage. The outlet of this stage was entered to the membrane setup. A flow diagram of the process is shown in Fig. 2.

2.5 Analysis

The feed of the experimental samples were analyzed for COD, TDS, pH and other contaminants. COD was performed by the dichromate closed refluxed colorimetric method using a spectrophotometer (APEL-PD-303). Concentrations of cations were determined by Atomic Absorption Spectrophotometery (AA-6300 SHIMADZU). Inions analyses were performed using Ionic Chromatography (761 Compact

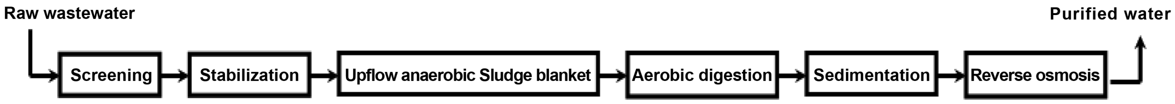

Fig 2. Diagram of the pilot plant for waste water treatment

IC, Metrohm). Concentration of Ca^{2+} and K^+ and Na^+ sample were determined by flame photometer Spectrophotometery (Corning 400). All experiments were carried out three times and the average values were reported.

3. Results and discussion

The water flux is one of the most important parameters in the evaluation of the performance of a filtration system. When the level of solute retention is met, the permeate flux turns to the fundamental factor in process optimization. The higher the permeate flux, the lower the necessary filtration area. The COD retention is influenced by the transmembrane pressure, temperature, cross-flow velocity and operation time (Mohammadi and Esmaeelifar 2004).

3.1 Flux behavior

Fig. 3 illustrates the flux versus time at 15 bars, 1 m/s and 25°C. Significant reduction in flux for the first 90 min indicates the development of fouling layer. The flux reduction from 22 to 11 kg/m^2.hr was observed. This is due to the deposition of small particles and colloidal on the membrane surface which led to the membrane fouling (Ahmad *et al.* 2005). The flux reached a constant value after 270 min.

3.2 COD removal

Fig. 4 represents the variation of COD rejection during time at constant feed temperature, transmembrane pressure and cross-flow velocity. This was improved from 72 to 100% during time.

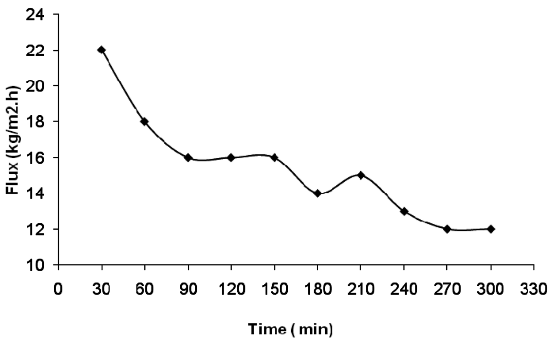

Fig. 3 Flux behavior for filtration of wastewater using the FT-30 RO membrane (T.M.P = 15 bar, Cross flow velocity = 1 m/s, Temp = 25°C)

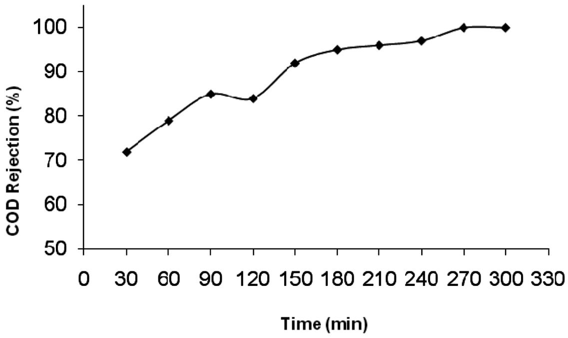

Fig. 4 COD rejection for filtration of wastewater using the FT-30 RO membrane (T.M.P = 15 bar, Cross flow velocity = 1 m/s, Temp = 25°C)

A layer of particles and macromolecules is deposited on the membrane surface, which leads to cake formation or a "secondary membrane". This layer increases the hydraulic resistance and decreases flux. Meanwhile the layer prevents the passage of the species through the membrane.

3.3 Effect of temperature

The variation of permeate flux with temperature is usually explained by the variation in the viscosity of the effluent. In the range of 15 to 45°C, the temperature strongly influences the permeate flux. This can be represented by Arrhenius equation as:

$$J = A_p \cdot \exp(-E_p/RT)$$

Where Ap is the coefficient and Ep is the nominal activation energy of permeation. Moreover increasing the temperature enhances the diffusivity, which results in an increase in permeation flux (Das and Gupta 2007).

The experimental data confirms this expectation. At high temperatures, viscosity is decreased and diffusivity is increased. Fig. 5 depicts the flux variations as a function of temperature at constant T.M.P (15 bars) and cross-flow velocity (1m/s). As temperature increased from 15 to 45°C, the flux was drastically increased from 16 to 34 kg/m^{2}hr. During filtration, solvent flux is increased and solute flux stays unchanged. This leads to high rejection of COD in the permeate [20]. Fig. 6 indicates that the removal of COD was enhanced by increasing the temperature. At 45°C, COD removal reached to 100%.

3.4 Effect of pressure

On the basis of Darcy's law, by increasing the pressure, the flux is linearly increased (Bhattacharjee *et al.* 2006).

Fig. 7 shows the variation of flux versus applied pressure for wastewater using FT-30 membranes. The flux is enhanced by the pressure due to the enhancement of the driving force. An increase in T.M.P from 5 to 20 bars at 25°C and 1 m/s, flux was increased from 4 to 26 kg/m2hr. In optimum pressure, the permeation flux is high and tendency to the cake layer formation is low. Generally a moderate pressure is considered as the optimum value. For the conditions of the current work, 15

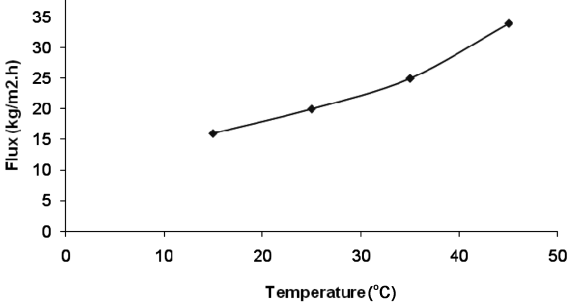

Fig. 5 Effect of temperature on the permeate flux for polyamide (FT-30) membrane (T.M.P = 15 bar, Cross flow velocity = 1 m/s)

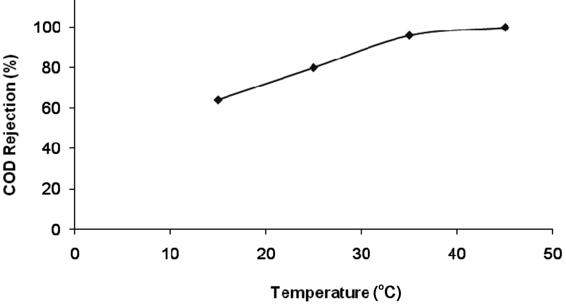

Fig. 6 Effect of temperature on COD retention for polyamide (FT-30) membrane (T.M.P = 15 bar, cross flow velocity = 1 m/s)

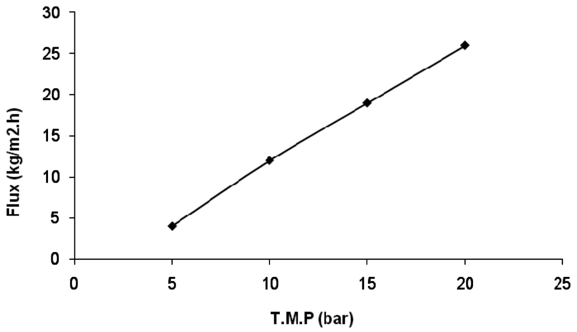

Fig. 7 Effect of pressure on the permeate flux for polyamide (FT-30) membrane (cross flow velocity = 1 m/s, Temp = 25°C)

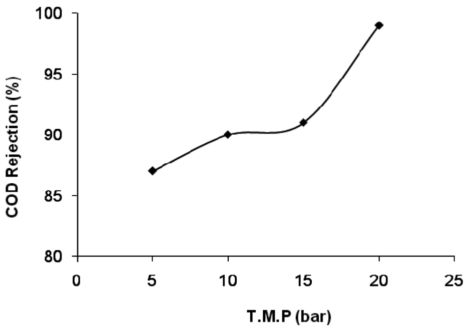

Fig. 8 Effect of pressure on COD retention for polyamide (FT-30) membrane (cross flow velocity = 1 m/s, Temp = 25°C)

bar was selected as the optimum pressure.

Variations of permeate COD with transmembrane pressure are shown in Fig. 8. An increase in transmembrane pressure improves the permeate quality. As the transmembrane pressure was increased from 5 to 20 bars, COD removal was increased to 100%. The solvent flux is increased, while the solute flux is nearly independent of the pressure. This increases the apparent solute removal. Another explanation is attributed to the deposit accumulation on the membrane surface which is increased with the operation pressure. The fouling layer acts as a barrier which increases the resistance for organic material to pass through. The adsorption or deposition of organic material on the fouling layer leads to lower COD content of permeates (Bhattacharjee *et al.* 2006).

3.5 Effect of velocity

Fig. 9 represents the flux variation at different cross-flow velocities from 0.5-2 m/s. An increase in cross-flow velocity increases the Reynolds number and turbulency, which lead to flux increment. Increasing cross-flow velocity enhances the back diffusion of solute accumulated on the membrane surface and decreases concentration polarization (Lobo *et al.* 2006). Accordingly the permeate flux is improved. The maximum flux was achieved at 2 m/s. At this velocity, the cake layer is thinner and permeation flux is higher.

COD removal was obviously influenced by variation of cross-flow velocity being higher for enhanced cross-flow velocity. Shear tangential to the membrane surface allows the sweeping the deposited particles; therefore, the fouling layer on the membrane surface is reduced. Consequently, more solvent can pass through the membrane leading to higher rejection. Fig. 10 indicates that increasing the cross-flow velocity from 0.5 to 2 m/s results in an enhancement in the COD rejection from 93 to 99%.

3.6 Application of treated industrial wastewater

The treated wastewater may be used in various parts of the industrial plant. Generally, the water used for industrial plants must be clear, colorless, without suspended solids and low content of hardness (Cuda *et al.* 2006). Apparently the quality of the produced water depends on the specific application. For instance the obtained water may be considered as cooling water or as a source of

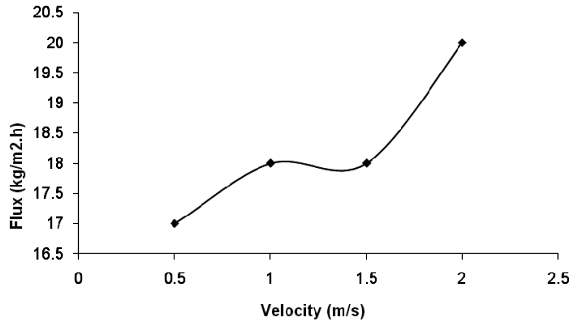

Fig. 9 Effect of cross flow velocity on the permeate flux for polyamide (FT-30) membrane (T.M.P = 15 bar, Temp = 25°C)

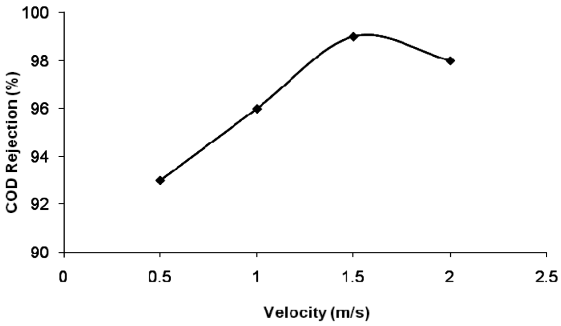

Fig. 10 Effect of cross flow velocity on COD retention for polyamide (FT-30) membrane (T.M.P = 15 bar, Temp = 25°C)

steam in power plant boilers. Apparently higher quality water is required for boiler feed water as compared to cooling water. The general guidelines for cooling and boiler water are presented in Table 3 together with the quality of the treated water. The guidline is based on minimization of corrosion, scale or fouling. Hardness is often responsible for scale forming in cooling towers and in pipes. Hardness is classified as carbonate and non-carbonate hardness, and with respect to the ions, calcium and magnesium (Dean Spatz 1991). The presence of deposits can provide habitats for the growth of microorganisms within the cooling system. Reverse osmosis can remove more than 99% of colloidal, suspended solids, 95-98% of inorganic ions, together with non-ionic contaminants and organic molecules. The reduction in particulates, suspended solids and total organic carbon (TOC) enhances turbine and boiler efficiency.

In the current study, FT30 reverse osmosis membrane was employed. This membrane removed most of the impurities and the product meets the requirements for reuse. The quality of the produced water for a specific raw wastewater in depicted in Table 3. Removal percentage of anions,

Table 3 Water quality guidelines for cooling and boiler feed water [11] and the characteristics of the treated water

Water quality parameter (all as mg/l)	Cooling Water	Boiler feed water	Treated wastewater
Conventional parameters			
Hardness, mg/l as CaC03	600	0.07-350	60
pH	6.9-9.0	7-10	7.3
Total dissolved solids	500	200-700	180
TSS	100	5-10	75
Organics			
BOD_5	25	1-30	10
COD	75	1-50	20
Phosphate, mg /l as P	4	2	8
Aluminum	0.1	0.01-5	NA
Chloride	500	Variable	25
Iron	0.5-1	0.05-1	1.1
Manganese	0.5	0.01-0.3	0.17
Sulfate	200	Variable	10

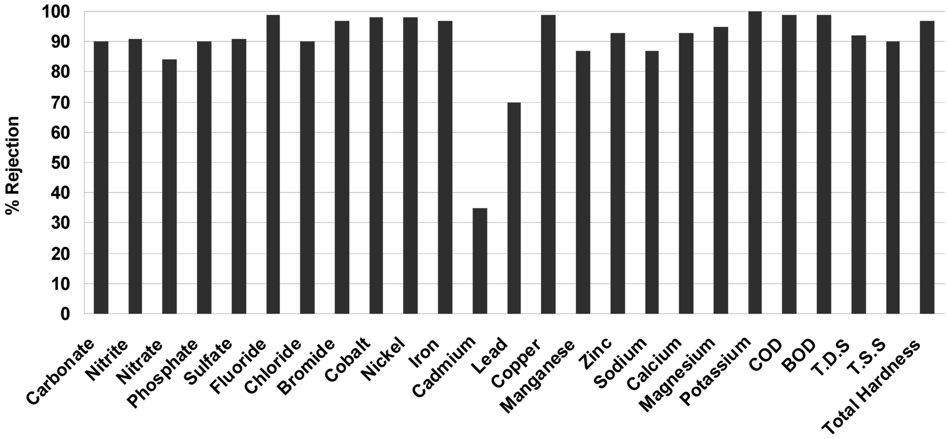

Fig. 11 Removal percentage for treatment of industrial wastewater using FT-30 polyamide membrane (T.M.P = 15 bar, Cross flow velocity = 1 m/s, Temp = 25°C, membrane soaked at (50%-50%) water-ethanol prior to experiment)

cautions, organic and inorganic matters are shown in Fig. 11. Most of the impurities were removed around or higher than 90%. In particular total dissolved solid (TDS) was reduced around 93%. The obtained data (Table 3) indicate that the produced water can be employed for cooling tower. The application of treated water for boiler needs further reduction of some of the components. This is the focus of a forthcoming research.

4. Conclusion

The transmembrane pressure and cross flow velocity imposed a direct effect on the permeate flux of aromatic polyamide (FT-30) reverse osmosis membrane. The permeate flux was higher for higher operating pressure. However flux was declined due to the concentration polarization phenomenon. Increasing the temperature and cross flow velocity led to an improvement in the steady-state fluxes. Higher applied pressure, cross flow velocity and temperature resulted in higher removal of impurities from the wastewater.

In general RO membrane is able to drastically reduce the COD concentration to an acceptable value for reusing the produced water from wastewater. The application includes but not limited to cooling tower water.

References

Ahmad, A.L., Ismail, S. and Bhatia, S. (2005), "Ultrafiltration behavior in the treatment of agro Industry effluent: Pilot scale studies", *Chem. Eng. Sci.*, **60**(3), 5385-5394.

Bes-Piá, A., Mendoza-Roca, J.A., Alcaina-Miranda, M.I. and Iborra-Clar, A. (2002), "Reuse of wastewater of the textile industry after its treatment with a combination of physico chemical treatment and membrane technologies", *Desalination*, **149**, 169-174.

Bhattacharjee, S., Datta, S. and Bhattacharjee, C. (2006), "Performance study during ultrafiltration of Kraft black liquor using rotating disk membrane module", *J. Clean. Prod.*, **14**, 497-504.

Bódalo-Santoyo, A., Gómez-Carrasco, J.L., Gómez, E. and Hidalgo-Montesinos, A.M. (2004), "Spiral wound membrane reverse osmosis and the treatment of industrial effluents", *Desalination*, **160**(3), 151-158.

Cowan, J.A.C., MacTavish, F., Brouckaert, C.J. and Jacobs, E.P. (1992), "Membrane treatment strategies for red meat abattoir effluents", *Water Sci. Technol.*, **25**(10), 137.

Čuda, P., Pospíšil, P. and Tenglerová, J. (2006), "Reverse osmosis in water treatment for boilers", *Desalination*, **198**, 41-46.

Das, C. and Gupta, S. (2007), "Treatment of soaking effluent from a tannery using membrane separation processes", *Desalination*, **216**(1), 160-173.

Dean Spatz, D. (1991), *Osmonics pure water handbook*, Minnetonka, USA.

Galambos, I., Molina, J., Járay, P., Vatai, G. and Bekássy, E. (2004), "High organic content industrial wastewater treatment by membrane filtration", *Desalination*, **162**, 117-120.

Ghabris, A., Abdel-Jawad, M. and Aly, J. (1989), "Municipal wastewater renovation by reverse osmosis", *Desalination*, **75**, 213-218.

Hussain, A.A., Nataraj, S.K., Abashar, M.E.E., Al-Mutaz, I.S. and Aminabhavi, T.M. (2008), "Prediction of physical properties of nanofiltration membranes using experiment and theoretical models", *J. Membrane Sci.*, **310**, 321-336.

Lee, J.W., Kwon, T.O. and Moon, I.S. (2005), "Performance of polyamide reverse osmosis membranes for steel wastewater reuse", *Desalination*, **177**, 69-82.

Lobo, A., Cambiella, Á., Manuel Benito, J. and Pazos, C. (2006), "Ultrafiltration of oil in water emulsions with ceramic membranes: Influence of pH and cross flow velocity", *J. Membrane Sci.*, **278**, 328-334.

Lynch, S., Smith, J., Rando, L. and Yauger, W. (1984), *Isolation or concentration of organic substances from water an evaluation of reverse osmosis concentration*, Report EPA-600 /1-84-018, US Environmental Protection Agency.

Madaeni, S.S. and Mansourpanah, Y. (2003), "COD removal from concentrated wastewater using membranes", *Filtr. Separat.*, **40**(1), 40-46.

Madaeni, S.S., Tahmasebi, K. and Kerendi, S.H. (2004), "Sugar syrup concentration using reverse osmosis membranes", *Eng. Life Sci.*, **4**(2), 178-190.

Mohammadi, T. and Esmaeelifar, A. (2004), "Wastewater treatment using ultrafiltration at a vegetable oil factory", *Desalination*, **166**, 329-337.

Nataraj, K.S., Hosamani, K.M. and Aminabhavi, T.M. (2006a), "Distillery waste water treatment by the membrane based nanofiltration and reverse osmosis processes", *Water Res.*, **40**(10), 2349-2356.

Nataraj, S.K., Hosamani, K.M. and Aminabhavi, T.M. (2006b), "Electrodialytic removal of nitrate and hardness of simulated mixtures using ion-exchange membranes", *J. Appl. Polym. Sci.*, **99**, 1788-1794

Nataraj, S.K., Hosamani, K.M. and Aminabhavi, T.M. (2007a), "Potential application of electrodialytic pilot plant containing ion exchange membrane in chromium removal", *Desalination*, **217**, 181-190.

Nataraj, S.K., Sridhar, S., Shaikha, I.N., Reddy, D.S. and Aminabhavi, T.M. (2007b), "Membrane-based microfiltration/electrodialysis hybrid process for the treatment of paper industry wastewater", *Sep. Purif. Tech.*, **57**, 185-192.

Pusch, W., Yu, Y. and Zheng, L. (1989), "Solute-solute and solute membrane interactions in hyperfiltration of binary and ternary aqueous organic feed solutions", *Desalination*, **75**, 3-14

Saffaj, N., Alami Younssi, S., Albizane, A., Messouadi, A., Bouhri, M. and Persin, M. (2004), "Preparation and characterization of ultrafiltration membranes for toxic removal from waste water", *Desalination*, **168**, 259-263.

Siler, J. and Bhattacharyya, D. (1985), "Low pressure reverse osmosis membrane: concentration and treatment of hazardous wastes", *Waste Hazard. Matter*, **2**, 45-65.

Šostar-Turk, S., Petrinić, I. and Simonič, M. (2005), "Laundry wastewater treatment using coagulation and membrane filtration", *Resour. Conserv. Recy.*, **44**(3), 185-196.

Stephenson, T., Judd, S. and Jefferson, B. (2000), *Membrane bioreactor for wastewater treatment*, IWA Publishing, London.

Williams, M., Deshmukh, R. and Bhattacharyya, D. (1990), "Separation of hazardous organics by reverse osmosis membranes", *Environ. Prog.*, **9**, 118-125.

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