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Recycle unit wastewater treatment in petrochemical complex using reverse osmosis process

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ABSTRACT

The implementation of reverse osmosis (RO) process is a solution for increasing water demand. In this work the treatment feasibility of effluent wastewater in Tabriz Petrochemical Complex was evaluated using RO pilot plant. After a pretreatment with cartridge filters, wastewater was introduced to RO unit with a rate of 2000–12,000 l/h. The permeated rate was 600–1500 l/h using different applied pressures of 5–22 bars. The results showed that Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Conductivity, Total Dissolved Solid (TDS), color, turbidity, SO_4, NH_4, Calcium Hardness (CaH), Total Hardness (TH), suspended solid (SS) and SiO_2 of the wastewater were decreased and removed extensively using RO membranes. The flux of permeated stream and the recovery rate were increased with the feed pressure. However the optimum operating pressure for the reverse osmosis pilot was determined as 15 bars leading to a recovery rate of 45%. The results indicate that achieving the "Zero Discharge" goal is possible using RO system. The plan for zero discharge is conducting the concentrated waste from the reverse osmosis system to evaporation pond.

1. Introduction

Nowadays wastewater reuse is not only possible and necessary but also affordable and cost effective. High water recovery rate is an essential concept in wastewater treatment. Membrane technology in general and reverse osmosis (RO) in particular has been used for seawater desalination and wastewater treatment for more than 30 years. However, these applications have been limited to some extent due to the sensitivity of RO membranes to fouling and the effectiveness of conventional pretreatment technologies.

The application of reverse osmosis for wastewater treatment can be regarded as state of the art [1]. The growing success of membranes in this application is related to improved membrane products and process design [2]. The applications of reverse osmosis membranes for wastewater treatment include beverage industry [3], tanneries wastewaters [4], chromium tanning processes [5] and greasy wastewater [6].

Key factors which play a vital role in operation of large-scale RO plants include pretreatment, low fouling membranes, flux rate, recovery and control of fouling and scaling. Ultrafiltration (UF) and microfiltration (MF) processes as pretreatment lead to high flux and increase life time of RO membranes. These technologies remove most of the suspended particles that would normally cause heavy fouling [5,6].

The required water quality can be achieved by RO using a cascaded operation. The problem is the water recovery rate. Contrary to seawater desalination with optimal water recovery rates between 30 and 50%, the water recovery rate in wastewater treatment processes must be very high – in many cases almost 100%. However the water recovery rate of RO is limited by scaling, fouling and/or osmotic pressure [7].

Improvement in membrane technology has resulted in low fouling RO membranes which minimize the strong adhesion of organic materials to the membrane surface. The success of such optimized system designs and low fouling membranes has been demonstrated [2].

The issue of membrane fouling is the primary issue limiting the use of RO technology. Previous studies [2,8] have shown that fouling of the RO membranes can lead to increasingly high pressures to maintain product water flow. At some point, it is more economical to stop the operation, clean the membranes, and then return the system to operation. However the pressure rises even more quickly after the initial fouling of the RO membranes. This makes the system difficult to operate and eventually shortens the life of the RO membranes.

In summary, the possibility of application of reverse osmosis membranes for wastewater treatment is widely accepted. However the localization of the process is a vital step in employment of the system for specific plants. In the present work a feasibility study was carried out for treatment of effluent wastewater in Tabriz Petrochemical Complex (TPC) by reverse osmosis. The effects of influencing parameters were investi-

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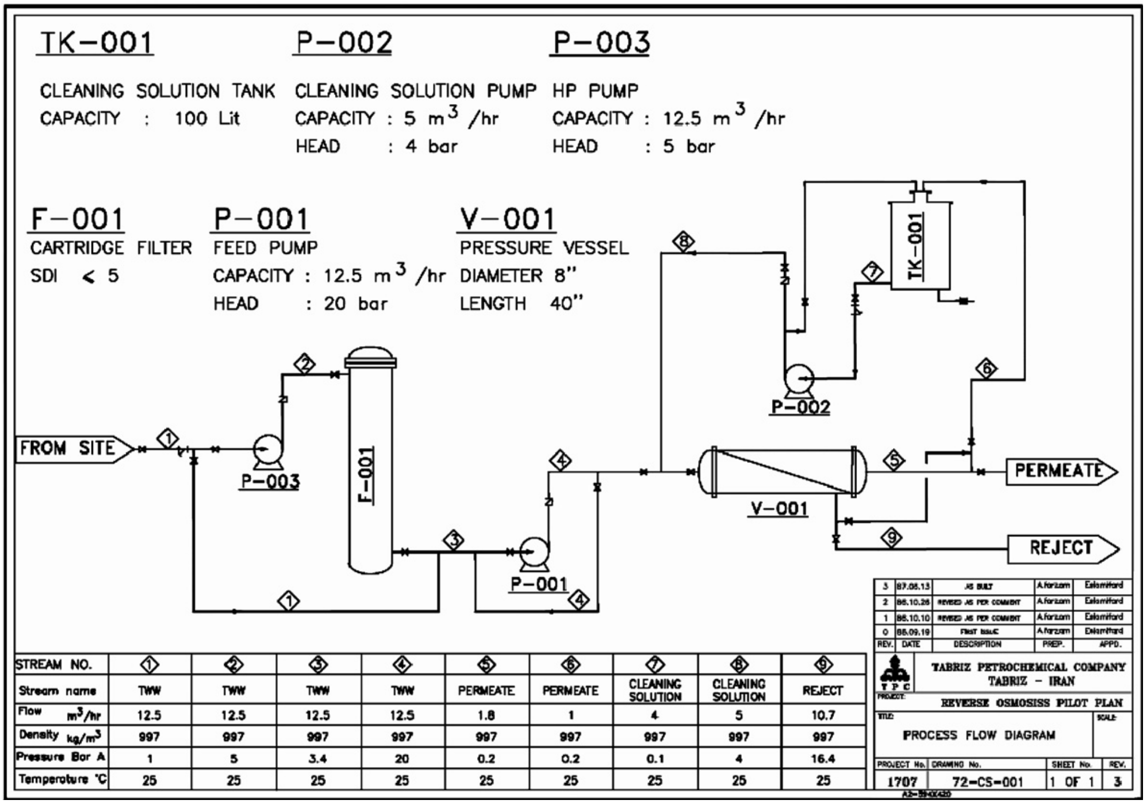

Fig. 1. Process flow diagram of the RO pilot plant.

gated using a home-designed and made reverse osmosis pilot plant.

2. Experimental

2.1. Equipment

Fig. 1 shows a process flow diagram (PFD) of the RO pilot designed and used in this work. The module consisted of a Hydranautics spiral wound with composite polyamide membrane. LSY-CPA2 membrane modules were used in this project. This is spiral wound configuration with a length of 1016.0 mm and a diameter of 201.9 mm. Maximum applied pressure and feed flow are 4.16 MPa and 17 m^3/h, respectively. Maximum pressure drop for each membrane is 10 psi. Operating pH range is between 3 and 10. Generally the permeate flow for the element is one fifth of the feed flow. The feed solution from the feed line (wastewater treatment unit) was drawn via a 4 kW pump through cartridge filters and carried to the pressure vessel (membrane) with a 15 kW pump. Analyses of the wastewater revealed that: TDS was between 750 and 2000 ppm, turbidity was between 2 and 8 NTU, TH was between 100 and 150 ppm, SO_4 was between 500 and 1100 ppm and COD was between 50 and 90 ppm.

Permeate and feed flow rates were measured using two flow meters placed on the streams entering and exiting the pressure vessel. A valve on the concentrate line was used to set the operating pressure. The inlet and outlet pressures to the membrane were measured by pressure gauges. The cleaning solutions from the chemical tank were drawn using a 1.5 kW pump to the pressure vessel (RO membrane). A photo of the RO pilot plant for wastewater treatment is represented in Fig. 2.

2.2. Procedures

Pretreatment is a vital step for RO systems in industrial scale. However this is not required and was not feasible for our pilot plant. The reason for not requirement of pretreatment is the estimation of the system performance in worst condition. In the current study, three cartridge filters were employed in the system. The filters are capable to partly remove the feed contaminants including COD, conductivity, suspended solids and sulfate.

The feed line was filled with wastewater. Then, the system power was switched on and the wastewater was pumped by the first pump (4 kW) into the cartridge filters and by the high-pressure pump (15 kW) into the RO pressure vessel at the constant feed pressure of 15 bars. This pressure was controlled by adjusting the concentrate control valve. The system was run for adequate time to reach steady state conditions and the flow rates of permeate and

Fig. 2. RO pilot plant for wastewater treatment.

Table 1
Procedures for measuring significant parameters.

Parameter	Test method	Number
pH	ASTM	D.1293-99
Conductivity	ASTM	D.1125-95
Hardness (CaH and TH)	ASTM	D.1126-02
Cl_2	ASTM	D.512-04
NH_4	ASTM	D.1426-03
COD	ASTM	D.1252-06
BOD	Standard Method	5210A,B,C
SS	Hach Method	8021
SO_4	ASTM	D.516
PH_4	ASTM	D.515
Turbidity	Hach Method (TPC-Lab)	022
Color	Hach Method (TPC-Lab)	DR-2000

Table 2
Instruments for measuring the significant parameters.

Parameter	Instrument or method
TDS	HACH (model DR/2000)
SS	HACH (model CO 150)
pH	Metrohm (pH meter model 691)
SO_4	HACH (model DR/2000)
Turbidity	HACH (model RATIO/XR)
SiO_2	HACH (model DR/2000)
COD	HACH (model DR/2000)
TH	Titration (EDTA)
CaH	Titration (EDTA)

feed streams were measured for feed pressures of 9–20 bars. The feed flow rate was controlled with a bypass valve in each constant pressure. The recovery rate and pressure drop were estimated for each run.

The samples were collected from pilot inlet (cartridge filter input stream), RO inlet and permeated water. Significant parameters of the samples such as Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Dissolved Solid (TDS), Conductivity, Suspended solid (SS), Calcium Hardness (CaH), Total Hardness (TH), SO_4, NH_4, turbidity, Cl_2, color, and pH were measured. A summary of the measuring procedures are presented in Table 1. A list of employed instruments for the analysis is presented in Table 2.

The cleaning of RO membranes were studied in five steps at ambient temperature (25 °C). In the first step the membranes were washed by permeated water (RO water). In the next step washing the membranes with the permeated water and 2% formaldehyde was performed for 45 min. This was followed by cleaning with 2% caustic (NaOH) at pH 10 for 45 min. In the fourth step citric acid (2%, pH 4) was employed for 45 min. Finally the membrane elements were rinsed with RO water. The reason for selecting the mentioned concentrations for chemical cleaning was the similarity with the concentrations used in the industrial scale plant. The optimum concentrations were found via a long period experience in the main reverse osmosis plant.

3. Results and discussions

3.1. Pilot plant performance (quantity)

After a pretreatment with cartridge filters, wastewater was introduced to RO unit with a rate of 2000–12,000 l/h. The permeated rate was 600–1500 l/h using different applied pressures of 5–22 bars. Various significant parameters were measured in 5 days interval. On the day 15th, some of the parameters in permeate were changed. Subsequently the flow rate of permeate was decreased. Chemical cleaning with formaldehyde 2% was conducted. After chemical cleaning, the permeate parameters and operating conditions changed to the normal conditions, i.e. the rejection and recovery were restored to the conditions prior to membrane fouling. The results from the 30th day showed that, permeate flow rate was decreasing again. Manual inspection of the membrane element indicated the presence of considerable iron. The presence of iron was easily observed in the flow meter and tubes. After removal of membrane elements from pressure vessel iron particles were detected by visual inspection. This was due to the occasional changes in the feed conditions and compositions. The fresh chemical cleaning was carried out to minimize the problem. Formaldehyde (2%), caustic (2%) and acetic acid (2%, pH 4) were employed for washing the membrane for half an hour. After chemical cleaning permeate and operating conditions were returned to the normal situation.

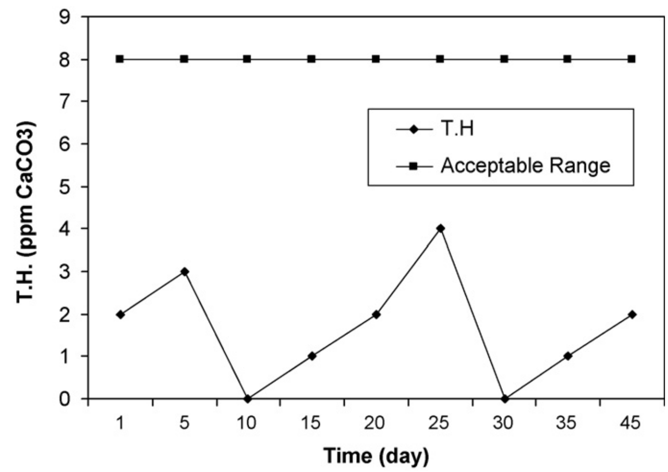

Fig. 3. TH of permeate versus time.

The feed in this study was the wastewater collected from various parts of the petrochemical complex. Accordingly the quality of feed is changed during time. By quality we mean the parameters such as COD, BOD, turbidity, SO_4, TDS, TH, etc. Consequently a precise schedule for membrane cleaning is impractical. Monitoring of permeate during time is an adequate indicator for required cleaning intervals.

3.2. Pilot plant performance (quality)

Several vital parameters were measured during the pilot plant experiments to elucidate the quality of permeate. During 45 days of quality monitoring, Total Hardness (TH) was fluctuated (between nil and 4 ppm Fig. 3) but remained well under the acceptable limit (8 ppm). This is the required concentration for various applications in TPC including cooling tower and DM (dematerialized water) water make up. The variation of TH was due to the diversification in wastewater composition. The same trend (parameter value below the acceptable range) was found for Calcium Hardness (CaH) (Fig. 4), Chemical Oxygen Demand (Fig. 5) and conductivity (Fig. 6). COD was zero in the first 10 days. The newly installed membrane was able to prevent the passage of most species. This capability was diminished during time due to accommodation of the unwanted foulants on the membrane surface.

The sulfate content (SO_4) of the feed altered during time but was around 1000 ppm for all days (Fig. 7). However most of the sulfate was removed by reverse osmosis process (Fig. 8). The average sulfate in permeate was around 2 ppm which is well below the 6 ppm of acceptable value. The other vital parameters such as Biological Oxygen Demand (BOD), Total Dissolved Solid (TDS), color, turbidity, SO_4, NH_4, Suspended solid (SS) and SiO_2 were measured. The results are not presented in the manuscript to avoid prolixity.

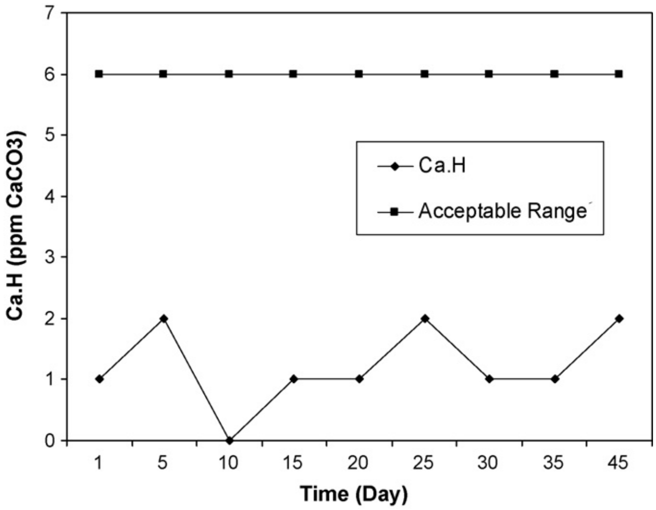

Fig. 4. CaH of permeate versus time.

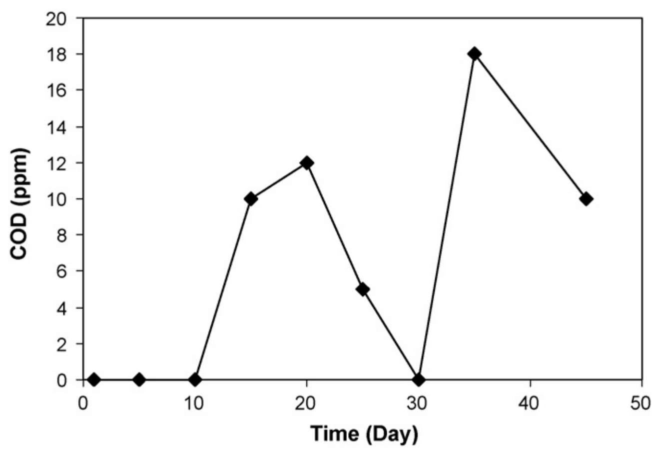

Fig. 5. COD of permeate versus time.

In summary the rejection of significant parameters by the membrane element was around 100% (Fig. 9). Moreover the permeate quality was not a function of the feed characteristics. In the current research the feed property was continually changed during the process. The feed variation range was demonstrated in Section 2. However one of the advantages of the reverse osmosis system is the constant quality of the permeate by changing the feed characteristics.

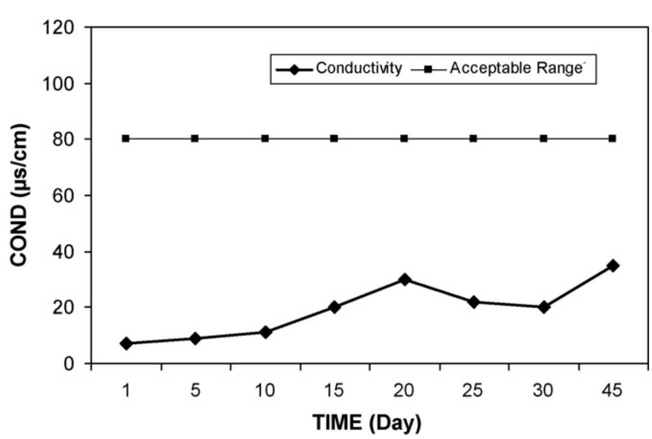

Fig. 6. Conductivity of permeate versus time.

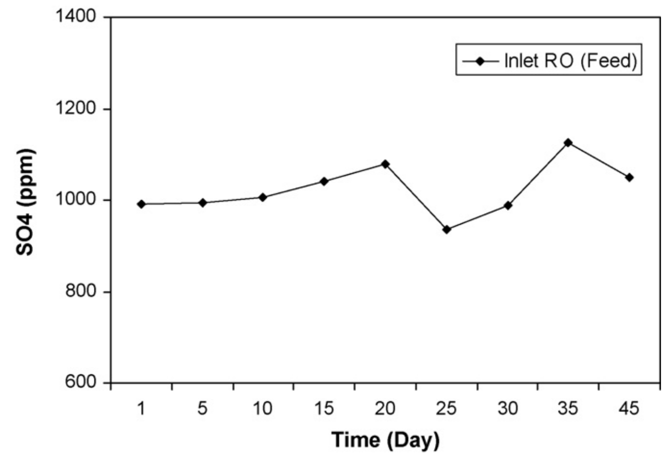

Fig. 7. SO_4 in feed versus time.

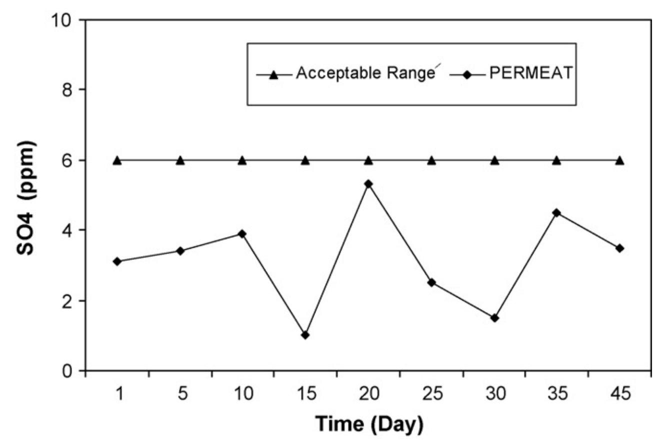

Fig. 8. SO_4 of permeate versus time.

The quality of membrane permeate was compared with cooling water, dematerialized water, softening water, potable water and reverse osmosis water. The analysis of permeate water indicated the similarity of the produced water with the product of reverse osmosis plant using fresh water as the feed. The permeate water from the current wastewater treatment plant may be mixed with the product of reverse osmosis process or as the make up water for cooling towers.

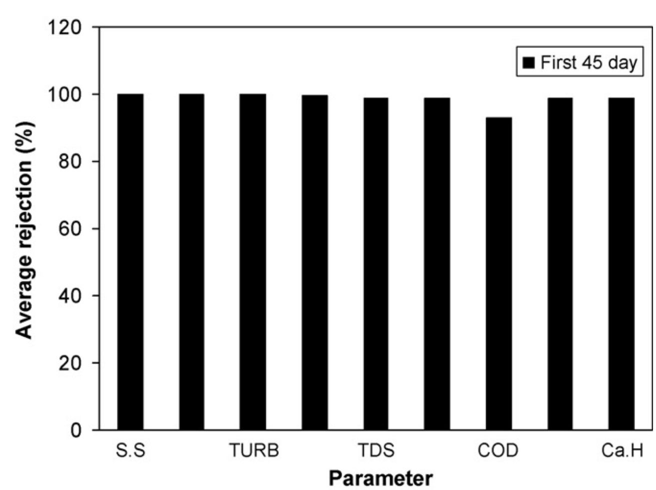

Fig. 9. Comparison of average rejection of parameters.

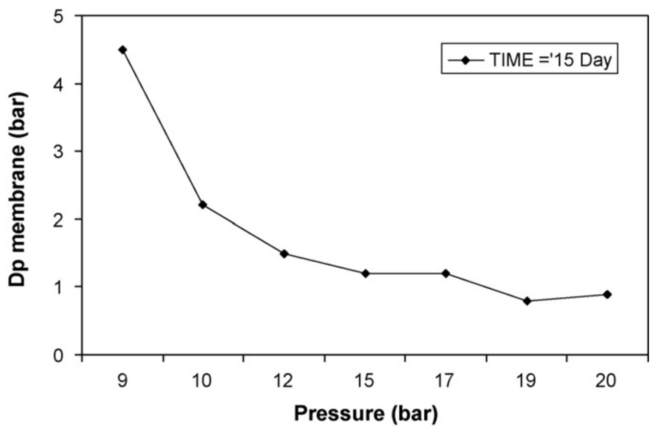

Fig. 10. RO pressure difference (Dp) versus feed pressure.

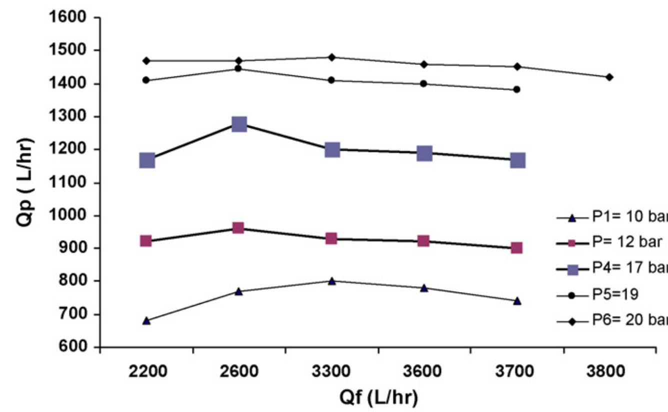

Fig. 12. Comparison of permeate flow versus feed flow.

3.3. Operating framework

The framework of the operating parameters such as permeate rate (Qp), feed rate (Qf), permeate pressure, feed pressure, RO pressure drop (Dp) and recovery (Qp/Qf) were elucidated.

Fig. 10 shows that the RO pressure drop is decreased with an increase in feed pressure. This may be explained due to higher cross-flow velocity obtained with increasing the feed pressure in the designed pilot plant. Enhancing the velocity removes most of the accumulated species on the membrane surface leading to lower resistance against the passage of flow. This leads to lower pressure drop for reverse osmosis element.

In accordance with Fig. 11 permeate water flow (Qp) is improved with increasing the feed pressure. This expected result is due to improvement of driving force by enhancing the applied pressure. However the initial sharp incline was followed by a moderate enhancement after 15 bars. The permeate rate was mainly constant after 19 bars.

The productivity depends on the various conditions including the feed condition that entering the membrane element. To elucidate the effect of feed conditions on productivity a series of experiments was conducted. Two significant feed conditions, i.e. feed pressure and feed flow rate were changed during the trials. The results of permeate rates versus feed rates for various applied pressures are depicted in Fig. 12. Clearly the permeate rate is increased with pressure increment without any pronounced effect of the feed rate.

One of the most important factors affecting the whole process is the wastewater recovery which is enhanced with feed pressure (Fig. 13) leading to a nearly constant value after 15 bars. Increasing the pressure possesses dual effects. In one side the driving force is increased leading to recovery improvement. On the other hand the tendency of material accumulation on the membrane surface is enhanced. This leads to recovery diminishment. At the early stages of filtration the recovery rate with pressure is sharply improved due to dominant effect of driving force. During time the fouling effect is more pronounced resulting in a reduction in recovery. However the increasing recovery rate is not stopped meaning that the overall effect of pressure is positive for the current study. Accordingly the applied pressure of 15 bars may be selected as the optimum pressure for the current pilot plant.

The fluctuation of wastewater recovery during days in several feed pressures is depicted in Fig. 14. The recovery was decreased during time showing a jump after chemical cleaning.

On the basis of obtained results calculation was conducted to elucidate the quantity of saved water. This study shows that by the implementation of reverse osmosis technology for wastewater treatment, 150 m^3/h of raw water is saved in Tabriz Petrochemical Complex. Moreover achieving the "Zero Discharge" goal is possible using continual reverse osmosis system. The plan for zero discharge is conducting the concentrated waste from the reverse osmosis system to evaporation pond. Accordingly there is no discharge from Tabriz Petrochemical Complex (TPC). Obviously before RO treatment, there is no possibility to evaporate all the wastewater generated in TPC. The associated problems include wasting the massive quantity of water in the wastewater and huge required space for the evaporation pond. However reducing the volume of

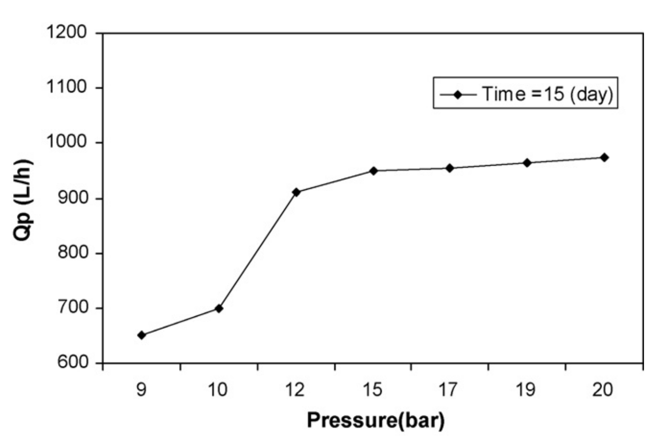

Fig. 11. Permeate water flow versus feed pressure.

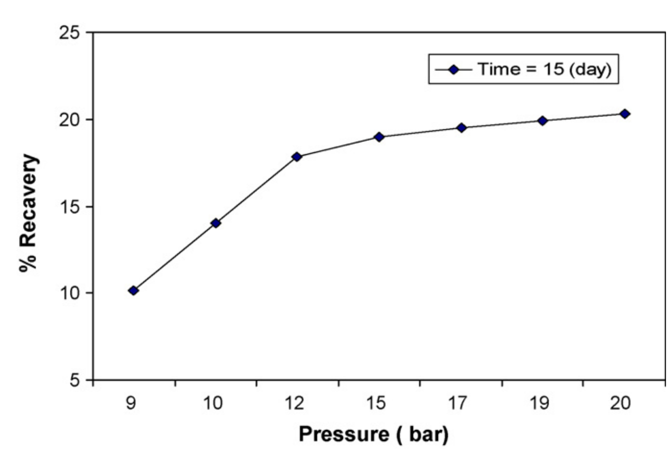

Fig. 13. Recovery of wastewater versus feed pressure.

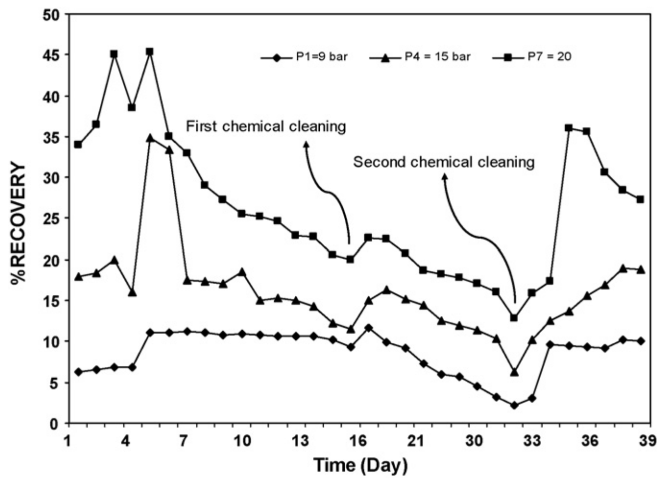

Fig. 14. Comparison of wastewater recovery versus time.

wastewater by obtaining the pure water is a solution for the problems.

Although the economical feasibility can be the focus of another study, we may emphasis that this is a cost effective process in TPC due to the following criteria: the required pretreatment and RO facilities have been previously installed. The spare RO section was the result of an overdesigned project. The environmental restrictions by law are maintained and the fines are prohibited.

4. Conclusions

The feasibility of wastewater treatment by reverse osmosis was conducted and the following results were obtained:

1. Treatment by reverse osmosis effectively decreases the turbidity, COD, BOD, TDS, SS, SO_4, NH_4, CaH, and TH of the wastewater up to 98%.
2. Performance of cartridge filters is extremely (90%) decreased with an increase in turbidity and suspended solids.
3. A recovery up of 45% may be obtained.
4. A reasonable quantity of water is saved by implementation of reverse osmosis technology for wastewater treatment.
5. Due to the instability of feed composition, parameters such as turbidity, SO_4, TDS, TH, are varied during time. Consequently a predicted schedule for membrane cleaning is impractical. A precise monitoring is required for optimization of cleaning program.
6. RO treated wastewater may be used as a make up water for cooling towers or feed water for water demineralization unit.

Acknowledgments

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