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Purification of Wastewater of Ion Exchange Plant of Shiraz Petrochemical Complex in Iran using Reverse Osmosis Method

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In present studies, the reverse osmosis (RO) is used for treatment of regeneration wastewater from ion exchange plant of Shiraz petrochemical complex, which at present the wastewater is discharged to evaporation lagoons without any treatment. Despite numerous research about using membrane processes for industrial wastewater treatment, there was no study about using reverse osmosis for treatment of wastewater form ion exchange regeneration process. So, considering the similarities between this kind of wastewater and brackish water or saline water, it has been hypothesized that reverse osmosis has the ability to remove dissolved solids from this kind of wastewater. Therefore, it is necessary to provide a pilot plant which has facilities for indicate and control of pressure, temperature and flux to evaluate and investigate the wastewater treatability. In this study, two variables, pressure and cross flow velocity have been chosen at three levels and each run of experiment continues for 5 h. Nine experiments have been done, to obtain the maximum flux and the minimum conductivity. Levels are 20, 25 and 30 bar for pressure and 0.27, 0.54 and 0.81 m/s for cross flow velocity. Results show that wastewater from ion exchange regeneration can be treated satisfactorily and during this study, conductivity has been decreased from 14400 μs/cm to about 558 μs/cm, under 30 bar pressure and 0.54 m/s cross flow velocity and the flux is 46.89 L/m^2 h. Considering results of treated wastewater, the percentage of dissolved solid removal is almost higher than 95. This treated wastewater can be used for irrigation or other purposes.

Key Words: Regeneration, Ion exchange, Membrane cell, Reverse osmosis.

INTRODUCTION

The shortage of the water forces different part of the society including industries to consider different methods for recycling and reuse of wastewater. Iran petrochemical industry tries to treat and reuse industrial wastewater using new methods for untreated wastewater. At this research in Shiraz Petrochemical Complex (SPC), we try to use reverse osmosis (RO) for treatment of regeneration wastewater from ion exchange plant which at present is discharged to evaporation lagoons without any treatment.

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In this study, first of all we introduce the source water of Shiraz petrochemical complex, the sequence of water treatment and the wastewater of ion exchange plant; next, recent ways of how to dispose of this kind of wastewater will be explained and finally the use of reverse osmosis (RO) method for the treatment of this wastewater is proposed.

Huge amount of industrial water is used in cooling systems of industries. In Shiraz petrochemical complex, the situation is the same. But, here deionized water is used for make up water in cooling system. This is because of the kind of cooling system of Shiraz petrochemical complex which is zero blow-down and they are not allowed to discharge this blow-down water which contains the poisonous chemical, zinc chromate to the environment. So, they have to use deionized water to compensate, the amount of water escaping from the system due to evaporation or other losses.

Deionized water is produced in ion exchange plant. The ion exchange resin saturation takes place after a few hours, regarding water quality, kind of resin and conditions of the process.

This saturated resin must be regenerated by acid or base, which causes the production of large volume of industrial wastewater containing large amount of dissolved solids. This wastewater, in turn, must be discharged. In brief, the water treatment plant of Shiraz petrochemical complex consists of intake, surface water provided by a dam, removal of suspended solids and colloidal matters and finally removal of dissolved solids in two-stage deionization plant.

The two-stage deionization plant is designed to supply deionized make up water for the process and power generation plant of Shiraz petrochemical complex. The plant consists of three duty streams with one standby stream. The streams treat waters, regenerate and standby in rotation. Each stream consists of a strongly acidic cation exchange unit, followed by a weakly basic anion exchange unit.

Between two regeneration processes, each stream produces deionized water about, 2000 m^3 to 2400 m^3 and generally in 24 h the amount of deionized water becomes 12000 m^3. For regeneration of the strongly acidic cation resin, 5 % nitric acid is used and for regeneration of the weakly basic anion resin, a 4 % strength ammonia solution is used. Besides, deionized water plant usually produces 1000 m^3/day regeneration wastewaters with 14000-20000 μs/cm conductivity which at present is discharged to evaporation lagoons. Common methods used for the disposal of these kinds of wastewater in the world consist of discharge to brackish or saline receiving waters, deep-well injection and in the case of small facilities, discharge to wastewater collection systems[1]. In some areas land application has been used for some low-concentration brine solutions and controlled thermal evaporation may be the only option available in many areas[2].

The treatment of effluents from the regeneration of cation exchanger by the membrane distillation process has been investigated, in the membrane distillation process, the two solutions at different temperatures are separated by a micro porous hydrophobic membrane. During this process the membrane pores are filled by the vapour phase. Therefore, the water vapour is only transferred across the membrane[3].

Membranes have been assigned a key role in water reclamation schemes that are aimed at higher water quality reuse application including aquifers recharge, indirect potable reuse and industrial process water[4].

Potential use of industrial wastewater in a thermal power station was carried out. There is significant water pumped from plant to the sewage plant and irrigation. Much of this wastewater could be treated by filtration, including RO and recycled in the plant as process water. The salty filtration and ion exchange backwash here are two sources of discharge from the sweage treatment plant could potentially be recycled into the plant[5].

In another research, power plant station faced with environmental and water shortage problems which have been solved by the installation of a spiral reverse osmosis plant to treat mine water and spent cooling water[6].

Despite numerous research using membrane processes for industrial wastewater treatment, there was no study or research using reveres osmosis for treatment of wastewater form ion exchange regeneration process. So, considering the similarities between this kind of wastewater and brackish water or saline water, it has been hypothesized that reverse osmosis has the ability to remove dissolved solids from this kind of wastewater. Therefore it is necessary to provide a pilot plant which has facilities for indicate and control of pressure, temperature and flux to evaluate and investigate the wastewater treatability.

Although, at this kind of pilot plant, usually spiral wound RO membrane is used, for achieving better results with low expenses, we can use bench scale instruments such as membrane cell. At this method, we can use a small sheet of membrane about 10 cm × 20 cm that sandwiched between two steel part which can tolerate high pressure[7].

In a research, to evaluate the production of high-quality water from secondary effluent, 4 different low operating pressure RO membranes in the RO simulator were used. Each of the four RO simulator contained a flat sheet of RO membrane overlaid with a spiral wound module[8]; the channel width was 25 mm, channel height 1 mm and the effective length 20 cm.

EXPERIMENTAL

The pilot plant designed and set up according to Fig. 1. The main parts of pilot plant consist of; wastewater tank, low pressure pump, cartridge filters high pressure pump, membrane cell and devices for pressure and temperature control.

Membrane cell has a key role in pilot plant, because at this part we must adjust pressure and cross flow velocity to obtain the maximum flux with the lowest conductivity and minimum fouling. After entering to the membrane cell, wastewater is divided to two streams, permeate or treated wastewater and concentrate. Permeate is collected in a separate container for volume and conductivity to be measured at specified time intervals. It is necessary to mention that, permeate and concentrate

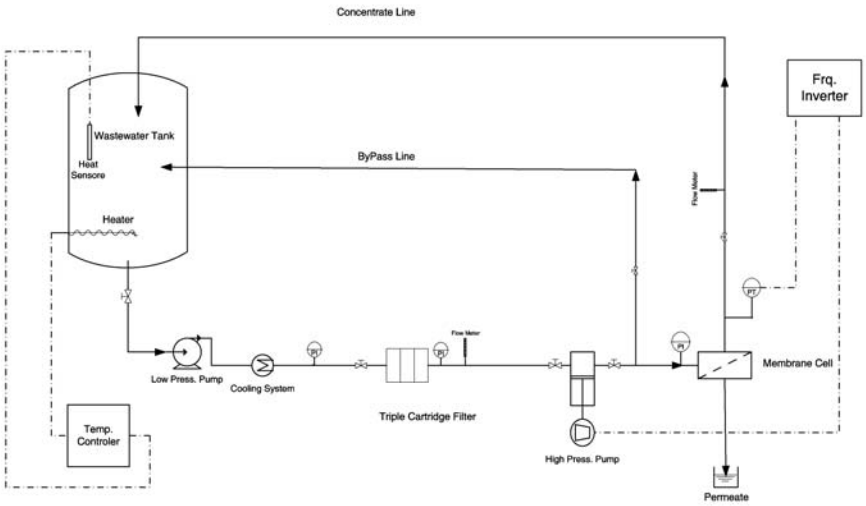

Fig. 1. Scheme of reverse osmosis pilot

are returned to the waste water tank to fix wastewater quality during the tests. To obtain precise result, pressure and temperature must be controlled. It is necessary to use frequency Inverter for pressure control and temperature controller with cooling system for adjust and control of temperature at 30 ± 0.5 ºC.

To conduct the study; TORAY osmosis membrane, model TM 810 for sea water is used.

Procedure and experiments: To start the experiment, wastewater tank is filled with ion regeneration wastewater and low pressure pump is put into operation; then, using bypass valve and the valve installed after membrane cell, we try to adjust flow and pressure according to predetermined figures. The process continues with fixed pressure and flow, with the use of frequency inverter. Fig. 2 shows the pilot plant.

Fig. 2. Pilot plant of the research

In this study two variables, pressure and cross flow velocity, have been chosen at 3 levels and each run of experiment continues for 5 h. Nine experiments have been done, to obtain the maximum flux and the minimum conductivity. Levels are 20, 25 and 30 bar for pressure and 0.27, 0.54 and 0.81 m/s for cross flow velocity. To ensure the lowest turbidity of wastewater, after cartridge filters silt density index (SDI) test has been performed and most of times the SDI has been below 4. Method of SDI test is available in the references[9].

Also to ensure that oxidizing agents are not present, the oxidation reduction potential (ORP) test has been performed and ORP has always been below 175 mv which is suitable for polymer membranes.

RESULTS AND DISCUSSION

Tables 1-3 shows, results of 9 experiments regarding pressure and cross flow velocity. Table-4 indicates results of 5th h of each experiment. It is necessary to mention that the feed of the pilot is regeneration wastewater with EC = 14400 μs/cm and pH = 7. In Table-5, parameters for regeneration wastewater and permeate are compared.

TABLE-1
FLUX AND EC AT 20 BAR PRESSURE AND THREE CROSS FLOW VELOCITY (0.27, 0.54, 0.81 m/s)

Pressure (bar)	Cross flow velocity (m/s)	Time (min)	EC (μS/cm)	Flux (L/m^2 h)
20	0.27	30	1800	28.06
		30	1505	28.80
		60	1395	28.94
		60	1440	29.54
		60	1432	29.17
		60	1430	29.54
20	0.54	30	1630	31.02
		30	1591	31.76
		60	1300	31.75
		60	1280	31.01
		60	1250	31.75
		60	1286	31.38
20	0.81	30	1508	33.32
		30	1200	33.96
		60	1210	34.11
		60	1190	34.70
		60	1175	33.97
		60	1170	34.34

From Tables 1-3, it is find out that in the first 0.5 h of all experiments, the flux of permeate is low and the conductivity is high due to the unsteady conditions. after 5 h, the flux of permeate and the conductivity are stable. So, the 5th h is selected as

TABLE-2
FLUX AND EC AT 25 BAR PRESSURE AND THREE CROSS FLOW VELOCITY (0.27, 0.54, 0.81 m/s)

Pressure (bar)	Cross flow velocity (m/s)	Time (min)	EC (μS/cm)	Flux (L/m^2 h)
25	0.27	30	1630	32.64
		30	1050	33.96
		60	960	34.70
		60	947	34.34
		60	950	33.97
		60	948	33.97
25	0.54	30	1510	38.40
		30	750	38.84
		60	698	39.13
		60	690	39.21
		60	695	38.77
		60	695	39.13
25	0.81	30	1205	42.09
		30	750	42.83
		60	530	43.20
		60	522	43.56
		60	518	43.20
		60	520	43.56

TABLE-3
FLUX AND EC AT 30 BAR PRESSURE AND THREE CROSS FLOW VELOCITY (0.27, 0.54, 0.81 m/s)

Pressure (bar)	Cross flow velocity (m/s)	Time (min)	EC (μS/cm)	Flux (L/m^2 h)
30	0.27	30	1520	38.40
		30	1105	40.61
		60	920	39.73
		60	910	39.87
		60	908	40.09
		60	907	39.87
30	0.54	30	1280	45.01
		30	950	45.75
		60	600	46.52
		60	585	46.52
		60	590	46.89
		60	585	46.89
30	0.81	30	1110	45.78
		30	735	46.59
		60	530	47.26
		60	520	48.59
		60	522	48.88
		60	520	48.73

a base for comparison of all experiments. Based on the mentioned facts, the best situation of experiment is the higher flux and the lower conductivity.

TABLE-4
COMPARISON OF 5TH HOUR OF THREE PRESSURES AND THREE CROSS FLOW VELOCITIES

Pressure (bar)	Cross flow velocity (m/s)	EC (µS/cm)	Flux (L/m^2 h)
20	0.27	1430	29.54
	0.54	1286	31.38
	0.81	1170	34.34
25	0.27	948	33.97
	0.54	695	39.13
	0.81	520	43.56
30	0.27	907	39.87
	0.54	585	46.89
	0.81	520	48.73

TABLE-5
ANALYTICAL RESULTS OF WASTEWATER FROM ION EXCHANGE REGENERATION PROCESS BEFORE AND AFTER TREATMENT USING REVERSE OSMOSIS

Parameter	Wastewater before treatment	Permeate after treatment	Removal (%)
Sodium (mg/L)	451.4	22.4	95
Potassium (mg/L)	8.4	1.6	81
Calcium (mg/L)	336.2	9.7	97
Magnesium (mg/L)	196.7	5.9	97
Ammonium (mg/L)	1500	67.1	96
Total hardness (mg/L)	1650.2	48.4	97
Chloride (mg/L)	7551.2	34.3	95
Phosphate (mg/L)	0.08	Nil	-
Silica (mg/L)	7.0	Nil	-
Nitrate (mg/L)	5600	412	93
COD (mg/L)	16.2	Trace	-
Bicarbonate (mg/L)	71.1	40.4	43
Sulphate (mg/L)	892.8	42.4	88
Iron (total)	Nil	Nil	-
Copper	Nil	Nil	-
Electrical conductivity (µS/cm)	14400	585	96

According to Table-4, when pressure is 30 bar and the cross flow velocity is 0.54 and 0.81 m/s, the amount of flux is higher and the conductivity is the minimum. Although it is obvious that in the higher flux and lower conductivity condition, probability of fouling and need for cleaning is more than moderate flux and conductivity. Therefore, selection of 0.54 m/s for cross flow velocity is better than 0.81 m/s; as approved by Toray guideline the maximum flux for seawater membrane is about 45 L/m^2 h that is nearly similar to flux for condition of 30 bar pressure and 0.54 m/s cross flow velocity.

Table-5 compares analysis of ion exchange regeneration wastewater and permeate obtained under the condition of 30 bar pressure and 0.54 m/s cross flow velocity regarding some parameters and the percentage of dissolved solids removal is over 95 %.

Conclusion

From these studies, it is concluded: (a) About 1000 m^3/day ion exchange regeneration wastewater is produced in Shiraz Petrochemical Complex which is almost clear, but with high dissolved solids (Conductivity = 14000-20000 µs/cm). (b) Industrial wastewater from ion exchange regeneration can be treated satisfactorily; and during this study, conductivity has been decreased from 14400 µs/cm to about 585 µs/cm, under 30 bar pressure and 0.54 m/s cross flow velocity and the flux is 46.89 L/m^2 h. (c) Considering results of Table-5, the percentage of dissolved solid removal is almost higher than 95 %. This treated wastewater can be used for irrigation or other purposes.

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REFERENCES

1. J. Crittenden, Water Treatment Principles and Design, John Wiley (2005).
2. Metcalt & Eddy; in ed.: G. Tchobanoglus, Wastewater Engineering, Treatment and Reuse, McGraw Hill, edn. 4 (2003).
3. M. Gryta, K. Karakulski and A. Morawski, *Desalination*, **197**, 50 (2006).
4. T. Wintgens, T. Melin, A. Schafer, S. Khan, M. Muston, D. Bixo and C. Thoeye, *Desalination*, **178**, 1 (2005).
5. M.S. Mohsen, *Desalination*, **167**, 75 (2004).
6. F. Buhrmann, M. van der Waldt, D. Hanekom and F. Finlayson, *Desalination*, **124**, 263 (1999).
7. R. Sheikholeslami and S. Zhou, *Desalination*, **132**, 337 (2000).
8. S.B. Sadr Ghayeni, P.J.Beatson, R.P. Schneider and A.G. Fane, *Desalination*, **116**, 65 (1998).
9. W. Byrne, Reverse Osmosis A Practical Guide for Industrial Users, Tall Oaks, edn. 2 (2002).

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