Spiral Wound Reverse Osmosis Membranes for the Recovery of Phenol Compounds-Experimental and Parameter Estimation Studies

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Abstract: Problem statement: Reverse osmosis is increasingly used as a separation technique in chemical and environmental engineering for the removal of organics and organic pollutants present in waste water. The removal of an organic compound, namely phenol, using a polyamide membrane was investigated in this study. Waste water containing phenol present a serious environmental problem and increasing attention is being given for its removal using RO membranes. Objective of this study is to (i) generate experimental data related to the removal of phenol using a spiral wound polyamide membrane (ii) analyze the performance of the membrane using solution-diffusion model and validate the model with the experimental data. **Approach:** Experiments were conducted on a laboratory scale spiral wound polyamide RO module. The permeate concentrations and rejection coefficient values were measured for various feed inlet pressures and feed concentrations. The total feed flow rate, 3.33×10^{-4} m^3 sec^{-1} (20 LPM) was not varied. The transport of solvent and solute through the membranes were analyzed using solution-diffusion model taking concentration polarization into account. **Results:** By varying inlet pressures from 4-14 kg$_f$ cm^{-2}) and feed concentrations of phenol from 200-1100 ppm, the rejection coefficients of the membrane were measured and found to vary from 64-91%. The solvent and solute transport parameters were determined by a graphical procedure using the experimental data and its values were 5.9×10^{-7} (m atm^{-1}) and 6.54×10^{-7} (m sec^{-1}) respectively. **Conclusion:** The model and the estimated parameter values were validated with the experimental data. The model was able to predict the rejection within 10% error. In view of the fact that not much information is available on the usage of spiral wound polyamide RO membrane modules for the removal of phenolic compounds, it may be concluded that the experimental results reported in this study is very significant in the scale up and design of RO system for treatment of industrial effluents containing phenolic compounds.

Key words: Reverse osmosis, polyamide membrane, spiral wound module, phenol

INTRODUCTION

Reverse Osmosis (RO) processes have been widely used for separation and concentration (recovery) of solutes in many fields. The use of RO in the treatment of various effluents of chemical (Bodalo-Santoyo *et al.*, 2003; 2004), petrochemical, electrochemical (Koops *et al.*, 2001), food, paper and tanning industries as well as in the treatment of municipal waste waters have been reported in the literature (Schutte, 2003). Also, the removal of individual contaminants by RO has been studied by very few researchers (Murthy and Gupta, 1999; Moresi *et al.*, 2002; Arsuaga *et al.*, 2006). These individual contaminants, though present at low level can cause problems. The potential of these RO processes to remove organic contaminants was first

demonstrated by Chian *et al.* (1975). A number of studies (Kimura *et al.*, 2003; Xu *et al.*, 2005; Bellona *et al.*, 2004; Yoon and Lueptow, 2006) have been reported on the application of RO for the removal of organics such as endocrine disrupting chemicals, plastic additives, pesticides, pharmaceutically active compounds (PhaC's), benzene and toluene. Typical RO membranes like cellulose acetate and polyamide show very high rejection of above 0.98 for inorganic salts like NaCl, Na$_2$SO$_4$. However, for organics, the rejection is reported to be lower and varies widely in the range of 0.3-0.96 (Pozderivic *et al.*, 2006; Senthilmurugan and Gupta, 2006). Phenol and its derivatives are important compounds used extensively in the synthesis of many organic compounds (Senel *et al.*, 2006). Phenolic compounds are found in industrial wastes from coal

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gas, gas coking, petroleum and pharmaceutical industries as well as in a wide variety of industrial wastes from process involving the use of phenol derivatives resembling those of phenol. In the present investigation, phenol is separated from synthetic aqueous binary solutions using a reverse osmosis thin film composite polyamide membrane and the separation data are analyzed to estimate membrane parameters.

Models that adequately describe the performance of RO membranes play a very significant role in the design of RO processes. Many mechanistic and mathematical models have been proposed to describe RO membranes. Two of the widely used models that describe the transport through the RO membrane are the solution diffusion model proposed by Lonsdale *et al.* (1965) and the irreversible thermodynamics model proposed by Kedem and Spiegler (1966). These models could be used to predict the solute and solvent transport characteristics of the membranes with reasonable success. In this research, the solution diffusion model will be used. The membrane parameters estimated using the experimental data generated will be utilized in this membrane transport model developed for the theoretical estimation of the rejection capabilities of the membrane.

MATERIALS AND METHODS

The Perma-TFC polyamide RO membrane in Spiral wound configuration (supplied by Permionics, Vadodara, India) was used in this study. The membrane has an effective area of 0.75 m^2 and the module length is 21" and diameter is 2.5 inches. The membrane is capable of withstanding pH values in the range of 2-12, Pressures up to 20 atm and temperatures up to 50°C. The flow diagram of the pilot plant unit is shown in Fig. 1.

The experimental RO system consisted of a Polyamide membrane kept inside a stainless steel cylindrical housing capable of withstanding high pressures. A feed tank of 80 L capacity made of stainless steel is provided for storage and supply of the feed to the system as well as for the collection of the recycled Permeate and Retentate. A high Pressure Pump capable of developing a pressure up to 300 Psi (20 atm) was installed for transporting the feed liquid through the membrane system at a fixed flow rate of 20 LPM. A micron filter installed in the upstream side of the membrane unit prevented entry of suspended solid particles which otherwise would damage the membrane. A manual needle valve was provided at the outlet of the retentate line to pressurize the feed liquid to a desired pressure indicated by pressure gauges installed in both the feed and retentate lines.
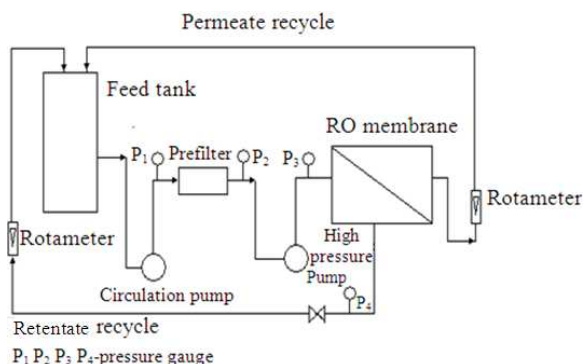

Fig. 1: Flow diagram of the pilot plant membrane unit

The permeate and the concentrate flow rates were measured by means of two glass rotameters containing metal floats. Since the feed gets heated by the high pressure pump, it was necessary to cool the feed reservoir by circulating cooling water through a cooling coil in the feed tank to keep the temperature at 35±2°C.

Solutions were prepared by dissolving definite quantities (in ppm) of pure phenol (>99.5% purity) in raw water in the feed tank of 80 liters capacity. The flow rate of the feed solution was set constant at 3.33×10^{-4} m^3 sec^{-1} (20 LPM. Operation was in a recycle mode, i.e., the feed-reject solution as well as permeate were recycled to the feed tank (closed loop). Samples of feed, permeate and retentate were taken at regular intervals during the run and the unit was operated for sufficient time to ensure steady state conditions. The concentrations of feed, permeate and retentate samples were analyzed using HPLC (Make: Perkin Elmer, USA) equipped with an UV detector and C-18 column. The mobile phase used was Acetonitrile-water (50:50%) delivered at a constant flow rate of 1.5 mL min^{-1}. The samples were analyzed soon after collection. A set of three samples were collected at a time and checked for consistency. The experiments were carried out using binary mixtures containing phenol compound in water of varying solute concentration in the range of 2.125×10^{-3}-10.6×10^{-3} Kmol m^{-3} (200-1100 ppm) and the feed inlet pressure in the range of 4-15 kg$_f$ cm^{-2}. The membrane system was first run with raw water to determine the solvent (water) transport parameter. Experiments are repeated for different feed concentrations of phenol. A total of 29 sets of readings obtained from these experiments are given in Table 1.

Theory: The solution diffusion model with concentration polarization is used for solute and solvent transport through the membrane.

Table 1: Experimental data obtained for rejection of phenol for feed flow rate $F_i = 3.33 \times 10^{-4}\,\text{m}^3\,\text{sec}^{-1}$

Sr. No.	$C_i \times 10^3$ (kmol m⁻³)	P_i (atm)	P_o (atm)	T (°C)	$C_p \times 10^3$ (Kmol m⁻³)	$C_o \times 10^3$ (Kmol m⁻³)	$F_p \times 10^6$ (m³ sec⁻¹)	$F_o \times 10^4$ (m³ sec⁻¹)	R
1	2.125	4.93	2.99	32.5	0.831	2.35	3.53	3.30	0.6462
2	2.125	6.90	4.96	33.1	0.647	2.37	5.20	3.30	0.7270
3	2.125	8.90	6.90	33.0	0.580	2.41	7.20	3.20	0.7593
4	2.125	10.90	8.90	33.2	0.524	2.45	9.60	3.16	0.7861
5	2.125	14.80	12.90	34.0	0.349	2.78	12.20	3.06	0.8745
6	4.250	4.93	2.99	32.2	1.240	5.30	3.30	3.33	0.7660
7	4.250	6.90	4.96	32.8	1.050	5.62	5.00	3.30	0.8132
8	4.250	8.90	6.90	33.5	0.600	5.60	7.00	3.25	0.8929
9	4.250	10.90	8.90	33.9	0.720	5.70	8.50	3.16	0.8737
10	4.250	12.80	10.90	34.5	0.685	5.74	10.25	3.00	0.8807
11	4.250	14.80	10.90	34.5	0.718	5.82	12.25	3.08	0.8766
12	6.375	4.93	2.99	32.5	1.400	6.94	3.20	3.33	0.7983
13	6.375	6.90	4.96	33.0	1.240	6.95	4.33	3.25	0.8216
14	6.375	8.90	6.90	33.2	1.176	7.11	5.93	3.20	0.8346
15	6.375	10.90	8.90	33.5	0.940	7.12	7.00	3.16	0.8680
16	6.375	12.80	10.90	33.8	0.870	7.24	8.70	3.08	0.8798
17	6.375	14.80	12.90	34.0	0.630	7.33	11.10	3.00	0.9141
18	8.500	4.93	2.99	32.0	2.610	8.88	3.13	3.20	0.7061
19	8.500	6.90	4.96	32.5	2.220	8.88	4.53	3.16	0.7500
20	8.500	8.90	6.90	32.8	1.930	8.91	6.20	3.13	0.7834
21	8.500	10.90	8.90	33.0	1.600	9.20	8.20	3.08	0.8261
22	8.500	12.80	10.90	33.2	1.470	9.20	9.30	3.03	0.8402
23	8.500	14.80	12.90	33.5	1.400	9.30	11.50	3.00	0.8495
24	10.600	4.93	2.99	31.5	3.090	10.70	2.66	3.25	0.7112
25	10.600	6.90	4.96	32.2	2.520	10.71	4.13	3.16	0.7647
26	10.600	8.90	6.90	32.6	2.020	11.00	5.86	3.13	0.8164
27	10.600	10.90	8.90	32.8	1.830	11.10	7.50	3.08	0.8351
28	10.600	12.80	10.90	32.8	1.690	10.99	9.00	3.00	0.8462
29	10.600	14.80	12.90	33.0	1.400	11.10	10.50	2.91	0.8739

Completely mixed flow pattern is assumed on both the retentate and permeate sides. The pressure on the retentate side of the membrane is taken as the average of feed inlet and outlet pressure. Atmospheric pressure is assumed on the permeate side:

$$\Delta P = [(P_i + P_o)/2] - P_p \tag{1}$$

The working equations of solution diffusion model (Mason and Lonsdale, 1990; Gupta, 1985) are:

$$J_s = (B_s)(C_w - C_P) \tag{2}$$

$$J_b = A_w(\Delta P - \Delta \Pi) \tag{3}$$

$$J_s = J_b C_P \tag{4}$$

Where:
J_s = The solute flux (Kmol m⁻² sec)
J_b = Solvent flux (m³ sec⁻¹ m²) = m sec⁻¹
A_w = The solvent transport parameter (m sec⁻¹.atm)
B_s = The solute transport parameter in m sec⁻¹
ΔP = The pressure difference across the membrane (transmembrane pressure)

$\Delta \Pi$ = The osmotic pressure difference across the membrane

The Osmotic pressure may be linearly related to Concentration (C) by the equation:

$$\Pi(C) = RTC \tag{5}$$

If:
C_w = The concentration at the membrane feed side
C_p = The concentration at the permeate side, then

$$\Delta \Pi = \Pi(C_w) - \Pi(C_p) \tag{6}$$

Intrinsic rejection coefficient:

$$R^\circ = 1 - \left(\frac{C_P}{C_w}\right) \tag{7}$$

Rejection coefficient:

$$R = 1 - \left(\frac{C_P}{C_O}\right) \tag{8}$$

$$\text{Recovery}\,\theta = \left(\frac{F_P}{F_i}\right) \tag{9}$$

and

$$\text{Separation coefficient} = \alpha = \left(\frac{A_w}{B_s}\right) \tag{10}$$

$$M = C_w/C_o \tag{11}$$

Accumulation of the impermeable solutes on the membrane surface leads to the development of a concentration polarization layer which may be determined by the concentration polarization model given by:

$$e^{\left(\frac{J_b}{k}\right)} = \frac{C_w - C_p}{C_b - C_p} \tag{12}$$

Here:

C_b = The concentration of solute in the bulk solution
k = The mass transfer coefficient which is estimated using the correlation as reported by Wankat (1990):

$$k = 1.177\left(\frac{U_b D^2}{hL}\right)^{1/3} \tag{13}$$

Where:

D = The diffusivity of the solute
U_b = The bulk velocity of the solution
h = The spacing between the plates

Substitution of Eq. 6, 7 and 10 in Eq. 11 gives the following relationship:

$$\frac{J_b}{e^{\frac{J_b}{k}}} = B_s\left[\frac{R}{1-R}\right] \tag{14}$$

Using the experimental values of J_b and R, a plot of $\dfrac{J_b}{e^{\frac{J_b}{k}}}$ Vs $\dfrac{R}{1-R}$ is made to estimate the solute transport parameter (B_S) for both phenol-water and chlorophenol-water solutions. The other membrane parameter, i.e., the solvent transport parameter (A_W) can be found out from a plot of J_b Vs $(\Delta P - \Delta \Pi)$. The values of A_w, B_S and k were substituted in the

theoretical model described earlier and the values of Rejection coefficient R, Permeate concentration C_P and flow rates were determined theoretically.

RESULTS AND DISCUSSION

The experimental separation data's obtained for Phenol-water are presented in Fig. 2 and 3, where the observed Rejection coefficient (R) and the permeate concentration are plotted against the inlet pressure, Pi for different feed concentrations. The rejection capabilities of the membrane for phenol are shown in the Fig. 2, where the measured rejection coefficient was plotted against the applied pressure across the membranes. It was found that the value of R increases with the increasing applied pressure. The maximum rejection obtained is around 90% for phenol. Figure 3 shows the variation of permeate concentration with inlet pressure for various feed concentration of phenol.
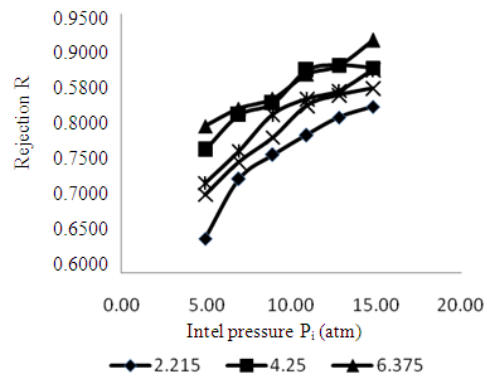

Fig. 2: Rejection Vs Inlet pressure for feed concentrations, $C_i \times 10^3$(kmol m^{-3}) of phenol
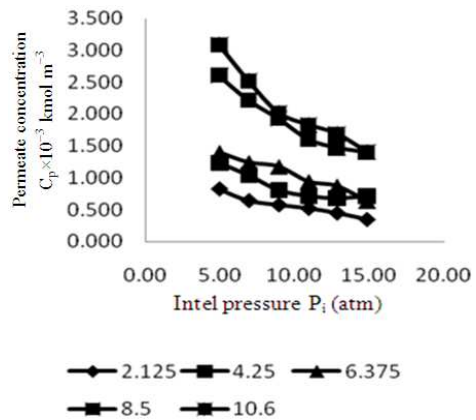

Fig. 3: Permeate concentration Vs Inlet pressure at various feed concentrations $C_i \times 10^3$ (kmol m^{-3}) of phenol
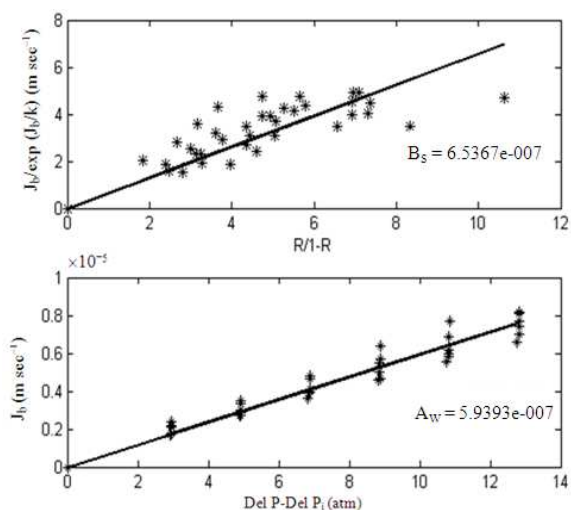
Fig. 4: Graphical plots for the estimation of parameters A_w and B_s

Table 2: Experimental and theoretical data showing rejection characteristics for phenol separation

Sr. No.	$C_i \times 10^3$ (kmol m^{-3})	P_i (atm)	R (exp)	R (theory)	Error (%)
1	2.125	6.93	0.646	0.642	0.59
2	2.125	8.90	0.727	0.698	4.00
3	2.125	10.90	0.759	0.733	3.45
4	2.125	12.90	0.786	0.758	3.62
5	2.125	16.80	0.874	0.790	9.70
6	4.250	6.93	0.766	0.680	11.23
7	4.250	8.90	0.813	0.737	9.38
8	4.250	10.90	0.893	0.772	13.53
9	4.250	12.90	0.874	0.796	8.88
10	4.250	14.80	0.881	0.813	7.67
11	4.250	14.80	0.877	0.813	7.25
12	6.375	6.93	0.798	0.696	12.83
13	6.375	8.90	0.822	0.754	8.21
14	6.375	10.90	0.835	0.790	5.39
15	6.375	12.90	0.868	0.814	6.27
16	6.375	14.80	0.880	0.830	5.63
17	6.375	16.80	0.914	0.844	7.68
18	8.500	6.93	0.706	0.704	0.30
19	8.500	8.90	0.750	0.764	-1.83
20	8.500	10.90	0.783	0.800	-2.08
21	8.500	12.90	0.826	0.824	0.28
22	8.500	14.80	0.840	0.840	-0.03
23	8.500	16.80	0.849	0.854	-0.52
24	10.600	6.93	0.711	0.708	0.42
25	10.600	8.90	0.765	0.770	-0.63
26	10.600	10.90	0.816	0.806	1.26
27	10.600	12.90	0.835	0.830	0.57
28	10.600	14.80	0.846	0.847	-0.11
29	10.600	16.80	0.874	0.861	1.52

The permeate concentration decreases steeply with increase in inlet pressure. Also, it may be found that for a particular inlet pressure, the permeate concentration increases with increase in feed concentration. It is evident from the Table 1 that permeate flux is seen to be decreasing with increasing feed concentration. This is because the osmotic pressure increases with increasing feed concentration and this reduces the driving force for the mass transfer, thus leading to lower permeate flux. Also, since the driving force for the mass transfer increases for higher feed pressures, the permeate flux is seen to increase with increasing applied pressures.

Experimental data obtained from the pilot plant RO spiral wound module for various operating conditions were used to obtain parameters of these systems using our parameter estimation program. The value of mass transfer coefficient 'k' using the correlation given in equation 13 is 12.230×10^{-6} m sec^{-1}. The solvent transport coefficient (A_W) was determined by using the pure water permeability data and were also verified with a plot shown in Fig. 4 and its value is found to be constant for all cases i.e., 5.9×10^{-7} (m atm^{-1}). The value of solute transport (B_s) parameter is found to be 6.54×10^{-7} (m sec^{-1}) for phenol as obtained from Fig. 4. These estimated parameters were used for the prediction of separation data as shown in Table 2 and compared with the experimental values obtained earlier (Table 1). The model is able to predict the rejection within error of 10%.

CONCLUSION

The research reported in this study dealt with product recovery and concentration reduction of pollutants in industrial wastewater using a RO spiral wound membrane. The pollutant investigated was phenol. The membrane was operated in a continuous steady state mode and the experimental data were obtained for the removal of phenol for a wide range of solute concentration and feed inlet pressures. The solution diffusion model with concentration polarization was used for solute and solvent transport through the membrane. Completely mixed flow pattern was assumed on both the retentate and permeate sides. The model was tested for its consistency and validated with the experiment data obtained for phenol. Also, the solute and solvent transport parameters of the membrane for phenol were estimated and used to predict the separation data. These predicted data were then compared with the experimental values and the percentage error was calculated.

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