CHAPTER IV

RESULTS AND DISCUSSION

The membrane experimental results and the data interpretations are presented in the following sections.

4.1 Concentration Polarization

### 4.1.1 Effects of operating transmembrane pressure and fluoride concentration in feed water on the permeate flux

The permeate flux can be determined as followed:

$$\text{Permeate flux } (m^3/m^2\text{-s}) = \frac{10 \text{ ml of permeate water}}{A \times T}$$

where A = the membrane area in the membrane module, $m^2 = 60 \times 10^{-4}$ m^2, and T = the time required for 10 ml of permeate water (sec)

The fluxes of the UTC-70 membrane as a function of operating time at 0.1, 0.3, and 0.5 MPa until the permeate water reached 1,000 ml. are shown in Figure 4.1.

For the fluoride concentrations in the feed solution at 0, 10, 25, and 50 mM, the range of the operating time until the permeate water reached 1,000 ml at 0.1, 0.3, and 0.5 MPa was 22.5 – 32 hr, 6-8 hr, and 3.5-6.5 hr, respectively. The results demonstrated that the lowest operating time was at 0.5 MPa, the highest operating transmembrane pressure.
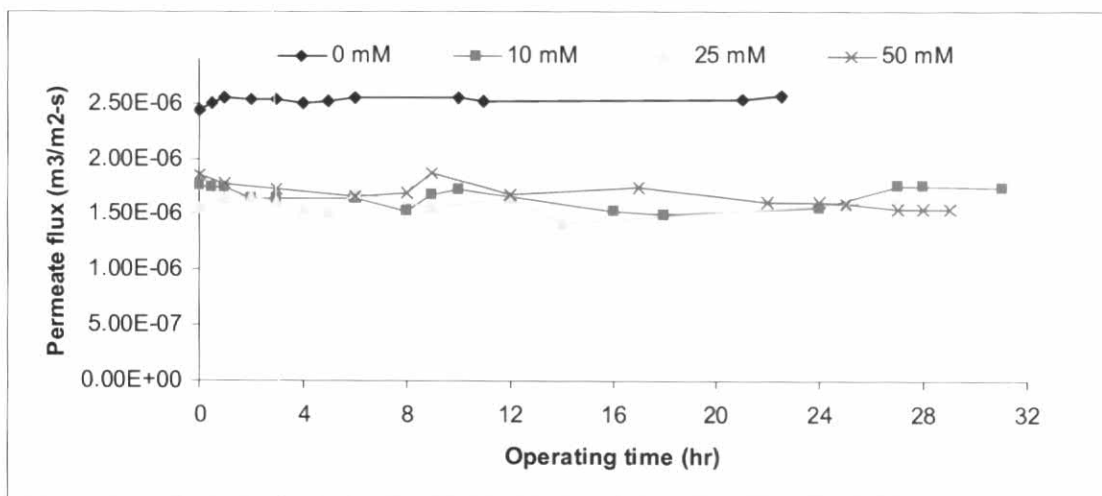
(a) Permeate flux as a function of operating time at 0.1 MPa
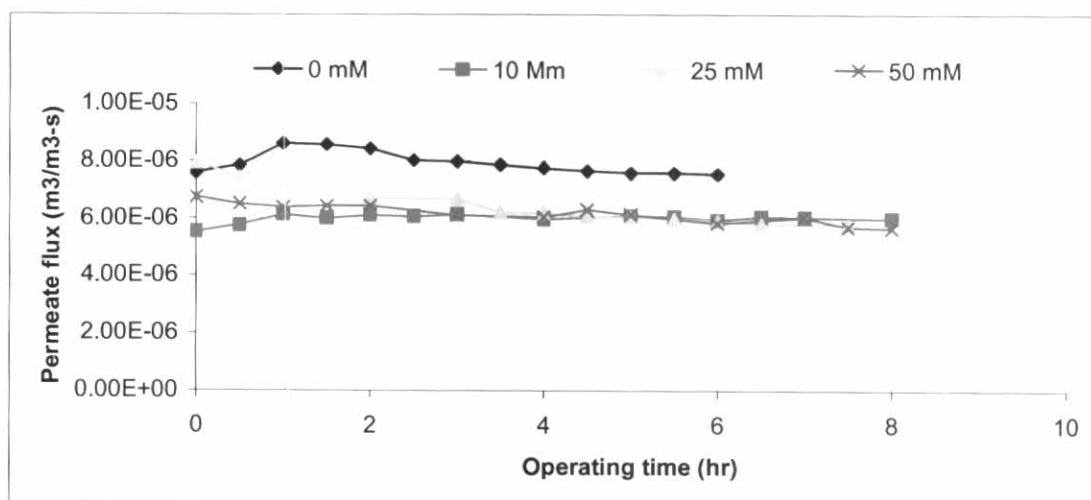
(b) Permeate flux as a function of operating time at 0.3 MPa
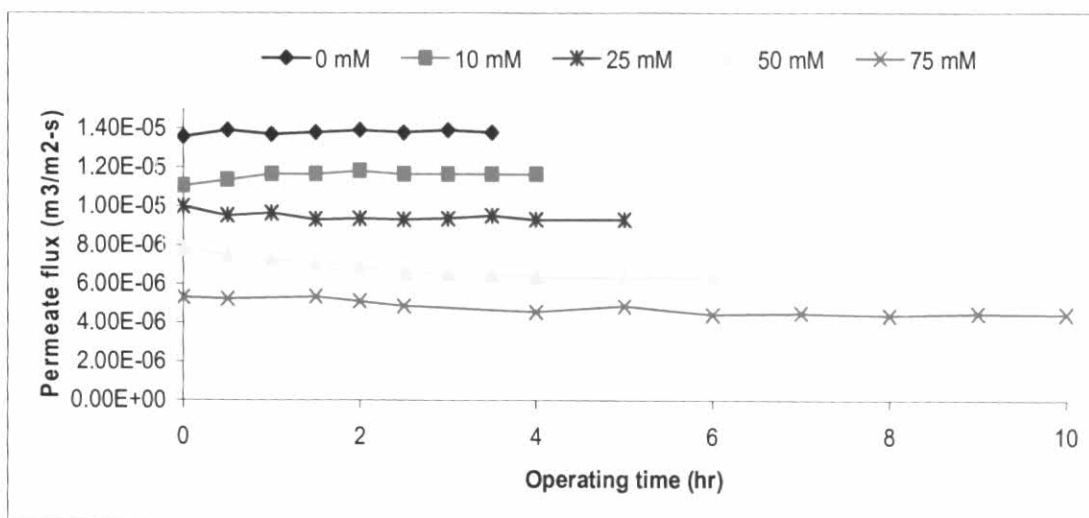
(c) Permeate flux as a function of operating time at 0.5 MPa

Figure 4.1 Permeate flux as a function of operating time

Figure 4.2 illustrates the effects of operating transmembrane pressure on the permeate flux of the UTC-70 membrane. The permeate fluxes obtained at 1,000 ml of permeate water from the UTC-70 membrane under the operating transmembrane pressures of 0.1, 0.3, and 0.5 MPa were investigated. When the fluoride concentration in the feed solution was 0 mM, the permeate fluxes were observed at 0.256×10^{-5}-1.380×10^{-5} m^3/m^2-s. When the feed solutions contained 10, 25, and 50 mM, the permeate fluxes were in the range of 0.174×10^{-5}-1.160×10^{-5}, 0.155×10^{-5}-0.930×10^{-5}, and 0.153×10^{-5}-0.630×10^{-5} m^3/m^2-s, respectively.
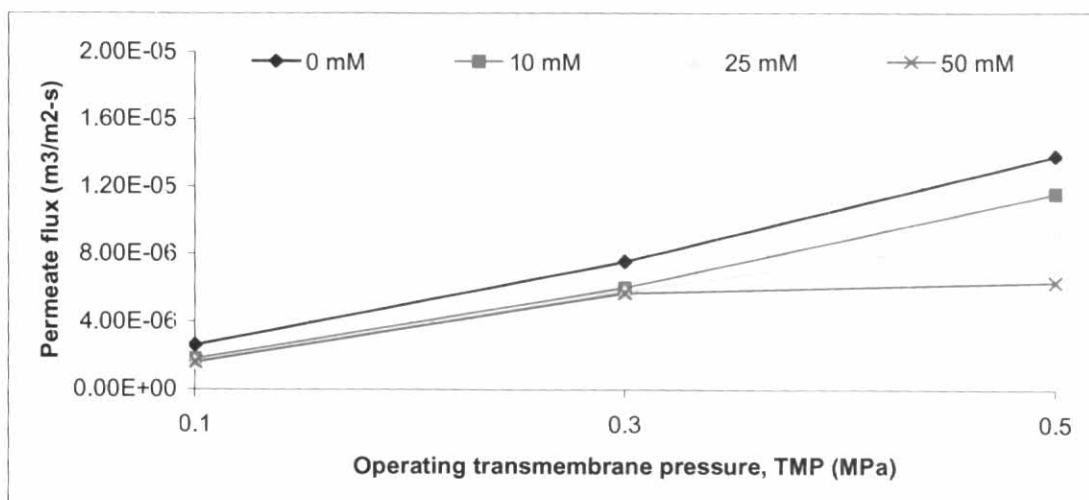
Figure 4.2 Permeate flux as a function of operating transmembrane pressure

The results found that the highest transmembrane pressure at 0.5 MPa presented the highest permeate flux. It was observed that the permeate fluxes of all feed solutions increased with the increment of the operating transmembrane pressure. As a result, the solution-diffusion model could be used to explain the relationship between the permeate flux and the transmembrane pressure by following equation:

$$(J_v)_{solute} = k_w [\Delta P - \Delta \pi] \qquad (4\text{-}1)$$

According to the equation, it can be found that the permeate flux (J_v) increased with the applied transmembrane pressure (ΔP), which is related with the study of Bhattacharyya et al., 1992 and Williams, M.E., 2003. It was reported that the operating pressure affected the performance of the membrane in the membrane separation processes.

At operating transmembrane pressure of 0.1, 0.3, and 0.5 MPa, the different fluoride concentrations in feed water presented different of permeate fluxes. Due to the osmotic pressure, the fluoride concentration at 0 mM had the highest permeate flux, followed by those at 10, 25, and 50mM, respectively. The osmotic pressure ($\Delta \pi$) of 10 mM is lower than 25 and 50 mM, respectively. In Equation (4-1), the permeate flux decreased while the osmotic pressure increased.

4.1.2 Mass transfer coefficient (k)

The fluoride concentration in the permeate water and concentrated water were measured and the osmotic pressures of each of the runs were calculated by using Equation (2-3). The results are shown in Table 4.1.

The mass transfer coefficient (k) was calculated by substituting the results in Equation (2-5). It was found that the mass transfer coefficient at 0.1, 0.3, and 0.5 MPa was in the range of 4.13×10^{-5}-5.32×10^{-5}, 3.47×10^{-5}-5.40×10^{-5}, and 2.85×10^{-5}-3.96×10^{-5} m/s, respectively.

Figure 4.3 illustrates the average mass transfer coefficient values of various operating transmembrane pressures. It was found that the average k values of NaF at 0.1, 0.3, and 0.5 MPa were 4.79×10^{-5}, 4.12×10^{-5}, and 3.24×10^{-5} m/s, respectively. Hence, the boundary layer thicknesses (δ) of 0.1, 0.3, and 0.5 MPa were estimated to be 2.92×10^{-5}, 3.40×10^{-5}, 4.32×10^{-5} m, respectively.

According to the Equation (2-5), it can be found that the mass transfer coefficient (k) decreased with the increasing of transmembrane pressure. Wongrueng (2007) found that the mass transfer coefficient at 0.8 MPa of NaF was $(3.20 \pm 0.01) \times 10^{-5}$ m/sec. It was indicated that the transmembrane pressure has an effect on the mass transfer coefficient.

$$k = \frac{\left(J_v\right)_{solute}}{\ln\left\{\dfrac{\Delta P}{\pi_B - \pi_P} \cdot \left[1 - \dfrac{\left(J_v\right)_{solute}}{\left(J_v\right)_{H_2O}}\right]\right\}}$$
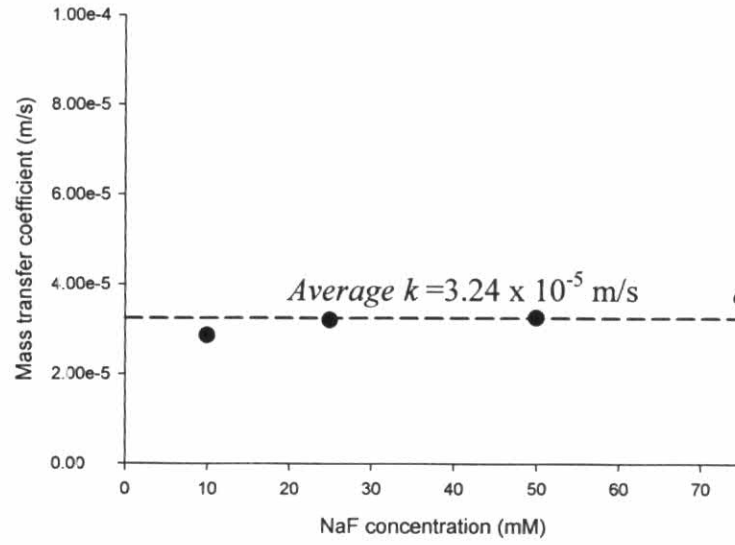
(2-5)

The average k values and the boundary thickness of 0.1, 0.3, and 0.5 MPa were then selected for use in the membrane fouling experiment.
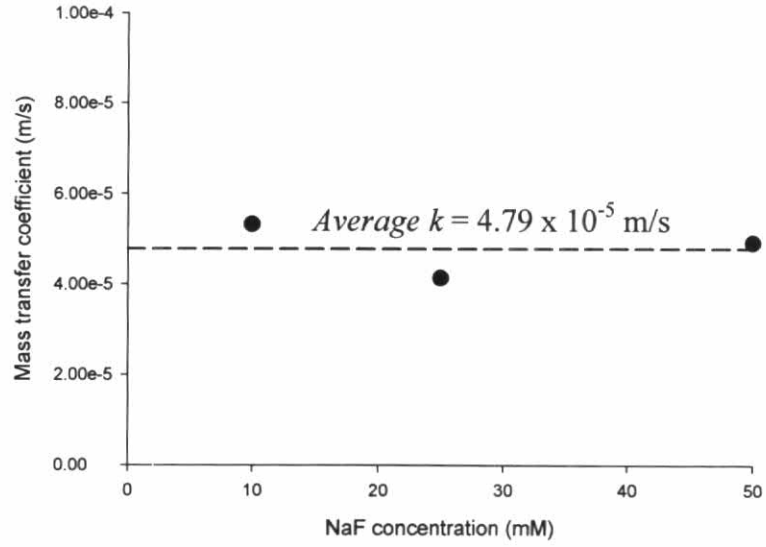
(a) Average mass transfer coefficient of 0.1 MPa
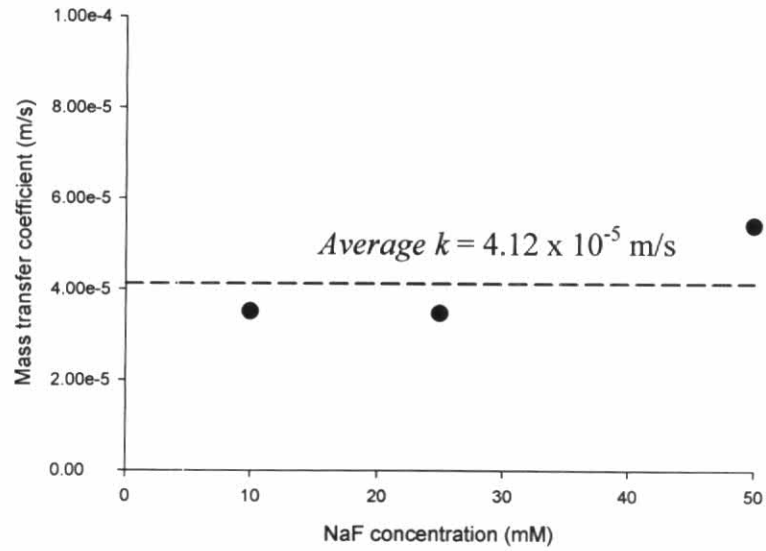
(b) Average mass transfer coefficient of 0.3 MPa

(c) Average mass transfer coefficient of 0.5 MPa

Figure 4.3 Average mass transfer coefficients of various operating transmembrane pressures

Table 4.1 Osmotic pressure and permeate flux results

Sample	TMP (MPa)	Concentrated water (C$_B$)		Permeate water (C$_P$)		$\Delta\pi$	Permeate flux J_v x 10^5
		mM	π_B	mM	π_P	$\pi_B - \pi_P$	m^3/m^2-s
C1	0.1	0.00	0.000	0.00	0.000	0.000	0.256
C2	0.1	9.71	0.045	3.01	0.014	0.031	0.174
C3	0.1	25.76	0.119	17.54	0.081	0.038	0.155
C4	0.1	52.47	0.241	43.98	0.202	0.039	0.153
C5	0.3	0.00	0.000	0.00	0.000	0.000	0.755
C6	0.3	12.52	0.058	1.32	0.006	0.052	0.599
C7	0.3	23.91	0.110	10.77	0.050	0.060	0.576
C8	0.3	48.78	0.225	33.96	0.156	0.068	0.565
C9	0.5	0.00	0.000	0.00	0.000	0.000	1.380
C10	0.5	11.67	0.054	0.59	0.003	0.051	1.160
C11	0.5	29.40	0.135	3.96	0.018	0.117	0.930
C12	0.5	54.04	0.249	7.42	0.034	0.215	0.630
C13	0.5	86.58	0.399	25.02	0.115	0.284	0.440

4.1.3 Concentration polarization phenomenon

The fluoride concentration on a membrane surface (C_M) can be estimated using the concentration polarization model expressed by Equation (2-4). The average k values of NaF at 0.1, 0.3, and 0.5 MPa were used to estimate the C_M. Table 4.2 shows the experimental results of the C_M, the concentration polarization level (f), the intrinsic rejection (R_{int}), and the observed rejection (R_{obs}).

Table 4.2 The experimental results of the C_M, concentration polarization level (f), intrinsic rejection (R_{int}), and observed rejection (R_{obs})

| Sample	C_B	C_P	C_M	$f = \dfrac{C_M}{C_B}$	R_{int}	R_{obs}
	mM	mM	mM		%	%
C2	9.71	3.01	10.07	1.037	70.1	69.0
C3	25.76	17.54	26.61	1.033	34.1	31.9
C4	52.47	43.98	54.17	1.032	18.8	16.2
C6	12.52	1.32	14.48	1.156	90.9	89.5
C7	23.91	10.77	27.50	1.150	60.8	55.0
C8	48.78	33.96	55.95	1.147	39.3	30.4
C10	11.67	0.59	16.71	1.432	96.5	94.9
C11	29.4	3.96	39.21	1.334	89.9	86.5
C12	54.04	7.42	65.68	1.215	88.7	86.3
C13	86.58	25.02	99.22	1.146	74.8	71.1

(Note: $R_{int} = 1 - C_P/C_M$ and $R_{obs} = 1 - C_P/C_B$)

The results indicated that the concentration of NaF on the membrane surface was higher than that of the bulk solution leading to an increase in the intrinsic rejection rate (R_{int}) which is higher than the observed rejection rate (R_{obs}). In some cases, the precipitation or formation of gel on the membrane surface was reported when the solute concentration exceeded its saturation limit due to the concentration polarization effect. The low concentration polarization level (f) was found at the high feed concentration.
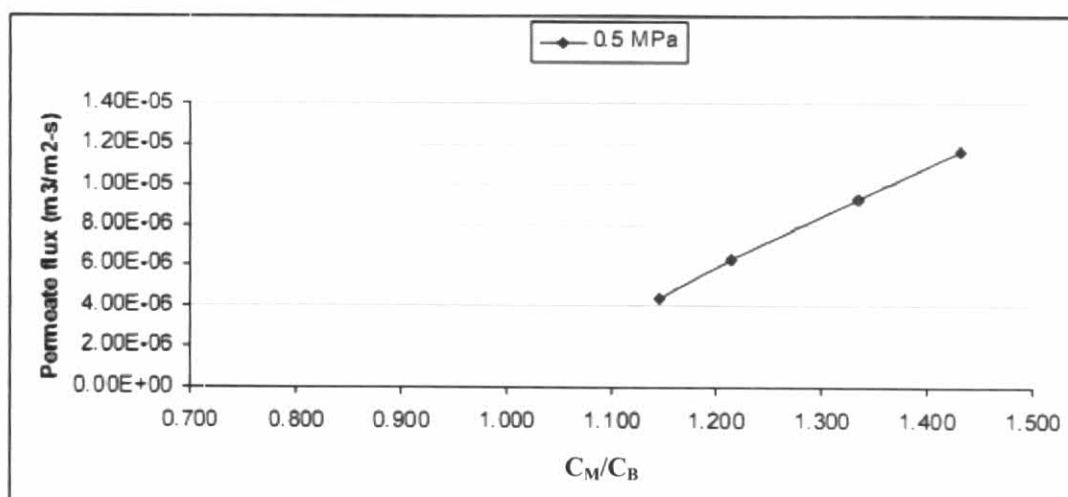
Figure 4.4 illustrates the concentration polarization level (f=C_M/C_B) at 0.1, 0.3, and 0.5 MPa as a function of permeate flux at 1000 ml of permeate water obtained. At transmembrane pressure of 0.1 MPa, it was found that the highest concentration polarization level (f=C_M/C_B) was 1.037. The highest concentration polarization level of 0.3 and 0.5 MPa was 1.156 and 1.432, respectively. The results showed the lowest feed fluoride concentration resulted in the highest degree of concentration polarization (C_M/C_B) and the highest of permeate flux.
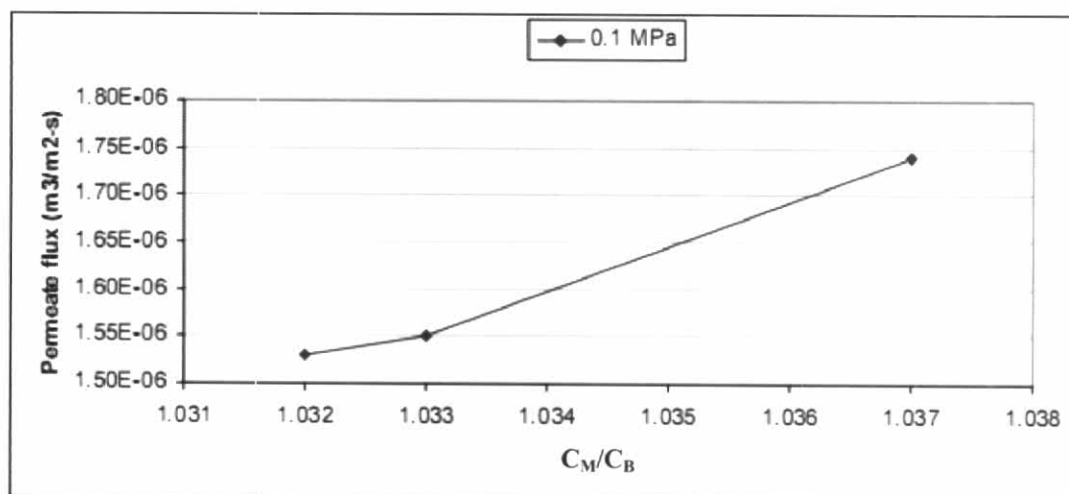
(a) C_M/C_B as a function of permeate flux at 1000 ml of permeate water obtained at 0.1 MPa
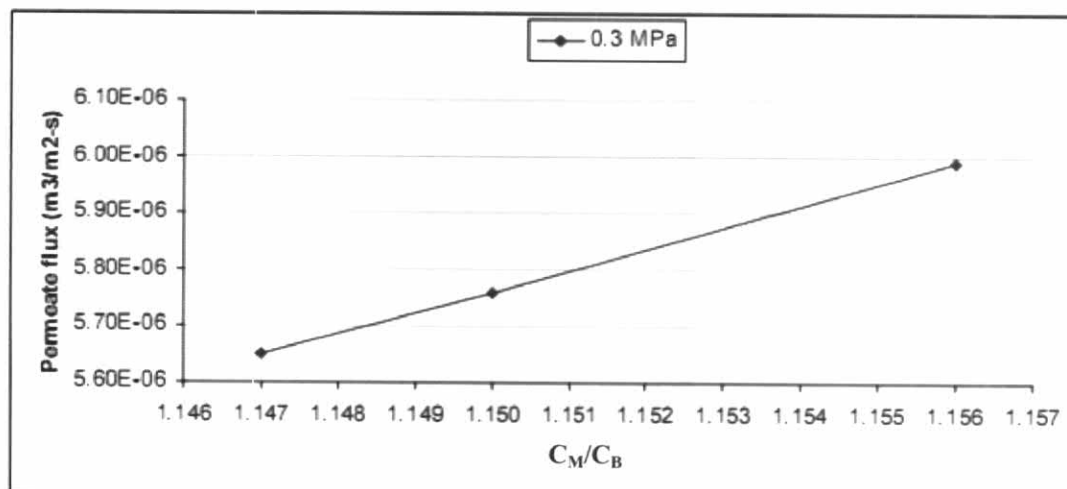

(b) C_M/C_B as a function of permeate flux at 1000 ml of permeate water obtained at 0.3 MPa

(c) C_M/C_B as a function of permeate flux at 1000 ml of permeate water obtained at 0.5 MPa

Figure 4.4 C_M/C_B as a function of permeate flux at 1000 ml of permeate water obtained

The concentration polarization level ($f=C_M/C_B$) as a function of percent rejection is shown in figure 4.5. The highest percent intrinsic rejection of 0.1, 0.3, and 0.5 MPa was 70.1, 90.9, and 96.5%, respectively and the highest percent observed rejection of 0.1, 0.3, and 0.5 MPa was 69.0, 89.5, and 94.9%, respectively. It was found that the highest concentration polarization level provided the highest percent intrinsic rejection and percent observed rejection.
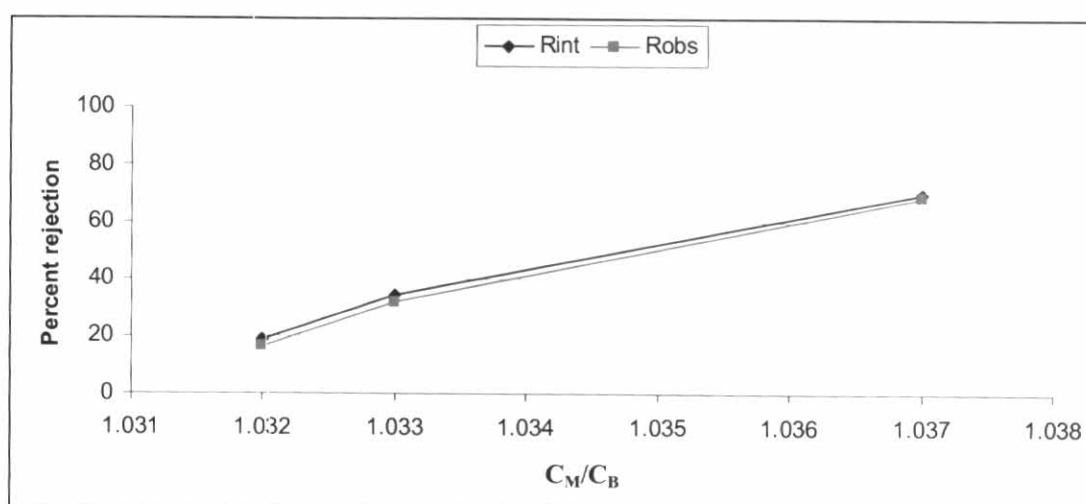
(a) C_M/C_B as a function of percent rejection at 0.1 MPa
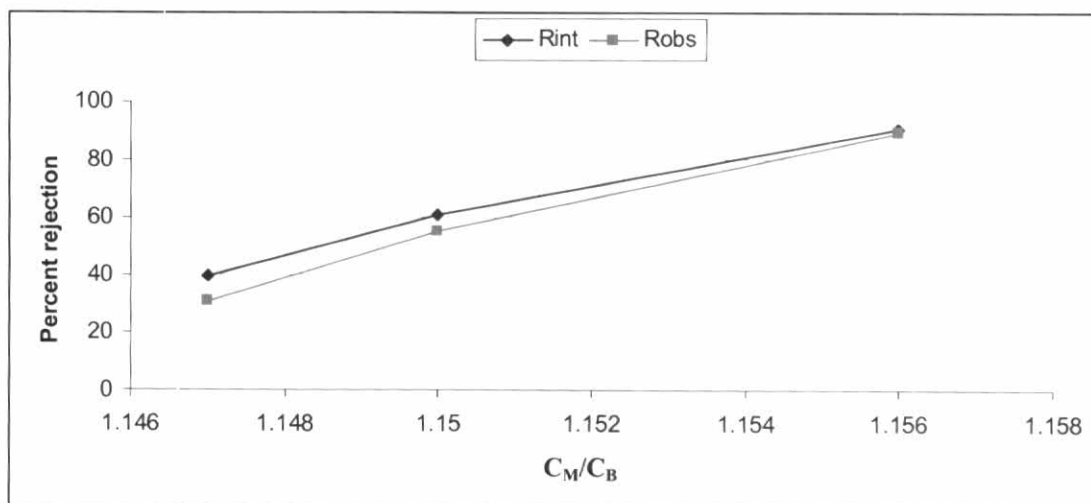
(b) C_M/C_B as a function of percent rejection at 0.3 MPa
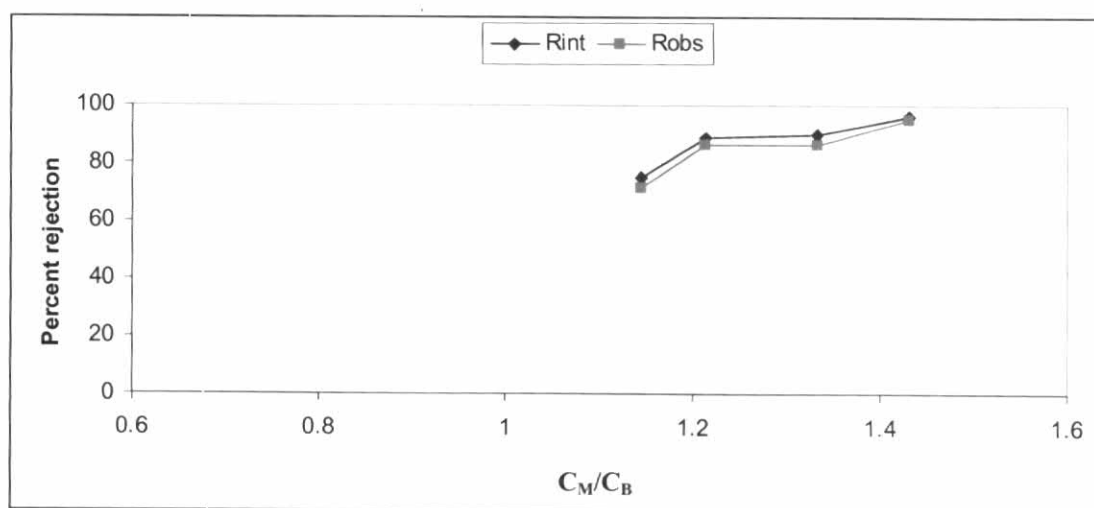
(c) C_M/C_B as a function of percent rejection at 0.5 MPa

Figure 4.5 C_M/C_B as a function of percent rejection

4.1.4 Solute mass transfer coefficient (k_i)

Wongrueng (2007) found that the solute mass transfer coefficient (k_i) through the UTC-70 membrane at a transmembrane pressure of 0.8 MPa was 1.06×10^{-7} m/s. Wang *et al.* (2007) studied salt concentration polarization on reverse osmosis membrane performance. The results indicated that the k_i was approximately constant at different transmembrane pressures. Thus, the k_i value of 1.06×10^{-7} m/s was applied in the membrane fouling experiment.

4.2 Silica Fouling

4.2.1 Effects of silica concentration and transmembrane pressure on the permeate flux

The permeate flux results at 1,000 ml of permeate water obtained is shown in Figure 4.6. It was found that the permeate fluxes at 0.1 MPa of runs 1, 2, and 3 were 0.255×10^{-5}, 0.219×10^{-5}, and 0.177×10^{-5} m^3/m^2-s; those at 0.3 MPa of runs 4, 5, and 6 were 0.734×10^{-5}, 0.728×10^{-5}, and 0.718×10^{-5} m^3/m^2-s; and those at 0.5 MPa of runs 7, 8, and 9 were 1.344×10^{-5}, 1.235×10^{-5}, and 1.217×10^{-5} m^3/m^2-s, respectively.
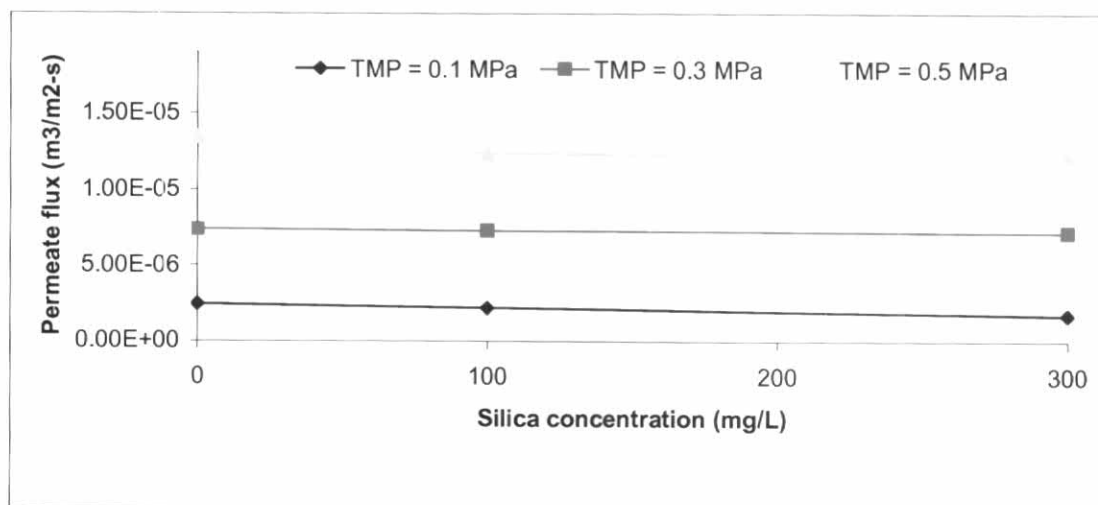

Figure 4.6 Permeate flux as a function of silica concentration

The results showed that the permeate fluxes increased with the transmembrane pressure. The highest transmembrane pressure at 0.5 MPa provided the highest permeate flux. The relationship between transmembrane pressure and permeate flux could be explained by the solution-diffusion flow model by using Equation (4-1). It was observed that the permeate flux declined, while the silica concentration in feed water increased. This may be attributed to the effect of the accumulation of silica in the feed water on the membrane surface (Liu et al., 1998).

4.2.2 Flux decline

The pure water fluxes of UTC-70 membrane at 0.1, 0.3, and 0.5 MPa were 0.256 x 10^{-5}, 0.755 x 10^{-5}, and 1.380 x 10^{-5} m^3/m^2-sec, respectively, which are denoted as J_0.

Table 4.3 Normalized flux at 1,000 ml of permeate water obtained

Run no.	TMP (MPa)	J_v (m^3/m^2-sec)	J_0 (m^3/m^2-sec)	Normalized flux (J/J_0)
1	0.1	0.254 x 10^{-5}	0.256 x 10^{-5}	0.99
2	0.1	0.219 x 10^{-5}	0.256 x 10^{-5}	0.85
3	0.1	0.177 x 10^{-5}	0.256 x 10^{-5}	0.69
4	0.3	0.734 x 10^{-5}	0.755 x 10^{-5}	0.97
5	0.3	0.727 x 10^{-5}	0.755 x 10^{-5}	0.96
6	0.3	0.718 x 10^{-5}	0.755 x 10^{-5}	0.95
7	0.5	1.344 x 10^{-5}	1.380 x 10^{-5}	0.97
8	0.5	1.235 x 10^{-5}	1.380 x 10^{-5}	0.89
9	0.5	1.217 x 10^{-5}	1.380 x 10^{-5}	0.88

As shown in Table 4.3, the runs containing high SiO_2 concentration (Run 3, 6, and 9) showed apparently lower normalized fluxes than those with the lower silica concentration (Run 2, 5, and 8). The results of normalized flux were attributed to the accumulation of silica on the membrane surface.

4.2.3 Fluoride rejection

The percent fluoride rejection was investigated. It was found that the percentages of fluoride rejection at 0.1 MPa were 87.0-96.1%, whereas those at 0.3 and 0.5 MPa were 94.9-98.7% and 95.1-98.8%, respectively.

When the silica concentration in the feed water was 100 mg/L, the percentages of fluoride rejection of 0.1, 0.3, and 0.5 MPa were 96.1, 98.7, and 98.8 %,

respectively. For the high silica concentration at 300 mg/L, the percentages of fluoride rejection were 95.8, 94.9, and 98.0% under the TMP of 0.1, 0.3, and 0.5 MPa, respectively. The higher percentages of fluoride rejection were observed when the silica concentration in the feed water was 100 mg/L. This might be a result of a polymerized silica fouled layer acting as a second filtration layer for a solute rejection at low silica concentrations. In contrast, the percentages of fluoride rejection dropped slightly as the silica concentration changed from 100 to 300 mg/L. This might be caused by the effect of a colloidal silica fouled layer, which is formed at high silica concentrations. The type of silica fouling is discussed further in the silica fouled layer section.

4.2.4 Silica fouled layer

The silica fouled layer on the membrane surface was investigated. The concentration of fluoride on the surface of the gel layer (C_G) was determined by Equation (2-4), when the C_M was considered as the C_G. The solute mass transfer coefficient (k_i) through the UTC-70 membrane was given as 1.06×10^{-7} m/s (Wongrueng, 2007). Thus, the fluoride concentration on the membrane surface (C_M) can be estimated by Equation (2-7). The fluoride concentrations in the bulk solution, on the surface of gel layer, on the membrane surface, and in the permeate solution are shown in Table 4.4.

Table 4.4 The fluoride concentrations in the permeate water, bulk solution, membrane surface, and gel layer

Run no.	TMP (MPa)	C_P (mg/L)	C_B (mg/L)	C_M (mg/L)	C_G (mg/L)	C_M/C_G
2	0.1	0.66	17.11	14.38	17.88	0.80
3	0.1	0.77	18.22	13.55	18.88	0.72
5	0.3	0.22	17.27	15.52	20.39	0.76
6	0.3	0.96	18.90	66.41	21.81	3.04
8	0.5	0.21	18.20	24.55	26.35	0.93
9	0.5	0.43	21.30	49.64	30.80	1.61

The fluoride concentrations on the membrane surface (C_M) in Runs 2, 3, 5, and 8 were lower than concentrations on the surface of the gel layer (C_G). It could be stated that the silica fouled layers in Runs 2, 3, 5, and 8 were expected to form the gel layer with the highly dense-gel layer, which is polymerized silica fouling. This might indicate that a dense-gel layer can be expected to form at low silica concentrations in feed water. The dense-gel acts as a second filtration layer for solute rejection. Thus, the fluoride in a dense-gel is mainly transported by the diffusion flow. Matsui (2007) reported that the gel layer formed by low silica concentrations is densely polymerized and has low permeability.

In runs 6 and 9, the fluoride concentrations on membrane surface (C_M) were found to be higher than the fluoride on surface of gel layer (C_G). Thus, a colloidal fouled layer (loose-gel layer) was formed. This colloidal silica fouled layer was found to form porous gel than polymerization. Consequently, the fluoride in gel layer dominated transportation by the convection flow.

The type of silica fouling depends on the condition of the system such as the silica concentration (Sahachiyaunta, P., et al., 2002).

Figure 4.7 illustrates fluoride concentration profile in bulk solution, on the surface of gel layer, on the membrane surface, and in the permeate solution. At 0.3 and 0.5 MPa, the formation of a polymerized silica fouled layer occurred at a low silica concentration of 100 mg/L, whereas the formation of a colloidal silica fouled layer appeared at a high silica concentration of 300 mg/L. At 0.1 MPa, the polymerized silica fouled layer was found at both the low silica concentration (Run 2) and high silica concentration (Run 3). It could be stated that the silica concentration has no effect on the formation of a silica fouled layer on the membrane surface at a low operating transmembrane pressure.
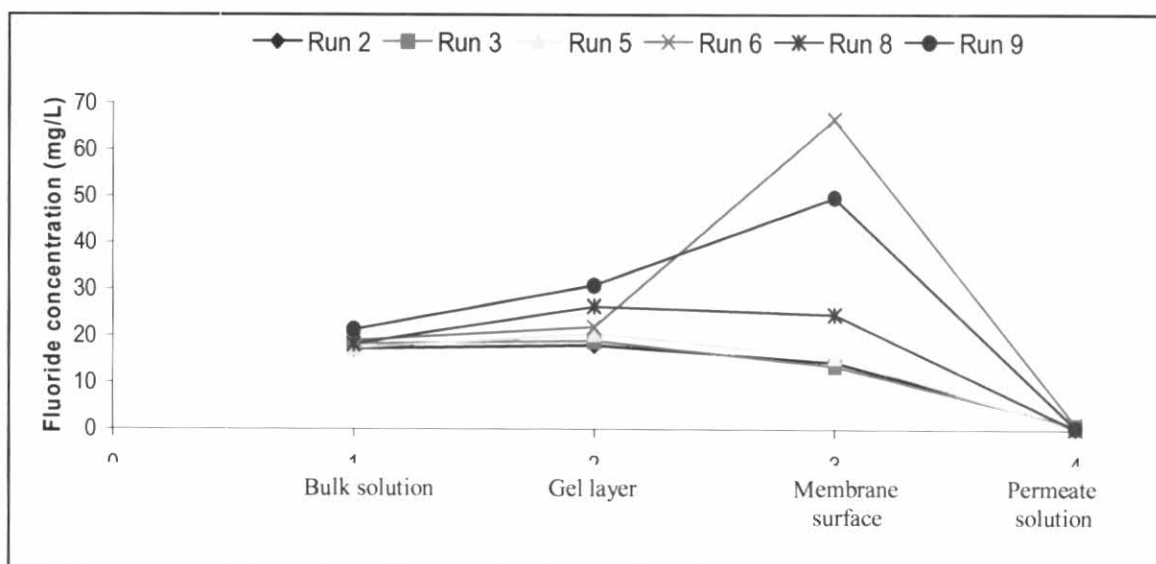
Figure 4.7 Fluoride concentration profile in bulk solution, on the surface of gel layer, on the membrane surface, and in the permeate solution