B−8 Effect of concentration polarization on fluoride removal by ULPRO membrane

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1. INTRODUCTION

ULPRO (ultra low pressure reverse osmosis) membrane is a promising technology for fluoride removal from groundwater. There are hundreds of millions who suffer from fluoride in groundwater in the world[1)]. Groundwater in Lamphun province, Thailand contained high fluoride and sodium[2)]. Thai government prompted small-scale membrane plants as community water systems to remove fluoride[3)]. Concentration polarization is a phenomenon, which can elevate solute concentration on membrane surface and lead to decrease in rejection rate. The objectives of this experiment were to study the effects of concentration polarization on fluoride removal by ULPRO membrane.

2. MATHEMATICS

According to the film model, the solute concentration on membrane surface can be estimated by the following equation:

$$(J_v)_{solute} = k \ln\left(\frac{C_M - C_P}{C_B - C_P}\right) \tag{1}$$

where k = mass transfer coefficient (D/δ), D = diffusion coefficient, δ = thickness of boundary layer, $(J_v)_{solute}$ = permeate flux of solute solution, C_M = solute concentration on membrane surface, C_P = solute concentration in permeate solution, and C_B = solute concentration in bulk solution.

The diffusion coefficient (D) for an electrolyte can be estimated as follow:

$$D = \frac{2 \cdot \mu_+ \cdot \mu_- \cdot RT}{(\mu_+ + \mu_-) \cdot F} \tag{2}$$

where μ_+ = ion mobility of cationic ion, μ_- = ion mobility of anionic ion, F = Faraday's constant, R = universal gas constant, and T = temperature.

The mass transfer coefficient (k) was based on evaluation of the permeate flux decline induced by a solute solution[4)]. It can be expressed as:

$$k = \frac{(J_v)_{solute}}{\ln\left\{\frac{\Delta P}{\pi_B - \pi_P} \cdot \left[1 - \frac{(J_v)_{solute}}{(J_v)_{H_2O}}\right]\right\}} \tag{3}$$

where $(J_v)_{H_2O}$ = permeate flux of pure water, ΔP = transmembrane pressure, π_B = osmotic pressure of bulk solution, and π_P = osmotic pressure of permeate solution.

In a diffusion flow model, it was assumed that solute flow through membrane was diffusion controlled and solvent flow through membrane was pressure controlled. Thus, permeate flux of solute solution, $(J_v)_{solute}$ and solute flux, J_i, through the membrane are given as:

$$(J_v)_{solute} = A[\Delta P - (\pi_M - \pi_P)] \tag{4}$$

$$J_i = B(C_M - C_P) \tag{5}$$

where A = water permeability of membrane, B = solute mass transfer coefficient through membrane, and π_M = osmotic pressure on membrane surface.

3. EXPERIMENTAL SET-UP

NaCl and NaF concentrations were varied as 10, 25, 50, 75, and 100 mM in the feed solutions. The bench scale dead-end filtration unit is illustrated in Fig.1. A flat sheet UTC-70U membrane, which is the ULPRO membrane type made by Toray Corporation, Japan, with diameter of 70 mm (38.5 x 10^{-4} m^2) was put on perforated plate and fixed by silicon O-ring. The cell volume is 700 mL on the primary side of the membrane. The filtration cell was pressurized by nitrogen gas (N_2) at a transmembrane pressure of 0.8 MPa and the temperature was controlled at 25 °C. The feed solution in the cell was mixed by a 5.5-cm magnetic stirring bar at a rate of 300 rpm. Permeate flux data were obtained at the volumetric concentration factor (*CF*) of 1.3 and the permeate flux at each time was calculated from the permeate volume, which was recorded by an electrical balance and connected to a PC. Water samples were analyzed by an electric conductivity meter (WM-22EP, TOA-DKK) and an ion chromatography (IC, 761 Contact IC, Metrohm Ion analysis).

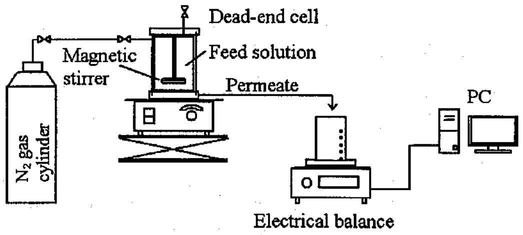

Fig.1 Bench scale dead-end filtration unit.

4. RESULTS AND DISCUSSION

Table 1 shows the average value of *k*, *D*, and *δ* of NaCl and NaF. It was found that average *k* value of NaCl was not significantly different from average *k* value of NaF.

Table 1 Average value of *k*, *D*, and *δ*

Solution	$k \times 10^5$ m/sec	$D \times 10^9$ m^2/sec	δ μm
NaCl	3.05 ±0.18	1.61	52.9 ±2.9
NaF	3.20 ±0.01	1.40	43.8 ±1.1

However, the average thickness of boundary layer (*δ*) of NaCl was higher than that of NaF. It might be due to the effect of hydration energy on solution viscosity and solute diffusion. The larger the hydration energy is, the higher the solution viscosity is, and the lower of solute diffusion were expected. The hydration energy of chloride and fluoride are 381 kJ/mol and 515 kJ/mol, respectively. Thus, NaF has a higher solution viscosity and lower solute back diffusion into the bulk solution. As a result, the thickness of boundary layer (*δ*) was smaller in NaF.

The experimental results of NaCl and NaF are reported in Table 2 and Table 3, respectively.

Table 2 Experimental results of NaCl.

Runs	Feed solution mM	C_B mM	C_M mM	C_P mM	C_M - C_P mM	Flux (m^3/m^2/sec) $J_v \times 10^5$	J_i mol m^{-2} s^{-1}	$f = C_M / C_B$	R %
2	10	18.1	30.5	0.5	30.0	1.58	7.90×10^{-9}	1.69	98.3
3	25	42.5	63.7	1.1	62.6	1.22	1.34×10^{-8}	1.50	98.3
4	50	81.1	101.7	2.1	99.6	0.79	1.65×10^{-8}	1.25	97.9
5	75	115.6	133.9	4.2	129.7	0.46	1.93×10^{-8}	1.16	96.9
6	100	145.1	157.4	9.9	147.5	0.29	2.90×10^{-8}	1.08	91.5

Table 3 Experimental results of NaF.

Runs	Feed solution mM	C_B mM	C_M mM	C_P mM	C_M - C_P mM	Flux (m^3/m^2/sec) $J_v \times 10^5$	J_i mol m^{-2} s^{-1}	$f = C_M / C_B$	R %
2	10	18.3	30.1	0.4	29.7	1.58	6.32×10^{-9}	1.65	98.7
3	25	44.9	65.2	0.7	63.9	1.20	8.40×10^{-9}	1.45	98.9
4	50	84.7	106.8	1.4	105.4	0.75	1.04×10^{-8}	1.26	98.7
5	75	117.7	139.0	2.8	134.7	0.46	1.28×10^{-8}	1.18	98.0
6	100	143.0	155.1	6.0	149.1	0.27	1.62×10^{-8}	1.08	96.1

It was indicated that due to the concentration polarization phenomenon, concentration of NaCl and NaF on membrane surface was higher than concentration of NaCl and NaF in bulk solution. It was noted that, although a lower concentration polarization level (*f*) was observed at a high feed concentration, the rejection rate at the high feed concentration was obviously decreased.

Fig.2 and Fig.3 illustrate the relationship between concentration gradient in UTC-70U membrane (C_M-C_P) of NaCl and NaF and their fluxes, respectively.

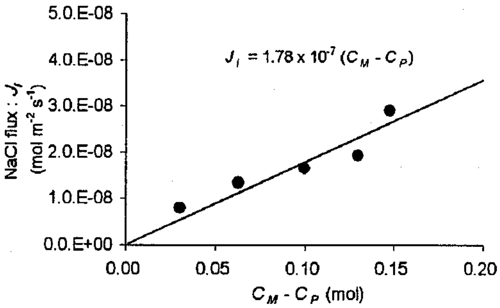

Fig.2 Concentration gradient in UTC-70U membrane vs flux of NaCl.

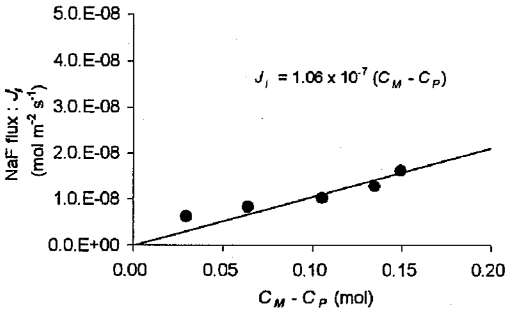

Fig.3 Concentration gradient in UTC-70U membrane vs flux of NaF.

The solute mass transfer coefficient (B) through UTC-70U membrane was estimated from the linear regression of the experimental results. For NaCl, the solute mass transfer coefficient (B) through UTC-70U membrane was 1.78×10^{-5} m/sec while that of NaF was 1.06×10^{-5} m/sec. According to the literature, it was indicated that higher hydration energy makes it the more difficult to pass through a membrane[5]. Thus, NaF was more difficult to pass through UTC-70U membrane than NaCl, and rejected with a higher efficiency.

5. CONCLUSION

The effect of concentration polarization on fluoride removal by ULPRO membrane was studied. It was noted that although a lower concentration polarization level (f) was observed at a high feed concentration, the rejection rate at the high feed concentration was obviously decreased. The larger the hydration energy is, the higher the solution viscosity is, and the lower of solute diffusion were expected. Thus, NaF has a higher solution viscosity and a lower of solute back diffusion into the bulk solution compared with that of NaCl. As a result, the thickness of boundary layer (δ) was smaller in NaF. The solute mass transfer coefficient through UTC-70U membranes of NaCl and NaF were observed at 1.78×10^{-5} m/sec and 1.06×10^{-5} m/sec, respectively. It was indicated that NaF was more difficult to pass through UTC-70U membrane than NaCl and rejected with higher efficiency.

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