Dialysis in parallel-flow rectangular membrane modules with external reflux for improved performance

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Abstract. The effect of external recycle on the performance of dialysis in countercurrent-flow membrane modules was investigated both theoretically and experimentally. Theoretical analysis of mass transfer in parallel-flow device with and without recycle is analogous to heat transfer in parallel-flow heat exchangers. Experiments were carried out with the use of a microporous membrane to dialyze urea aqueous solution by pure water. In contrast to a device with recycle, improvement in mass transfer is achievable if parallel-flow dialysis is operated in a device of same size with recycle which provides the increase of fluid velocity, resulting in reduction of mass-transfer resistance, especially for rather low feed volume rate.

1. Introduction

Dialysis is a process where solutes diffuse from one side of the membrane (the feed side) to the other side (the dialysate) according to their chemical potential gradients. Separation between the solutes is obtained as a result of differences in the diffusion rates across the membrane (Mulder 1991). The diffusion rates of solutes through membrane depend on their molecule sizes and solubilities. Usually, the feed and dialysate of dialysis are composed of the same solvent differing only slightly in concentration, it may be assumed that the chemical potential of solutes are proportional to their concentration. Thus, the concentration gradients may be used satisfactorily as the driving force in dialysis.

The early applications of dialysis were the recovery of NaOH from cellulose steeping liquors and the recovery of sulfuric acid from copper leaching solution (Kessler and Klein 1992). The famous applications of dialysis are hemodialysis for removing the metabolic waste from blood such as urea, creatine, phosphates and uric acid (Mulder 1991, Waniewski 2006), and the recovery of acids from various waste solutions by employing ion exchange membranes (Kobuchi, *et al*. 1986, Narebska and Warszaski 1994, Oh, *et al*. 2000, Palatý, *et al*. 1996, 2000, 2007).

Mass transfers for dialysis (Michaels 1966, Grimsurd and Babb 1966, Cooney, *et al*. 1974), as well as for dialysis coupled with ultrafiltration (Yeh, *et al*. 1997, 2000, Cheng and Su 2002), in microporous membranes were analyzed. Recently, both the effects of diffusion (dialysis) and convection (ultrafiltration) on the cocurrent flow membrane mass exchanger were investigated by theoretical and experimental approaches (Tu, *et al*. 2006). Actually, mass transfer in microporous membrane modules can be analogous to heat transfer in heat exchangers (Bowman, *et al*. 1940, Jakob 1957). The effect

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of dialysis in the double-pass membrane mass exchanger has been investigated by the method analogous to heat transfer in heat exchanger (Yeh and Chang 2005). The resistance of mass transfer in dialysis is the sum of resistances in feed side, in membrane and in dialysate side. The performance of dialysis process can be enhanced by maintaining at a higher driving force and/or decreasing the transfer resistance. Since reflux has much influence on the heat and mass transfer (Yeh, *et al*. 1999), it is the purpose of present study to investigate the effect of external reflux on the performance of dialysis in countercurrent-flow rectangular modules for improved performance.

2. Theory

The schematic diagram shown in Fig. 1 may serve to explain the nomenclature to be employed for countercurrent-flow device. The system consists of two channels for retentate (channel *a*) and dialysate (channel *b*), respectively, which are separated by a microporous membrane sheet through which the solute in feed solution diffuses perpendicularly to the dialysate. Before entering the channel *a*, the feed solution with inlet volume rate Q_a and concentration $C_{a,i}$ will mix with the recycling fluid existing from the outlet of channel *a* with volume rate $Q_a R$, which is controlled by means of a conventional pump situated at the beginning of channel *a*. The dialysate with inlet volume rate Q_b flows oppositely through channel *b*. The analysis is based on the following assumptions: steady state, no chemical reaction, uniform concentrations, $C_a(x)$ and $C_b(x)$, over the cross section of flow, constant rates of flow, constant overall mass-transfer coefficient.

2.1. Concentration distributions

We follow the procedure of Underwood (Bowman, *et al*. 1940) for the analysis of heat transfer in heat exchangers. The mass balances for the solute in differential length *dx* are
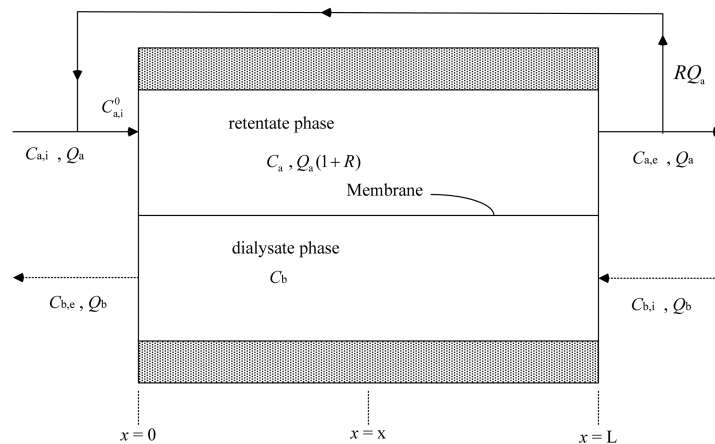
$$Q_a(1 + R)dC_a = Q_b dC_b \tag{1}$$

Fig. 1 Schematic diagram of a parallel-flow rectangular membrane module

$$-Q_a(1 + R)dC_a = KW(C_a - C_b)dx \tag{2}$$

where K is the overall mass-transfer coefficient and W denotes the width of dialyzer. The outlet concentration of solute in channel a can be obtained by solving Eqs. (1) and (2), simultaneously, with the use of the following boundary conditions

$$C_a = C_{a,i}^0 \quad \text{and} \quad C_b = C_{b,e} \quad \text{at} \quad x = 0 \tag{3}$$

$$C_a = C_{a,e} \quad \text{and} \quad C_b = C_{b,i} \quad \text{at} \quad x = L \tag{4}$$

The results are

$$C_{a,e} = C_{a,i}^0 + (C_{a,i}^0 - C_{b,i})\,\xi_{a,e} \tag{5}$$

where

$$\xi_{a,e} = \frac{\exp[KWL\{(1/Q_b)-(1/Q_a)\}]-1}{1-(Q_a/Q_b)\exp[KWL\{(1/Q_b)-(1/Q_a)\}]} \tag{6}$$

Inspection of Eq. (5) shows that the mixed inlet concentration of feed solution $C_{a,i}^0$ is not specified a priori. Mathematically, one more relation is needed for solving this problem. For this purpose, a mass balance for solute at the inlet of channel a is readily obtained as

$$C_{a,i} + RC_{a,e} = (1 + R)C_{a,i}^0 \tag{7}$$

Substitution of Eq. (7) into Eq. (5) to eliminate $C_{a,i}^0$, gives the expression for calculation of outlet concentration for feed solution (retentate) as

$$C_{a,e} = \frac{C_{a,i}[(1+\xi_{a,e})/(1+R)]-C_{b,i}\xi_{a,e}}{1-(1+\xi_{a,e})[R/(1+R)]} \tag{8}$$

2.2. Mass transfer rate

Once the outlet concentration of retentate, $C_{a,e}$, is calculated from Eq. (8), the mass transfer rate is readily obtained from the following equation

$$M = Q_a(C_{a,i} - C_{a,e}) \tag{9}$$

2.3. Overall mass transfer coefficient

The equation for calculating overall mass-transfer coefficient, K, combined diffusive and convective transport in a dialyzer, is (Jaffrin, *et al.* 1981, Yeh, *et al.* 1999, Legallais, *et al.* 2000, Galach, *et al.* 2003):

$$\frac{1}{K} = \frac{1}{k_a} + \frac{1}{k_m} + \frac{1}{k_b} \tag{10}$$

where k_a, k_b and k_m are mass-transfer coefficients in retentate phase (channel a), in dialysate phase (channel b) and within the membrane, respectively.

Since mass transfer within the membrane is due to the molecular diffusion alone, the following expression may be used for calculating the mass-transfer coefficient in the membrane (Kiani, *et al*. 1984)

$$k_m = \frac{D_m \varepsilon}{\tau t} \tag{11}$$

where D_m is the diffusivity of solute in membrane, ε and t denote the porosity and thickness of membrane, respectively, and τ is the pore tortuosity of membrane. Since the mass transfers in both sides of the microporous membrane are convective, k_a and k_b are a function of fluid properties, flow pattern, etc. Blatt, *et al*. (1970) pointed out that for all thin-channel lengths of practical interest, Graetz or L'evêque solution for convective heat transfer in laminar-flow channels, could be suitably modified for mass transfer. For flow over a microporous membrane sheet

$$k_a = 0.816 \left[\frac{6Q_a(1+R)D_a^2}{Wh_a^2 L} \right]^{1/3} \tag{12}$$

$$k_b = 0.816 \left[\frac{6Q_b D_b^2}{Wh_b^2 L} \right]^{1/3} \tag{13}$$

where D_a and D_b are the mass diffusivities of solute in phases a and b, respectively, L is the length of a microporous membrane sheet, and h_a and h_b are the heights of channels a and b, respectively.

3. Experiments

Dialysis with external recycle was carried out with the use of a membrane sheet (L = 0.185 m, W = 0.105 m) made of microporous cellulose ester (Spectrum, tortuosity = 2.6, porosity = 21% and thickness = 178 μm) as a permeable barrier to dialyze urea (reagent ACS grade, Shimakyu's Pure Chemicals) from aqueous solutions ($C_{a,i}$ = 1.0, 1.5 and 2.0 M or 10^3 mol/m³) by pure water ($C_{b,i}$ = 0). The diffusivity of urea in aqueous solution is about 1.378×10^{-3} m²/s. The porous cellulose ester membrane is very hydrophilic, the diffusivity of urea in membrane phase can be assumed to 1.378×10^{-3} m²/s. The membrane sheet was inserted in parallel between two parallel plates of stainless steel, with same distance from them to divide the conduct into two channels (channel a and b) of same height ($h_a = h_b = 1.9 \times 10^{-3}$ m). Fig. 2 shows the schematic diagram of experimental apparatus. Five rotameters (L-03214-34, Cole Parmer Co.) were installed at the inlet and the outlet of both flow channels, as well as the recycle line, and no water flux through the membrane was observed by checking the
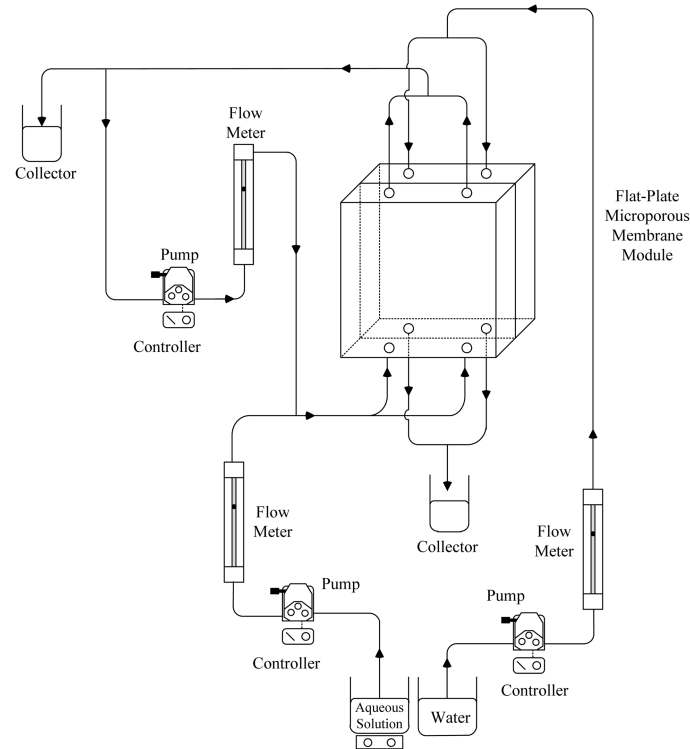
Fig. 2 Schematic diagram of experimental system

same flow rates at both ends of a channel. Flow rates (Q_a = 0.248 to 1.241×10^{-7} m^3/s, Q_b = 0.739×10^{-7} m^3/s) were adjusted by three controlled pumps (L-07553-20, Cole Parmer Co.). Under specific operation conditions, samples of outlet streams were analyzed at 10 min intervals until steady state was reached as indicated by no change in urea concentrations ($C_{a,e}$ and $C_{b,e}$) by UV spectrum detector over a period of 1h. The experiment was conducted at 25°C under continuous operation. The time for steady state was about 30 min.

Experimental results were obtained from the outlet concentration, $C_{a,e}$, and the experimental mass transfer rate values, M, were calculated from Eq. (9). Some of the experimental results for M are plotted in Figs. 3-5. The theoretical predictions were calculated from Eqs. (6), (7) and (9) with the use of Eqs. (10)-(13), and the results are listed in Table 1 and also plotted in Figs. 3-5 for comparison. The variations of Reynolds numbers (Re) inside the channel a were also shown in Table 1, and the assumption of laminar flow is acceptable for the system of present interest. As shown in Figs. 3-5, the theoretical predictions are in qualitative agreement with the experimental results. Therefore, presented model can be used satisfactorily for membrane mass exchanger with reflux operation.

4. Results and Discussion

It is seen in Figs. 3-5 and Table 1 that the mass-transfer rate M increases when reflux ratio R, as

Table 1 Improvement of performance with $Q_b = 0.739 \times 10^{-7}\,\mathrm{m^3/s}$ and $C_{b,i} = 0$

$Q_a \times 10^7$ (m³/s)	R	Re	$M \times 10^6$ (mol/s)			I (%)
			$C_{a,i} = 1.0\,\mathrm{M}$	$C_{a,i} = 1.5\,\mathrm{M}$	$C_{a,i} = 2.0\,\mathrm{M}$	
0.248	0	0.52	3.129	4.711	6.254	0
	1	1.04	3.449	5.193	6.894	10.23
	3	2.08	3.646	5.489	7.287	16.52
	5	3.11	3.707	5.581	7.485	18.47
	7	4.15	3.745	5.639	7.485	19.69
	9	5.19	3.759	5.659	7.513	20.13
0.496	0	1.04	3.642	5.462	7.274	0
	1	2.08	3.841	5.770	7.671	5.46
	3	4.15	3.962	5.942	7.913	8.79
	5	6.23	3.994	5.990	7.977	9.67
	7	8.30	4.017	6.024	8.023	10.30
	9	10.38	4.026	6.038	8.041	10.54
0.745	0	1.56	3.916	5.881	7.832	0
	1	3.12	4.049	6.081	8.098	3.40
	3	6.24	4.168	6.260	8.336	6.44
	5	9.35	4.194	6.299	8.388	7.10
	7	12.47	4.209	6.321	8.418	7.48
	9	15.59	4.217	6.333	8.434	7.69

well as the flow rate Q_a or inlet concentration $C_{a,i}$, in the retentate phase, increases. The application of recycle operation to a mass exchanger actually has two conflicting effects: the desirable effect of increasing fluid velocity, resulting in increase of mass-transfer coefficient, and the undesirable effect of lowering the concentration difference due to mixing of inlet fluid with the recycling stream, resulting in decrease of driving force for mass transfer.

The dialysis improvement I from using an external recycle-device is best illustrated by calculating the percentage increase in mass-transfer rate M based on the mass-transfer rate M_0 obtained in a device of same size without recycling ($R = 0$), i.e.

$$I = \frac{M - M_0}{M_0} \tag{14}$$

Some of the results are listed in Table 1. We found in this table that I increases with R, while it is independent on $C_{a,i}$. This is easy to explain as follows. Eq. (8) may be rewritten with $C_{b,i} = 0$ as

$$C_{a,e} = \frac{C_{a,i}(1 + \xi_{a,e})}{1 - R\xi_{a,e}} \tag{15}$$

Substitution of Eqs. (9) and (15) into Eq. (14) with $R = 0$ for M_0 results in
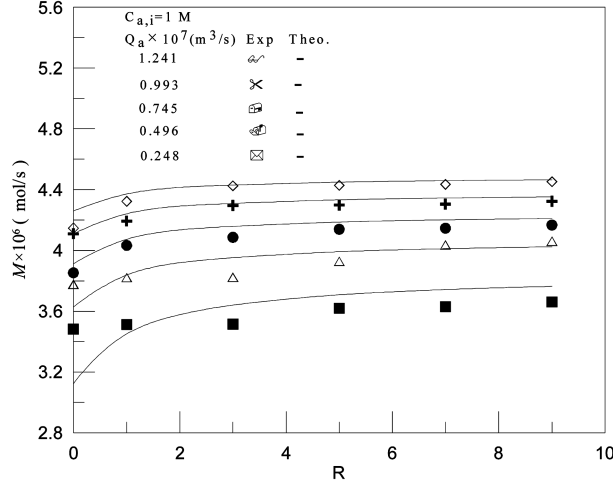
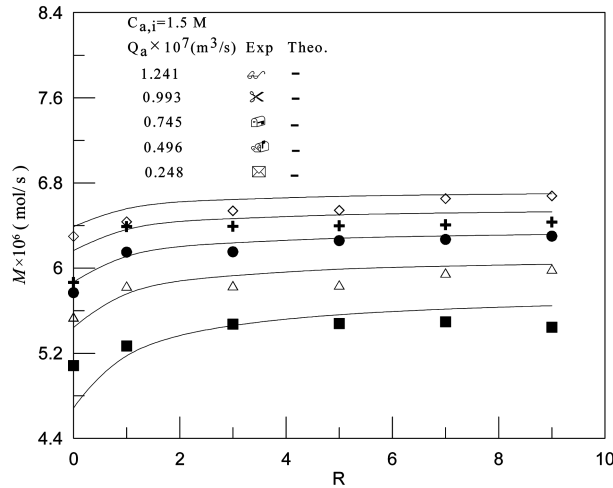Fig. 3 Experimental results and theoretical predictions of mass transfer rate for $C_{a,i}$ = 1.0 M

Fig. 4 Experimental results and theoretical predictions of mass transfer rate for $C_{a,i}$ = 1.5 M

$$I = \frac{M}{M_0} - 1 = \frac{Q_a C_{a,i}[1-(1+\xi_{a,e})/(1-R\xi_{a,e})]}{Q_a C_{a,i}[1-(1+\xi_{a,e})]} - 1 = \frac{R(1+\xi_{a,e})}{1-R\xi_{a,e}} \tag{16}$$

Therefore, the fact that the improvement of mass-transfer rate I by recycle is independent of feed concentration $C_{a,i}$, is confirmed. Further, differentiating I with R, one has

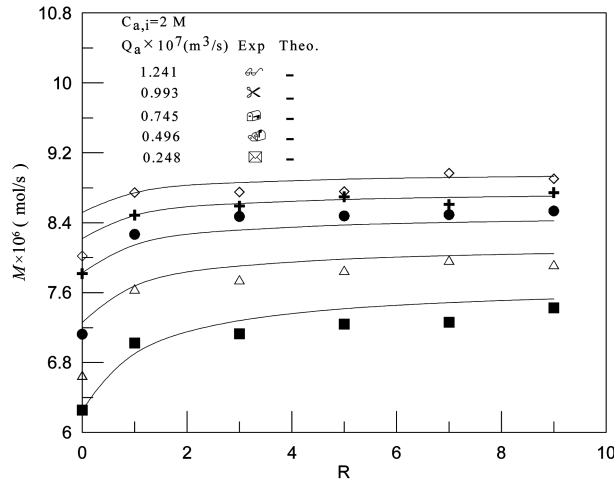$$\frac{dI}{dR} = \frac{1+\xi_{a,e}}{(1+R\xi_{a,e})^2} \tag{17}$$

From Eq. (5)

Fig. 5 Experimental results and theoretical predictions of mass transfer rate for $C_{a,i}$ = 2.0 M

$$1+\xi_{a,e} = 1+\frac{C_{a,e}-C_{a,i}^0}{C_{a,i}^0-C_{b,i}} = \frac{C_{a,e}-C_{b,i}}{C_{a,i}^0-C_{b,i}}>0$$

Consequently, $dI/dR > 0$ and the fact that I increases with R, is also confirmed.

It is also seen in Table 1 that the improvement of performance I decreases as the inlet volume rate in retentate channel Q_a increases. In fact, the improvement of the process due to the improvement of the hydrodynamic conditions in channel a has its limits. The resistance in the retentate decreases with the increase of the fluid velocity inside channel a, at a critical point, however, this resistance will have no influence on the global mass-transfer resistance. Therefore, further improvements in the fluid velocity, either by changing the feed flow rate or by changing the reflux rate, will have no effect in the mass transfer. This is clear also in Figs. 3-5, no significant change in the mass-transfer rate was achieved for the higher reflux rates. It is concluded that the application of recycle operation to mass transfer is limited at high inlet volume rate. The comparison in performance enhancement between increasing recycle and increasing the flow pass (Yeh and Chang, 2005) will be studied in the further work.

5. Conclusions

The equation for predicting the mass-transfer rate in rectangular dialyzer operated with external recycle was derived by following the procedure for the analysis of heat transfer in heat exchangers. The calculation of the outlet concentration, total mass-transfer rate and the improvement in performance may be generally based on Eqs. (8), (9) and (14), respectively. Experiments were carried out with the use of a microporous membrane sheet to dialyze urea aqueous solutions by pure water, under various feed concentrations, inlet volume rates and reflux ratios. Theoretical predictions are in qualitative agreement with the experimental results. The improvement of mass-transfer rate by recycle was estimated based on the mass-transfer rate obtained in the device of same size without

recycle. It was found that mass transfer rate as well as the improvement of performance *I* increases with the reflux ratio, while *I* increases as the inlet volume rate decreases. Actually, increasing the feed rate, or applying the recycle operation, has two conflicting effects on the mass transfer in membrane separation. One is the increase in fluid velocity, as well as the enhancement in mass-transfer coefficient, which is good for performance, while the other is lowering the concentration difference between the retentate and dialysate phases due to remixing and dilution, resulting in decrease of driving force for mass transfer. At a critical point, therefore, further increasing in the fluid velocity, either by changing the feed flow rate or by changing the reflux ratio, will have no effect in the mass transfer, as shown in Table 1 and Figs. 3-5. It is believed that for rather low volume flow rate, considerable improvement in mass transfer is obtainable in dialyzers by recycling operation, which provides the increase of fluid velocity, resulting in substantially decreasing mass-transfer resistance.

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Nomenclature

C_a, C_b	bulk solute concentration in phase a, phase b (mol/m^3)
$C_{a,i}^0$	mixed inlet concentration in phase a (mol/m^3)
$C_{a,i}$, $C_{b,i}$ C_a, C_b	at the inlet (mol/m^3)
$C_{a,e}$, $C_{b,e}$ C_a, C_b	at the outlet (mol/m^3)
D_a, D_b, D_m	solute diffusivity in phase a, phase b, membrane (m^2/s)
h_a, h_b	height of flow channel in phase a, phase b (m)
I	improvement of separation defined by Eq. (14)
K	overall mass-transfer coefficient defined by Eq. (10)
K_a, K_b, K_m	mass-transfer coefficient in phase a, phase b, membrane (m/s)
L	effective length of a mass extractor (m)
M	total mass-transfer rate (mol/s)
M_0	total mass-transfer rate without recycling (mol/s)
m	KS/Q_b
n	$KS/Q_a(1+R)$
Q_a, Q_b	volume flow rate in retentate phase, dialysate phase (m^3/s)
R	reflux ratio
Re	Reynolds number, $\mathrm{Re} = \dfrac{2\rho Q_a(1+R)}{\mu(W+h_a)}$
S	mass-transfer area, WL (m^2)
t	thickness of membrane sheet (m)
W	membrane width (m)
x	rectangular coordinate (m)

Greek letters

ε	porosity of membrane
μ	viscosity of feed solution (kg/m-s), is approximately equal to pure water, 0.894×10^{-3} kg/m-s
ρ	density of feed solution (kg/m^3), is approximately equal to pure water, 1000 kg/m^3
τ	pore tortuosity of membrane
$\xi_{a,e}$	dimensionless outlet concentration defined by Eq. (6)