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Abstract: This study investigates the effect of operation parameters on the separation of nitric acid-water mixture using air gap membrane distillation (AGMD). Porous hydrophobic PTFE membrane was used. The performance was evaluated based on the permeate flux and the nitric acid selectivity. Operating parameters such as feed solution temperature, feed concentration, flow rate, and air gap width were varied. Nitric acid selectivity was found to increase with the increase in feed solution temperature, feed concentration, flow rate, and air gap width. Permeate flux increased, when the feed temperature and the flow rate were increased. The effect of recirculation of the feed solution was also studied. With the recirculation mode, at different initial solution volumes, it was observed that the nitric acid concentration in the feed and the permeate, increased. The rate of flux decline was greater, when the initial feed solution volume was lower.

Keywords: Air gap membrane distillation (AGMD), nitric acid, azeotropic, selectivity, flux

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INTRODUCTION

Nitric acid is widely used in fertilizers and explosives industries. It is also used in the manufacture of nylon and polyurethane. Dehydration of nitric acid streams is a complicated and hazardous process in the chemical separation industry. The separation is not performed by conventional distillation, due to the presence of an azeotropic in the nitric acid/water system at 68 wt. % nitric acid (Fig. 1) (1). Although, the addition of sulfuric acid to the nitric acid/water mixture will shift the azeotropic point and act as an entrainer, this method is not a viable alternative (2, 3). With the addition of sulfuric acid, nitric acid can be separated from the water/nitric acid mixture. However, the sulfuric acid/water mixture must then be separated again.

Membrane distillation (MD) is a separation process of liquid mixtures through porous hydrophobic membranes. The hydrophobic nature of the membrane prevents penetration of an aqueous solution into the pores. Therefore, only volatile components of the feed may be transported through the membrane. The driving force of the process is supplied by the vapor pressure difference caused by the existing temperature difference between the liquid-vapor interface and the composition in the layers adjacent to the membrane surface (4). This technology has been gaining recognition lately, as it is proving to be a low cost energy saving alternative to conventional separation processes, such as distillation and reverse

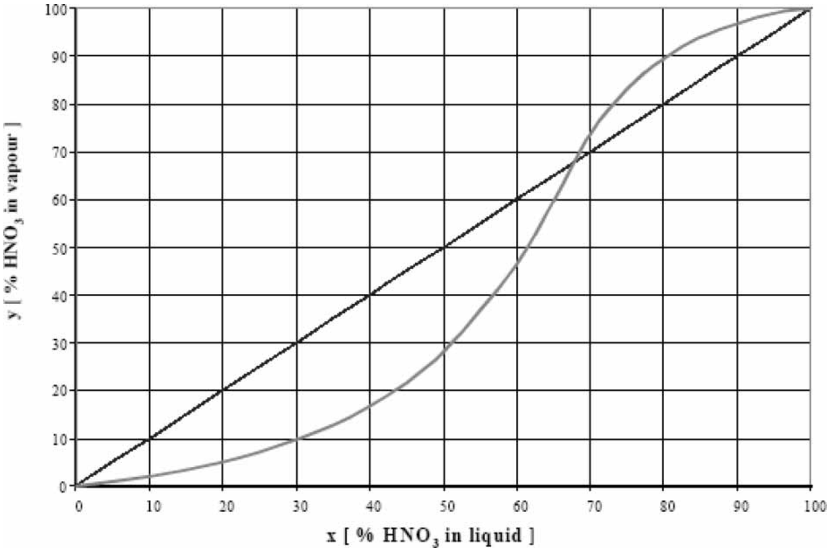

Figure 1. Vapor liquid equilibrium nitric acid-water.

osmosis. Depending on the method of permeate collection, a mass transfer mechanism through the membrane and the reason for driving force formation, various types of MDs exist; direct-contact MD (DCMD), air gap MD (AGMD), sweeping gas MD (SGMD), vacuum MD (VMD), and osmotic MD (OMD) (5, 6). The major applications of MD have been in the area of desalination for the production of ultra pure water (7, 8), concentration of several non-volatile solutes in aqueous solutions (salt, sugar, fruit juices, etc.) (9–11), water treatment (12) and more recently, its application in the separation of volatile solutes in aqueous mixtures, is gaining ground. This includes separation of alcohol-water mixtures (13–16), extraction of stable isotopes 18O-enriched water (17), breaking azeotropic mixtures (18), and in concentration of acids (3, 19).

Ames et al. (19), and Sportsman et al. (3), have studied the dehydration of nitric acid, using vacuum assisted MD with a specially made Nafion composite ionomer membrane. The objective of the present study was to systematically investigate the influence of relevant operating parameters on the performance of the separation of nitric acid and water and permeate flux, using simple PTFE (Teflon) membrane by AGMD.

In AGMD of aqueous nitric acid solutions, water and nitric acid are evaporated from the liquid–vapor interface at the feed side of the membrane, the vapors of both species are transported through the membrane pores and are condensed on a cold surface separated from the membrane by an air gap. The main advantage of the air gap membrane distillation against other configuration of membrane distillation, such as direct contact membrane distillation, arises from the possibility to condense the permeate vapors on a cold surface, rather than directly in a cold liquid.

EXPERIMENTAL

The experiments using AGMD were carried out with the apparatus shown schematically in Fig. 2. The setup consists of three compartments, namely, feed (bottom cell), permeate (middle part), and the cooling compartment (top cell). The compartments were made of Teflon to resist corrosion by the acid solution. The cooling plate on which the permeate vapors condense, was made of stainless steel. The feed and permeate was separated by a hydrophobic porous PTFE membrane (Millipore). The membrane used had an average pore diameter of 0.2 μm, porosity $\sim$70%, and a tortuosity factor $\sim$2. The effective surface area of the membrane was 0.01368 m^2. The nitric acid-water feed solutions were prepared from analytical grade 60% nitric acid (Dongwon Chemicals, Korea) and ultra pure water (RO and UP System, P.NIX Power III, Human Corp., Korea).

The cooling water was maintained at 15°C and was recirculated. The effects of the various operating parameters, such as feed and cooling water temperatures, feed flow rate, feed concentration, and air gap thickness were

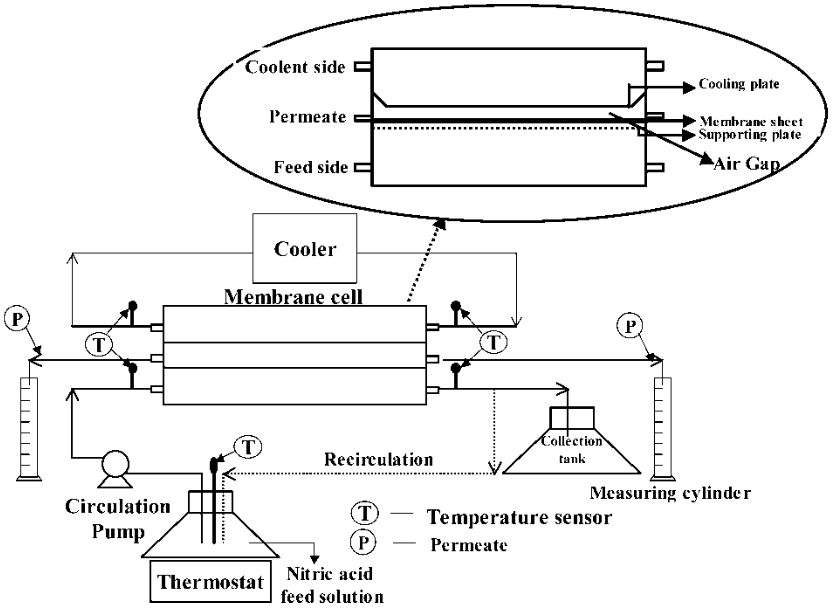

Figure 2. Schematic of AGMD.

studied under a non-recirculation feed solution and co-current (with cooling water) mode. Hence, at any given experimental run, the concentration of the inlet solution fed into the system remains the same throughout the experiment. Further, under a specific constant operating condition, feed solution was operated in a recycle mode.

The separation performance was evaluated in terms of permeate flux, concentration of nitric acid, and selectivity. Selectivity represents the measure of the preferential transport of nitric acid based on the chemical analysis of the permeate. A calibrated graduated cylinder was used to collect the permeate solution, directly. The concentration of nitric acid in the permeate solution was obtained by titration (APHA 1998). This information was used to calculate the selectivity using the formula:

$$\alpha_E = \frac{(y_E/x_E)}{(1 - y_E/1 - x_E)} \qquad (1)$$

where y_E and x_E are the mole fraction of nitric acid in the permeate and in the feed, respectively. The flux was determined by knowing the volume of permeate collected, membrane area, and the time of the experimental run. Temperatures were measured at the inlet and outlet positions of the feed solution and cooling water.

RESULTS AND DISCUSSION

Effect of Feed Solution Temperature

The effect of the feed solution temperature on flux and nitric acid selectivity is shown in Fig. 3. Initially, the permeate gets collected slowly in the permeate

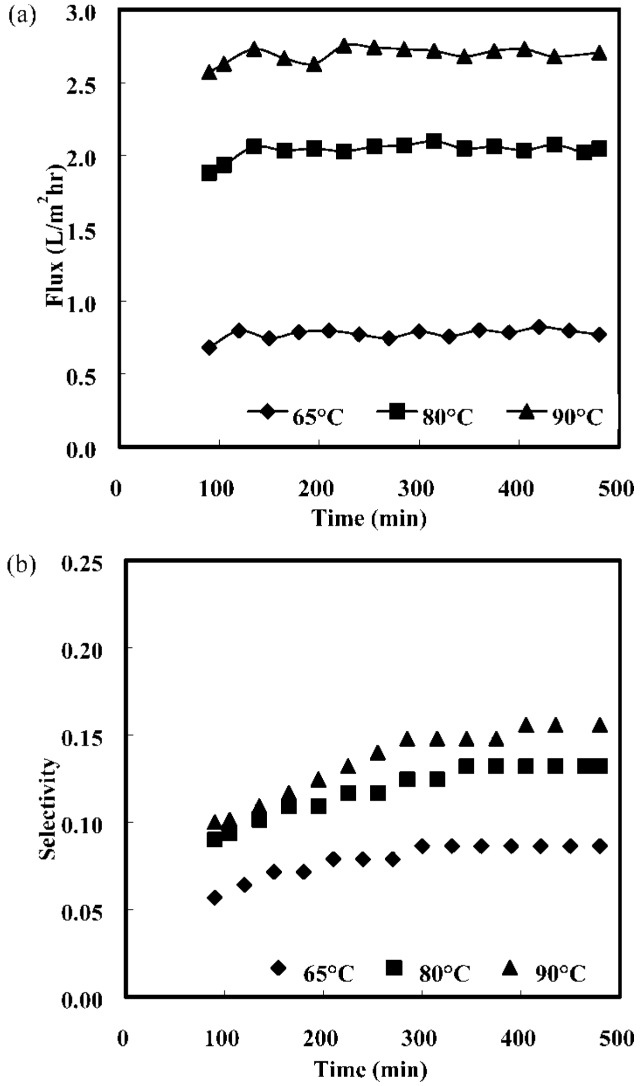

Figure 3. Flux (a) and nitric acid selectivity (b) at different feed solution temperatures (nitric acid feed concentration 4 M, feed flow rate 50 ml/min).

side and takes about 90 minutes for the permeate chamber to be completely filled and the permeate flows continuously, thereafter. Hence, the flux values were noted from 90 minutes. As shown in Fig. 3a, increasing the temperature significantly increases the flux. However, as shown in Fig. 3b, with the rise in the feed temperature, the nitric acid selectivity increases initially and upon further increase in the feed solution temperature, a marginal increase in nitric acid selectivity was observed. On the other hand, the selectivity of water decreases with the increase in feed solution temperature for a given feed concentration (4 M nitric acid). Similar patterns of the separation and the permeation flux were observed by Banat et al. (15), and Ahn et al. (20), in studying ethanol-water and trifluroethanol-water mixtures, respectively.

This phenomenon is due to the combined effect of feed concentration and vapor pressure, as the evaporation of the binary mixture at the membrane pore entrance would be affected by the vapor-liquid equilibrium of the nitric-acid mixture at a given temperature and concentration. The mass transfer coefficient is strongly dependent on the hydrodynamic conditions, as well as feed temperature and concentration. Increasing the mass transfer coefficient will reduce the difference between the bulk and the membrane surface concentration and vice versa. Similarly, both the temperature and the concentration polarization (16) are affected by the values of mass flux, heat, and mass transfer coefficients in the liquid film bounding the membrane surface and feed concentration. The flux increase with temperature rise will require more heat of vaporization. A higher flux increases the temperature drop at the liquid membrane interface and increases the gas–condensate interfacial temperatures, which will lower the driving temperature difference, resulting in lower vapor pressure gradient. Thus the combined effect of feed concentration and vapor pressure affects the permeation flux and selectivity.

During the course of the study, mild fluctuations in the selectivity (though very minimal) were observed. There could be slight variations in pore size of the membrane (pore size distribution would exist) (although nominal pore size of the membrane used was 0.2 μm), which could cause minor fluctuation in selectivity. The existence of pore size distribution has been reported by Schofield (21) and further sited by Banat and Simandal (16). Another aspect in the present study on the separation of the nitric acid-water mixture, the system takes about 6 hours (360 min) to reach a state of equilibrium beyond which the selectivity values plateau. Until this time and especially during the first 200–300 minutes, the system is set to be in a quasi steady state, where there is a gradual increase in selectivity, as expected.

Effect of Feed Concentration

The effect of nitric acid concentration on the permeate flux and its selectivity is shown in Fig. 4. It was found that the total permeation flux decreased as the water in the feed decreased (Fig. 4a). This trend was followed up to a point

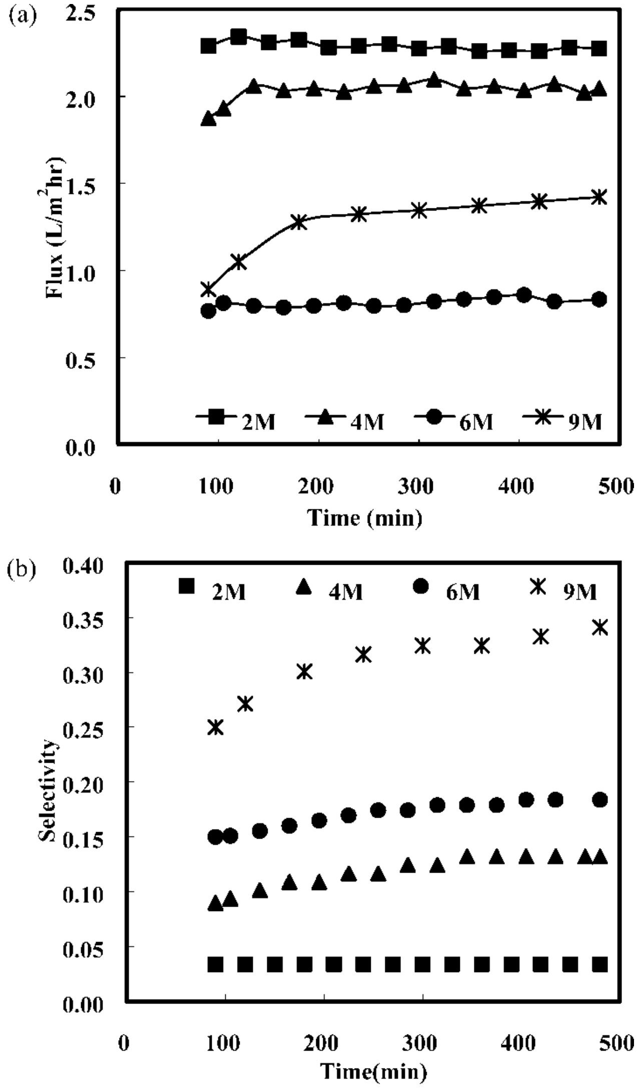

Figure 4. Flux (a) and nitric acid selectivity (b) at different feed concentration (feed solution temperature 80°C, feed flow rate 50 ml/min).

where the azeotropic concentration (68% wt – Fig. 1) was reached, beyond which (9 M), there is an increase in flux. A similar pattern of permeation flux was observed in the concentration of nitric acid by DCMD (22). With the increase in nitric acid concentration in the feed, the selectivity (Fig. 4b) of nitric acid increased gradually, until the azeotropic concentration, beyond which the increase in selectivity was much higher. In the case of mixtures of nitric acid and water, there is a maximum boiling point of 120.5°C when the mixture contains 68% by mass of nitric acid. That compares with the boiling point of pure nitric acid at 86°C, and water at 100°C. In the case of dilute nitric acid feed solutions, the vapor produced is richer in water than the organic acid, whereas for concentrated nitric acid feed solution (9 M) the vapors formed and hence the permeate solution is richer in nitric acid. The selectivity of nitric acid and the permeate flux is significantly increased.

Effect of Feed Flow Rate

Figure 5 shows the effect of the feed flow rate on permeate flux and nitric acid selectivity. It can be seen that both flux (Fig. 5a) and selectivity (Fig. 5b) increased with the increase in the feed flow rate. The permeate flux increases rapidly with the feed velocity and the amount of increase seems to reach maximum values at higher feed velocities. A similar asymptotic increasing trend of permeate flux with the increase in the feed flow rate was reported by Garcia-Payo et al. (13), in the separation of aqueous alcohol solutions. Generally, Banat et al. (15), Banat and Simandl (16) Garcia-Payo et al. (13), Lee and Hong (23), have all consistently observed an increasing trend in flux and selectivities with the increase in the flow rate of feed solutions and hence the feed turbulence. An increase in permeate flux with the increase in feed flow rate can be attributed to the temperature polarization effect (16). Since the separation involves simultaneous heat and mass transfer, the heat required for species evaporation at the membrane–liquid interface has to be supplied from the bulk solution. This creates temperature gradients in the liquid film adjoining the membrane. The increased heat transfer coefficients by the temperature polarization effect at higher feed flow rate results in an increased permeate flux. Similarly, an increase in turbulence increases the nitric concentration at the liquid-membrane interface, which lowers the film resistance for nitric acid diffusion through the membrane. Hence the selectivity of nitric acid increases with an increasing feed flow rate.

Effect of Air Gap Width

At a constant inlet feed concentration of nitric acid aqueous solution of 4 M and a temperature of 80°C, and a constant feed flow rate of 150 ml/min, the air gap thickness was varied. As can be seen in Fig. 6a, the permeate flux was inversely proportional to the gap width. The wider the air gap, the higher the mass transfer resistance, and thus the lower is the flux. However, an increase in air gap width increased the nitric acid selectivity. As the selectivity is increased at the expense of decrease in flux, a balance must be struck in selecting the optimum operating condition, based on the required objective of a particular separation.

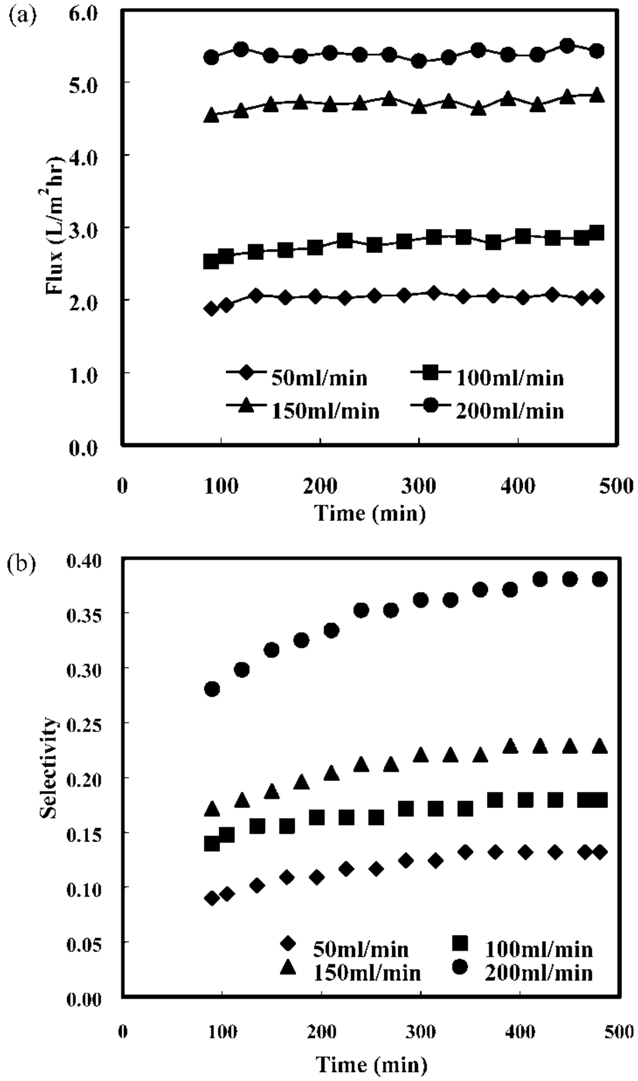

Figure 5. Flux (a) and nitric acid selectivity (b) at different feed flow rate (nitric acid feed concentration 4 M, feed solution temperature 80°C).

Recirculation of Feed Solution

The feed solution was recirculated. At the start of the experiments the inlet nitric acid feed concentration was fixed at 2 M. However, due to the recirculation mode, during the course of the experiments, the inlet concentration of the feed was constantly varying. The initial volume of the fed solution was also varied (1L, 2L, and 5L). The feed flow was maintained at 150 ml/min.

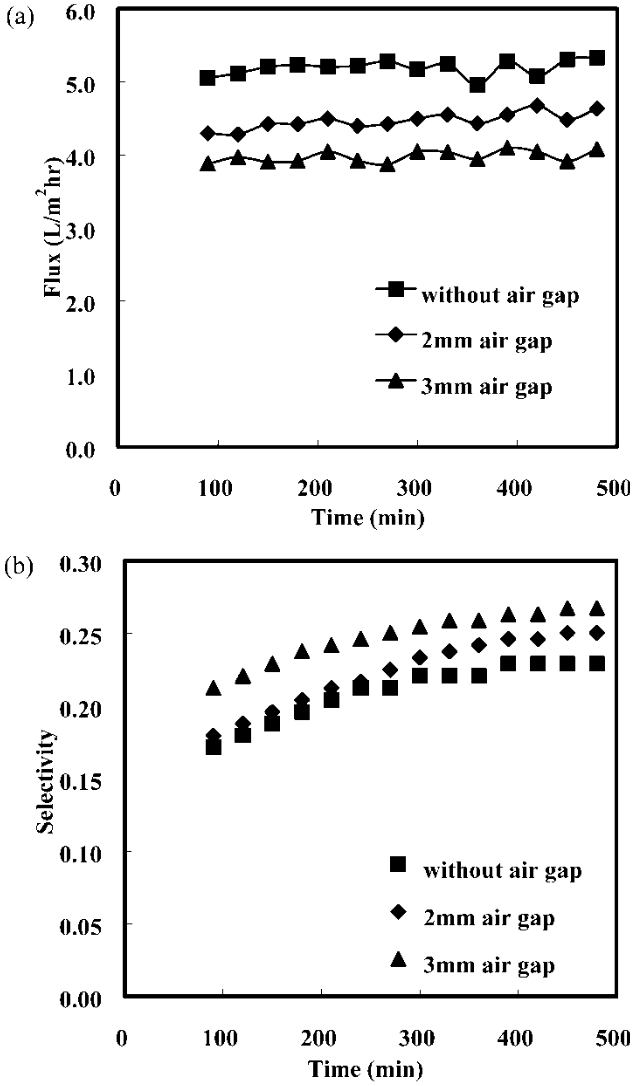

Figure 6. Flux (a) and nitric acid selectivity (b) at various air gap width (nitric acid feed concentration 4 M, feed solution temperature 80°C, feed flow rate 50 ml/min).

Under such operating conditions, Fig. 7 shows the concentrations of nitric acid for feed and permeate solutions during the course of the experiments. It can be seen that both the feed and the permeate concentration of nitric acid increased and the amount of increase in concentration was lower, when the initial volume of the feed solution was higher. The rate of rise was also lower.

Flux decreased with the increase in initial feed solution volume (Fig. 8). In the case of 1 L of initial feed solution, as the feed concentration rises rapidly

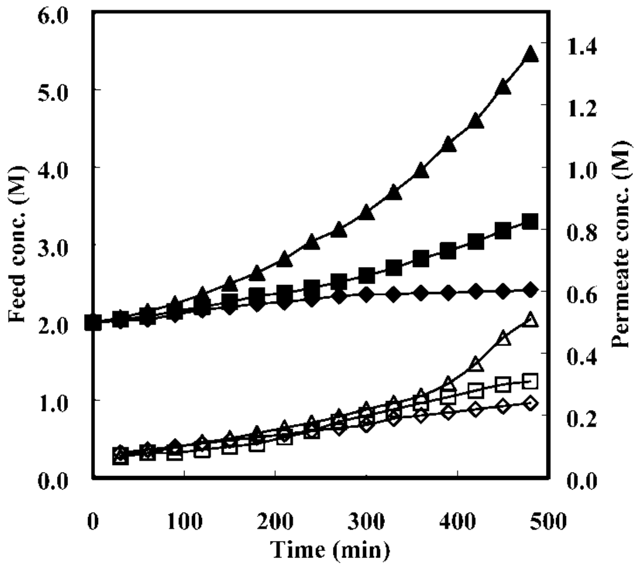

Figure 7. Nitric acid concentration in the feed and permeate solutions at different initial feed volumes operated under recirculation mode (shaded symbols: feed, unshaded symbols: permeate; -▲- 1L, -■- 2L, -◆- 5L; initial nitric acid feed concentration 2 M, flow rate 150 ml/min, feed temperature 80°C, cooling water temp. 15°C).

(though below the azeotropic concentration), the decline in permeate flux was greater. If the experimentation had been carried out for a longer time, based on the declining rate, the flux would have reached the values lower than 2L and 5L.

CONCLUSIONS

The effects of operating parameters on the separation of nitric acid-water mixture using AGMD were evaluated.

- At a constant feed flow rate and concentration, the permeate flux and the nitric acid selectivity increased with the increase in the feed solution temperature.
- With the increase in feed concentration, nitric acid selectivity increased, whereas the flux decreased below the azeotropic concentration region. When the initial feed solution was operated above the azeotropic concentration, the flux increased.
- Both the flux and selectivity increased appreciably with the increase in feed flow rate.
- The electivity increased at the expense of decrease in flux, when the air gap width was increased.

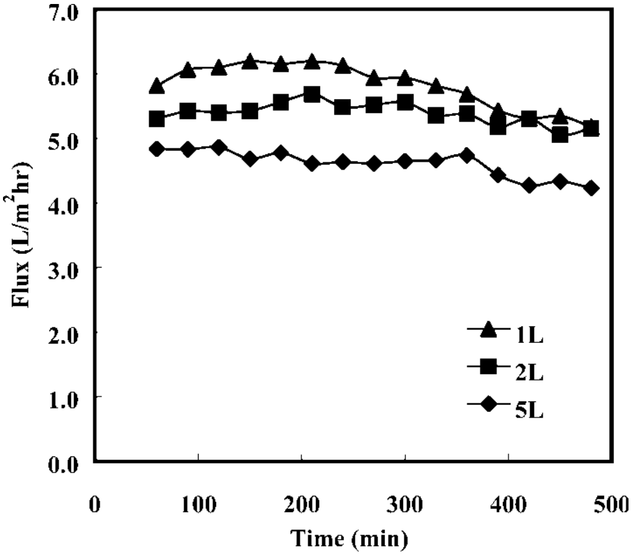

Figure 8. Permeate flux with different initial volume of feed solution and under feed recirculation mode (initial nitric acid feed concentration 2 M, feed flow rate 150 ml/min, inlet feed temperature 80°C, inlet cooling water temperature 15°C).

- When the feed solution was operated in a recirculation mode, the initial nitric acid solution concentration and the volume of the initial feed solution plays an important role in determining the flux and nitric acid concentration in the permeate.

AGMD was successfully applied for the separation of nitric-acid water mixture, using PTFE hydrophobic porous membrane.

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