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Stability and Performance of Ultrafiltration Membranes in Aqueous Ethanol

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ABSTRACT

The stability of several polymeric ultrafiltration membranes in aqueous ethanol was evaluated with an ethanol-soluble protein. Concentration polarization effects were observed at concentrations of 5–150 g/L of the protein, with flux becoming independent of pressure above 100–200 kPa. The data followed the film theory, resulting in a C_g value of 340 g/L with the model protein. Protein rejections for the selected membranes were 80–95%. However, even with prior conditioning, some membranes (polysulfone, polyacrylonitrile, and cellulosic) that initially appeared to give good performance and stability failed over a period of 10 weeks, resulting in an increase in flux or decrease in protein rejection.

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Polysulfone hollow fibers gave good initial performance but degraded in less than 24 hours of cumulative use.

Key Words: Ultrafiltration; Organic separations; Ethanol; Protein; Zein.

INTRODUCTION

Most studies on application of membrane technology in nonaqueous systems have focused on nanofiltration or reverse osmosis.[1–11] There are fewer reports on ultrafiltration (UF) applications,[12–14] and almost none on their long-term stability on exposure to organic solvents. Many were done with small benchtop systems for periods of minutes or hours. The stability of polymeric membranes in high concentrations of organic solvents is crucial to their successful commercialization. Most polymers or their supports that are used for membranes are first dissolved in organic solvents during manufacture. Thus, during use, either the membrane or the support could swell or dissolve in the solvent, leading to changes in solvent flux or solute rejection.[2,3,6,11] Solvents with solubility parameters similar to the polymer result in the greatest changes in the polymer matrix. Because certain solvents act as polymer plasticizers, they can significantly reduce the glass transition temperature of the membrane polymer. This will reduce the ability of the membrane to resist high transmembrane pressures.[14] This is why experiments performed at low pressure or a single pressure are inconclusive. Ceramic membranes are more stable to nonaqueous solvents, but they are significantly more expensive than polymeric membranes and are often limited by low surface area-to-volume ratios.

Iwama and Kazuse[15] examined stability of polyimide membranes in different organic solvents and reported no change in flux behavior up to 300 days. However, these tests were conducted at a single low pressure. Niwa et al.[16] reported membrane swelling and loss of separation properties of reverse osmosis membranes with 1% to 8% methyl ethyl ketone, tetrahydrofuran, and ethyl acetate solutions. Nguyen et al.[12] found that membrane permeability remained unchanged up to 3 to 4 weeks after a decline in the initial few days.

To use these membranes with organic solvents, it may be important to provide appropriate "conditioning" to the polymer matrix, in which the membrane is soaked in a series of successive baths of solvents of decreasing polarity. We recently reported on the effect of conditioning on the performance of 18 UF membranes in ethanol–water solutions.[13] It was

evident that membranes of a particular chemistry marketed by different companies are usually not compatible with organic solvents to the same extent. In most cases, these membranes are sold either without appropriate instructions for solvent conditioning and consequently fail in field tests, or are not stable in the long term and hence cannot be used.

This article reports on the effect of long-term exposure of selected polymeric membranes to 70% aqueous ethanol. The parameters studied were time of exposure, transmembrane pressure, and concentration of the protein on flux and rejection of an ethanol-soluble protein.

MATERIALS AND METHODS

Seven membranes were selected for this study (Table 1) based on our prior membrane screening work.[13] With the flat-sheet membranes, three samples of each membrane were conditioned by the solvent exchange procedure 1 described previously.[13] Experiments with these membranes were first conducted using a benchtop Amicon (Millipore, Bedford, MA, USA) dead-end stirred cell (Model 502). The cell was capable of withstanding pressures up to 500 kPa and holds a 62 mm membrane disc of area 28.7 cm^2. Pressure was generated by a nitrogen cylinder and turbulence was created by a magnetic stirrer operated at 300 RPM. Potable ethanol and deionized water used for these experiments were microfiltered through a 0.2 μm filter. All stirred cell experiments were at room temperature (24°C).

A model ethanol-soluble protein from maize (corn) was used for the tests with the flat-sheet membranes. The model solution contained 5–150 g/L zein (F4000, Freeman Industries, Tuckahoe, NY) in the aqueous ethanol solvent, which was 70% ethanol-30% water (v/v). The concentration of ethanol in the binary solvent was 0.42 M. In each experiment, the conditioned membrane was contacted with 250 mL protein solution and pressurized to the desired pressure. Flux measurements were made until at least three consecutive flux values were constant. All experiments were repeated within 24 hours and average values are reported.

The independent variables in this study were transmembrane pressure and protein concentration, and the dependent variables were flux and rejection. Flux is the volume of permeate per unit membrane area per unit time and is expressed as liters/m^2/hour (LMH). Rejection (R) is defined as:

$$R(\%) = (1 - C_P/C_R) \times 100 \quad (1)$$

where C_p and C_R are the concentrations of zein in permeate and retentate, respectively.

Table 1. Ultrafiltration membranes selected for stability studies.

Material[a]	Membrane	MWCO[b]	Configuration[c]	Manufacturer
Cellulose acetate	Cell	10,000	FS	Pall Filtron, Northborough, MA
Composite[d]	U20S	20,000	FS	Koch Membrane Systems, Wilmington, MA
PAN-m	MX25	25,000	FS	Osmonics, Minnetonka, MN
PAN-based	U20T	20,000	FS	Koch Membrane Systems, Wilmington, MA
PS	UFP10	10,000	HF	A/G Technology, Needham, MA
PS	PM10	10,000	HF	Koch Membrane Systems, Wilmington, MA
R. cellulose	YM10	10,000	FS	Millipore, Bedford, MA

[a]PAN = polyacrylonitrile; PS = polysulfone; R = regenerated; -m = modified.
[b]MWCO (molecular weight cut-off) values from manufacturers' specifications.
[c]FS = flat sheet; HF = hollow fiber.
[d]Composition is proprietary.

Membranes were cleaned by rinsing in multiple fresh solutions of 70% ethanol. If necessary, a cleaning solution consisting of 5 g/L NaOH in 70% ethanol was used. Each membrane was again thoroughly rinsed with multiple fresh solutions of 70% ethanol before use.

Upon completion of the experiments and cleaning, the membranes were stored in 70% ethanol at 24°C for periods up to 10 weeks. Flux and rejections with the model zein solution were measured at the end of each week.

Based on results from the dead-end cell studies, three of the more stable polymeric membranes (MX25, U20S, and U20T) were tested in the cross-flow mode using the Osmonics SEPA CF cell. The SEPA CF cell has an effective membrane area of 138.7 cm^2 and the stainless steel cell construction is capable of withstanding pressures up to 6.9 MPa (1000 psi). A Procon C0107A rotary positive displacement pump was used for recirculation. The independent variables were pressure, temperature, and protein concentration and the dependent variables were flux and rejection of the protein solution. Temperature was adjusted between 24°C and 50°C as required with a heater-stirrer. Cross-flow rate was set at the maximum capacity of the pump (5.4 L/min). Experiments were performed at zein concentrations of 5 g/L, 50 g/L, and 150 g/L at 138, 275, and 413 kPa (20, 40, and 60 psi).

Two hollow fiber modules were studied: a benchtop unit from A/G Technology (Needham, MA; UFP10-C4) and a pilot-scale module from Koch (Romicon HF15-PM-45). They had also been conditioned, as described earlier.[13] A peristaltic pump at a cross-flow rate of 2.2 L/min was used with the A/G Technology module. The Romicon hollow fibers were studied on pilot equipment using a centrifugal pump at a cross-flow rate of 25 L/min and a transmembrane pressure of 103 kPa. Both hollow fiber modules were evaluated with ethanol extracts of whole ground corn prepared as described by Shukla et al.[17] The experiments were carried out in a batch concentration mode. The volume concentration ratio (VCR) is defined as:

$$\text{VCR} = \frac{\text{Volume of feed}}{\text{Volume of retentate}} \tag{2}$$

Zein concentrations for model solutions (in feed and permeate) were measured spectrophotometrically using the procedure of Craine et al.[18] Zein concentration for the real feed (ethanol extract of corn) was measured by the Kjeldahl procedure.[17]

RESULTS AND DISCUSSION

Figures 1 through 5 show results of long-term stability studies with several membranes using a model solution of zein dissolved in 70% ethanol. In each case, the same membrane piece was exposed to 70% aqueous ethanol continuously for the period indicated. It was tested on a weekly basis with a fresh solution of 5 g/L zein in 70% ethanol as described earlier. The most striking feature of these data is the apparent failure of the membranes within a few weeks, especially at the moderately high pressures typical of UF systems. Initial rejections at all pressures, even 413 kPa (60 psi), are high in almost all cases. However, exposure to the solvent for even 1 week causes the rejection to drop significantly with a concomitant increase in flux (see Fig. 1–3). This is possibly the result of membrane swelling and pore dilation under pressure. Of the five membranes tested, the PAN-based membranes (MX25 and U20T) and the composite (U20S) appear to have the longest stability periods. The cell and YM10 membranes, which are cellulose based, show high rejection and fluxes in the first week of exposure, after which their rejection declines continuously.

When a membrane is exposed to an organic solvent, there is usually a decrease in flux which, in some cases, can be accounted for by changes in viscosity.[5,11,13] If this is the prevailing mechanism, a plot of flux versus the reciprocal of viscosity should be linear, according to the Hagen–Poiseuille and

Darcy models of fluid flow. All the membranes studied here, except the U20S, displayed almost linear behavior with the pure solvent.[13] However, in the presence of the protein and in a cross-flow mode of operation, all the membranes displayed classic concentration polarization effects, as shown in Figs. 6 through 8. Two different flow regimes can be identified: a pressure-controlled and a mass-transfer controlled region.[19] At low concentrations of protein in the feed (5 g/L) flux increases with increase in pressure. At higher zein concentrations of 50 g/L and 150 g/L, there is little or no increase in flux when pressure is increased above a certain critical value (about 138 kPa, 20 psi). Protein rejections are generally high (80–95%) and increases with protein concentration with the MX25 membrane, but generally decreases at higher protein levels with the two U20 membranes.

Flux with the U20S membrane shown in Fig. 7 (2–18 LMH) are lower than those for the MX25 membrane shown in Fig. 6 (8–43.3 LMH). The U20T is a PAN-based prototype membrane with the same support as the relatively more hydrophobic U20S membrane and is claimed by the manufacturer to be

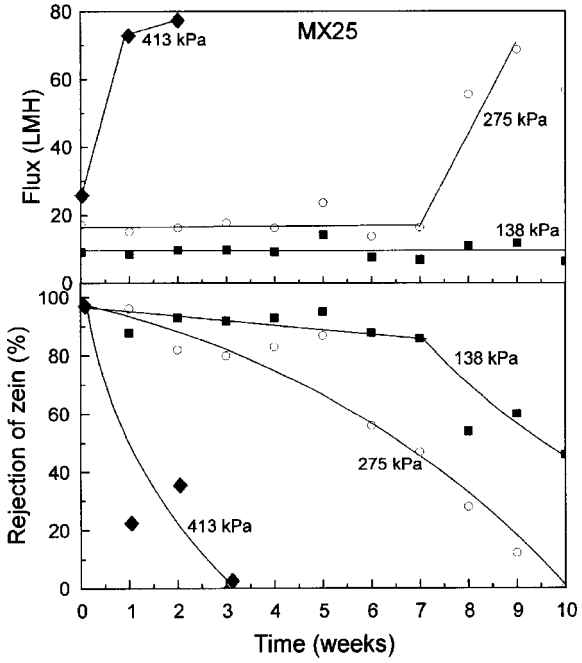

Figure 1. Effect of pressure on the stability of the MX25 membrane with a model zein solution containing 5 g zein/L in 70% ethanol.

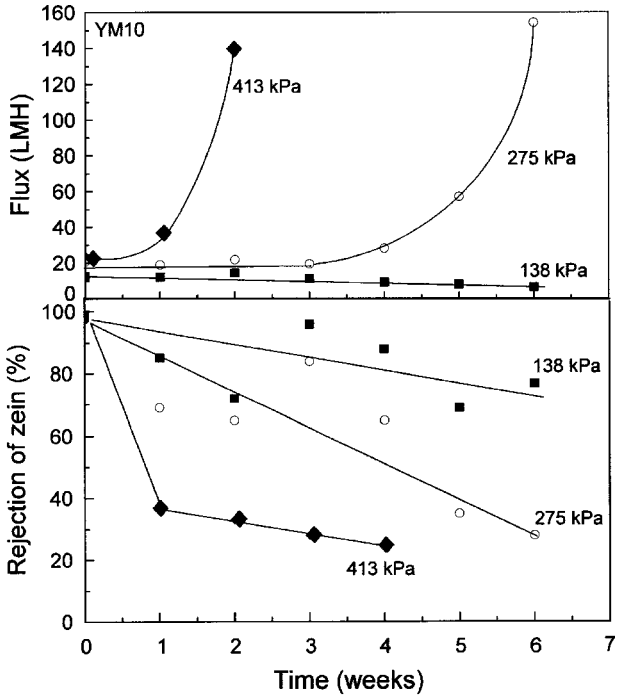

Figure 2. Effect of pressure on the stability of the YM10 membrane with a model zein solution containing 5 g zein/L in 70% ethanol.

as solvent stable as the U20S membrane. The U20T displayed higher fluxes (18–25 LMH) for 5 g/L protein solutions although flux at higher feed concentrations (50 g/L and 150 g/L) were nearly identical to those observed with the U20S membrane. But protein rejections were consistently lower (73–90%) than those observed with U20S. Rejection increases in most cases when the transmembrane pressure is increased possibly because of compression of the protein layer on the membrane surface. Higher rejections observed with 50 g/L and 150 g/L protein in feed support this reasoning.

Concentration Effects

The mass transfer/film theory model states that flux decreases exponentially with increasing protein concentration in the feed.[19]

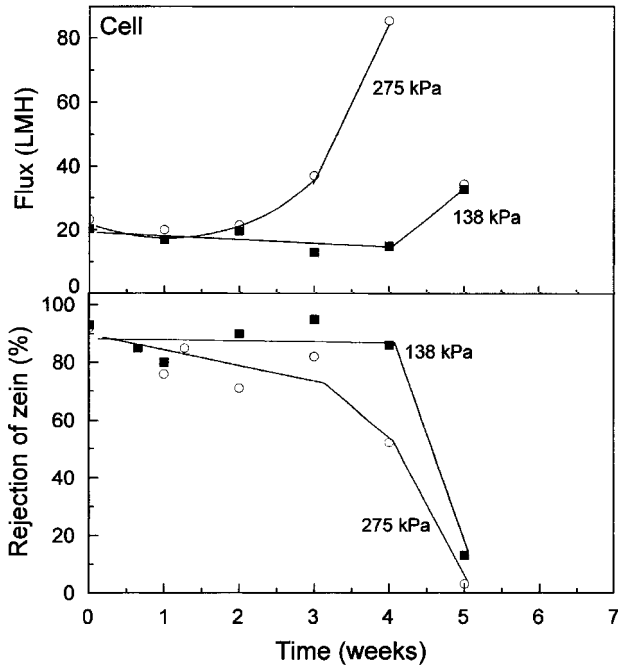

Figure 3. Effect of pressure on the stability of the cell membrane with a model zein solution containing 5 g zein/L in 70% ethanol.

This relationship is supposed to hold true regardless of flow conditions, membrane, turbulence, or temperature. Based on this approach, the steady state fluxes obtained in Figs. 6 through 8 were plotted against feed concentration at different pressures. As shown in Fig. 9, the plots appear to converge on the x-axis at one point, which the theory says is the "gel" concentration (C_g) of the solute on the membrane. The C_g value, as determined from all the plots together using the least squares approach, was 340 g/L.

Ethanol Extracts of Corn

Ethanol extracts of corn typically contain about 5 to 20 g/L total solids, of which 50% is the protein zein and the rest low molecular weight impurities,[17]

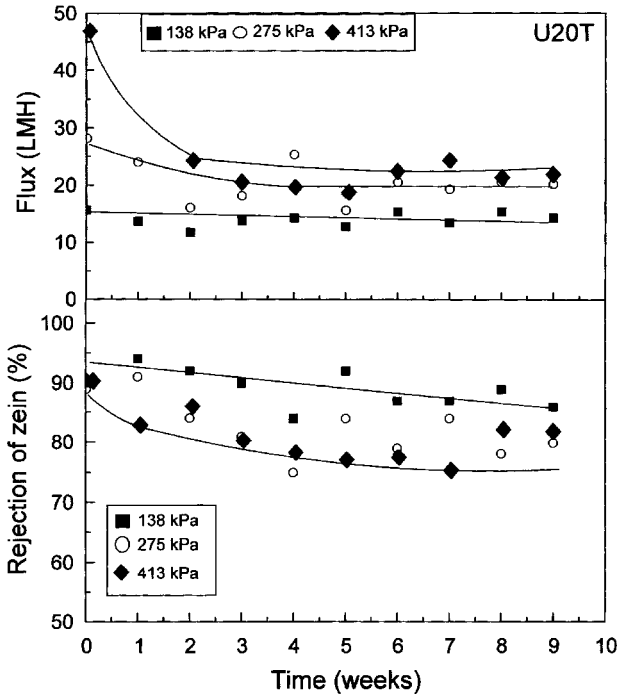

Figure 4. Effect of pressure on the stability of the U20T membrane with a model zein solution containing 5 g zein/L in 70% ethanol.

which can be removed by ultrafiltration. The extract was processed with the pilot scale Romicon HF15-45-PM10 hollow fibers from Koch and the laboratory scale UFP10C4 module from A/G Technology. As shown in Fig. 10, the PM10 hollow fibers gave a good rejection of protein with a flux of 10–15 LMH at a pressure of 103 kPa (15 psi). The flux dropped rapidly initially and stabilized after VCR 2. However, after two similar experiments were performed with this PM10 membrane, representing less than 24 hours of cumulative use, extensive fiber swelling and elongation were observed and the fibers were prone to rupture. Similar results were obtained with the UFP10C4 fibers: after two runs, the fibers were distorted and it became difficult to maintain flow and pressure.

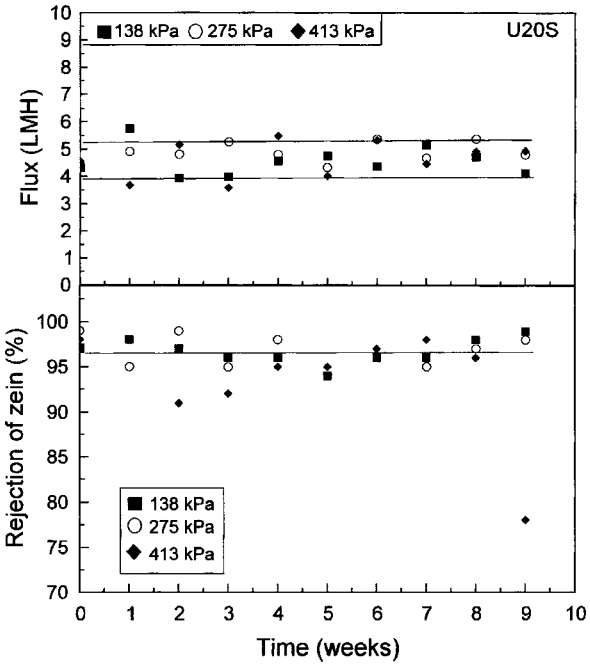

Figure 5. Effect of pressure on the stability of the U20S membrane with a model zein solution containing 5 g zein/L in 70% ethanol.

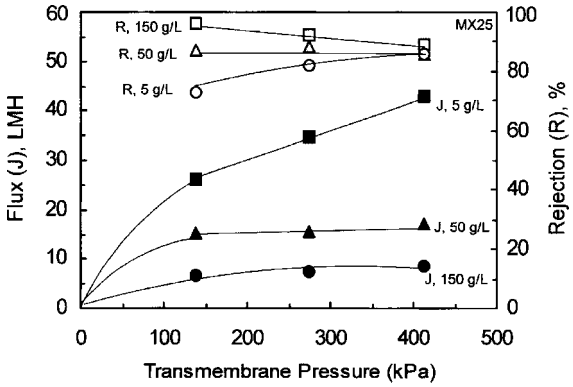

Figure 6. Pressure–flux relationships for MX25 membrane. Feed solutions were model zein in 70% ethanol.

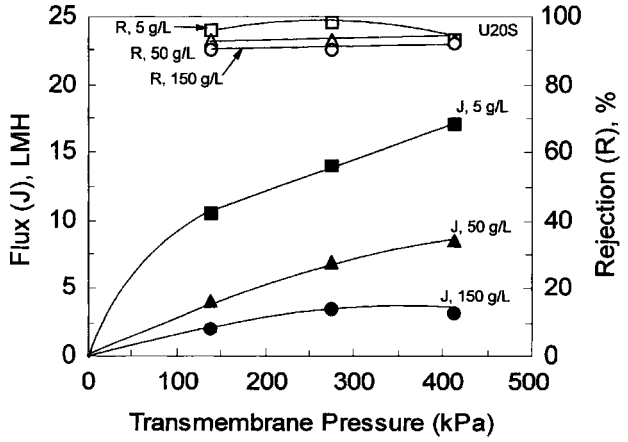

Figure 7. Pressure–flux relationships for U20S membrane. Feed solutions were model zein in 70% ethanol.

Fouling and Cleaning

Fouling, as indicated by a decline in flux or reduction in relative permeability of the membrane, was observed in all cases. Flux declined 20–50% from the initial value in 1–3 hours and then tended to remain steady. With organic solvent systems, cleaning membranes will be a challenge.

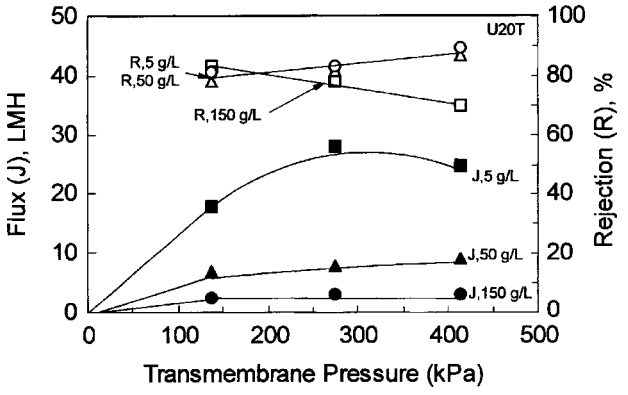

Figure 8. Pressure–flux relationships for U20T membrane. Feed solutions were model zein in 70% ethanol.

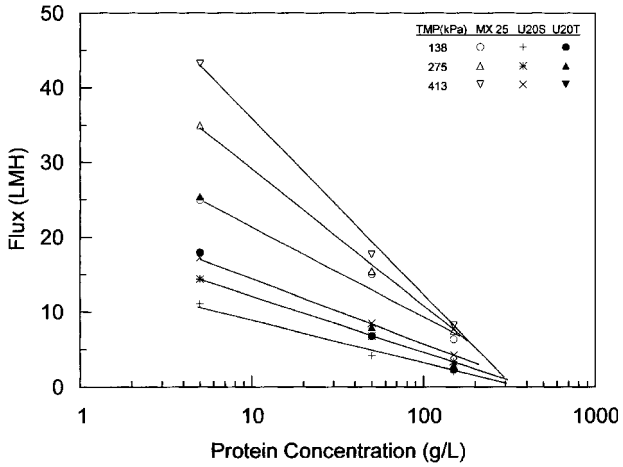

Figure 9. Effect of protein concentration and transmembrane pressure on flux for MX25, U20S and U20T membranes with model zein solutions.

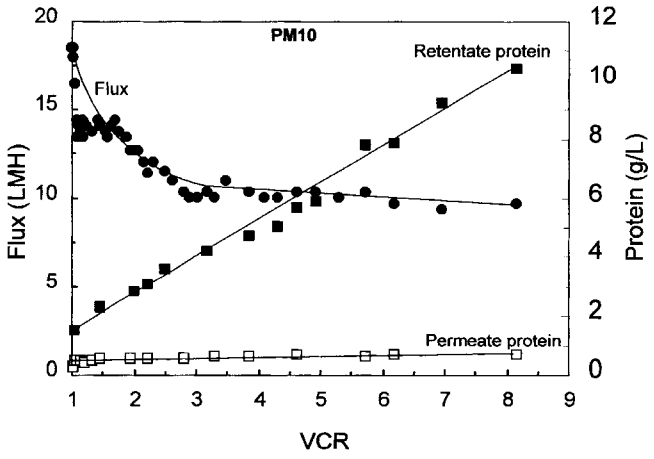

Figure 10. Ultrafiltration of ethanol extract of corn with the PM10 hollow fibers from Koch-Romicon. Effect of volume concentration ratio (VCR) on flux and protein concentrations in the retentate and permeate.

For the work described here, a cleaning solution of 5 g/L NaOH dissolved in 70% ethanol was used. If the time of exposure of the soiled membrane to this cleaning solution was no more than a few hours, flux could be recovered to about 80% of the original solvent flux. However, NaOH dissolved in 70% ethanol tends to precipitate on the membrane surface over long periods (24 hours or more), which essentially destroys the membrane for all practical purposes. Despite consultations with membrane manufacturers and manufacturers of cleaning chemicals, no chemical cleaning agents that could be used in ethanol solutions were found. Enzymes stable in organic solvents are not commercially available in the market. Attempts were made to use SPEZYME FAN, a protease from Genencor International that is used to increase the efficiency of ethanol fermentation. However, although it might be effective at the low 10–15% ethanol concentration in fermenters, it was ineffective at the 70% ethanol concentrations of our process. Flushing membrane systems with large volumes of fresh organic solvents as was done in this research can get expensive. It is usually not possible to clean the membrane intermittently with water between the organic solvent runs because frequent solvent exchange could damage the membrane. This problem of cleaning membranes in organic solvents needs attention before this technology can be successfully commercialized.

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