Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Benzinger, W. D. , Parekh, B. S. and Eichelberger, J. L.(1980) 'High Temperature Ultrafiltration With Kynar® Poly(Vinylidene Fluoride) Membranes', Separation Science and Technology, 15: 4, 1193 — 1204
To link to this Article: DOI: 10.1080/01496398008076294
URL: http://dx.doi.org/10.1080/01496398008076294

SEPARATION SCIENCE AND TECHNOLOGY, 15(4), pp. 1193-1204, 1980

HIGH TEMPERATURE ULTRAFILTRATION WITH KYNAR® POLY(VINYLIDENE FLUORIDE) MEMBRANES

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ABSTRACT

Ultrafiltration membranes prepared from KYNAR® poly(vinylidene fluoride) have excellent stability to high temperature and to harsh chemicals such as acids, strong oxidants, and many organic solvents. These membranes can be dried and rewetted without degradation of their properties, and they can be autoclaved.

Spiral-wound modules with reproducible performance have been fabricated from these membranes and used in pilot plant studies on a simulated textile sizing waste. Flux rates up to 15 gal/ft^2 day and retentions of 97% of the poly(vinyl alcohol) have been achieved routinely. No degradation in performance has been observed during continuous operation at 186°F and 20 to 25 psi for 7 months.

INTRODUCTION

Most commercial ultrafiltration membranes are useful only in a limited range of operating conditions because they are damaged by extremes of temperature, high and low pH, many organic solvents, and aggressive chemicals such as chlorine and other strong oxidants. Most membranes are also destroyed by drying. These drawbacks limit the usefulness of membranes for many industrial applications of ultrafiltration, including the concentration of textile sizing wastes, processing of food products, and concentration of industrial wastes. When the modules are stable only at low temperature, hot feed streams must be cooled with a resulting waste of energy. In addition, fluxes are lower at lower temperatures.

In industrial-scale ultrafiltration systems the membranes are fabricated into modules. In order for a module to be useful for separations involving high temperature or harsh chemicals, not only the membrane but also all other materials used in the module must be inert under the expected conditions of operation. In addition, the design and methods of construction of the module must minimize stress areas and mechanical weaknesses so that the module can operate for long periods without replacement.

Pennwalt Corporation has been developing ultrafiltration modules based on KYNAR® poly(vinylidene fluoride) membranes that are mechanically tough, resistant to harsh chemicals, and stable at high temperatures. This paper reports some of the data we have obtained on the chemical and thermal stability of KYNAR® membranes and on use of the modules containing KYNAR® membranes for concentration of poly(vinyl alcohol) solutions at high temperature.

EXPERIMENTAL

The poly(vinylidene fluoride) membranes were prepared in our laboratory from KYNAR® polymer by a proprietary process. For comparison purposes polysulfone membranes were prepared in our laboratory from Udel P-1700 polysulfone resin (Union Carbide) by a proprietary process.

Membranes were characterized by measuring distilled water flux and the flux and retention of 1% Carbowax 20M solutions at 30 psi in an Amicon TCF 10 thin-channel ultrafiltration cell. For chemical stability tests, membrane samples with known flux and retention were soaked in the specified solution or solvent for a given period (usually ∿1 month) and then thoroughly rinsed and retested. If no significant change in flux or retention was found, the sample was returned to the chemical solution for an additional period.

Elvanol T-25, fully hydrolyzed poly(vinyl alcohol), from E. I. DuPont de Nemours & Co. was used in all the process studies. The average molecular weight is 125,000.

Flux was determined by collecting time-measured grab samples of permeate. All feed and permeate samples were analyzed gravimetrically for Carbowax or Elvanol.

Module tests and process studies were carried out in a pilot-scale ultrafiltration system that was equipped with instrumentation for automatic recording and control of all process variables. The two test lines each had independent control of pressure and flow rate but were fed from a single feed tank.

RESULTS AND DISCUSSION

Chemical and Thermal Stability of Membranes

The results shown in Table 1 demonstrate the superior resistance of poly(vinylidene fluoride) membranes to high concentrations of strong oxidants. The KYNAR® membranes also have excellent long term stability in concentrated solutions of mineral acids and in dilute alkaline solutions, but no superiority over polysulfone in acids has been shown. The exposure tests of polysulfone in acids have not been in progress for the same length of time as those KYNAR membranes. Polysulfone is definitely superior to poly (vinylidene fluoride) in resistance to 10% caustic.

KYNAR® membranes are not harmed by soaking in a number of common organic solvents as shown in Table 2. Conversely, polysulfone membranes were instantly disintegrated by ethyl acetate, tetrahydrofuran, toluene, and chlorobenzene, and they shrank during long term soaking in ethanol, butanol, and 1:1 acetone:water.

The KYNAR® membranes can be dried without loss of physical strength, flexibility, flux, or retention properties. They are normally stored in a dry state. No treatment with a surfactant or humectant is required prior to drying. The dry membranes are conditioned for use by a short soaking in a water-soluble solvent such as alcohol followed by thorough rinsing with water.

The membranes can be used at temperatures up to at least 200°F for long periods, and they can be autoclaved.

TABLE 1
Pennwalt Ultrafiltration Membranes
Stability Data - Acids, Bases, and Oxidants

Exposure	KYNAR® Poly(vinylidene fluoride)		Polysulfone	
1% NaOCl	6 mo. 8 mo.	OK[1] failed[2]	1 mo.	failed[2]
10% $Na_2Cr_2O_7$ in 96% H_2SO_4	1 week 1.5 mo.	OK[1] failed[2]	2 hr.	disintegrated
5% $Na_2Cr_2O_7$ in 48% H_2SO_4	5 mo.	OK[1]	<2 weeks	disintegrated
10% H_2O_2	1.5 mo. 5 mo.	OK[1] failed[2]	1 week 1.5 mo.	OK[1] failed[2]
48% H_2SO_4	25 mo.	OK[1]	5 mo.	OK[1]
18% HCl	25 mo.	OK[1]		
35% HNO_3	25 mo.	OK[1]	5 mo.	OK[1]
42% H_3PO_4	25 mo.	OK[1]		
10% NaOH	1 mo. 3 mo.	OK[1,3] failed[2,3]	24 mo.	OK[1]
1% NaOH	24 mo.	OK[3,4]		
1% Na_2CO_3	24 mo.	OK[1]		

1. No significant change in flux or in retention of Carbowax 20M.
2. Became brittle, cracked and chipped.
3. Became discolored.
4. Flux has increased and retention of Carbowax has decreased; however, ∿90% of the Carbowax still retained.

Preliminary Test of Spiral Modules

A spiral module formed from KYNAR® membranes was operated successfully for 1000 hr in a pilot-scale test cell with a feed of deionized water at 196°F and 20 psi. Retention of Blue Dextran 2000 by the module was quantitative both at the beginning and at the end of the test.

TABLE 2
Pennwalt Ultrafiltration Membranes
Stability Data - Organic Solvents

Exposure	KYNAR® Poly(vinylidene fluoride)		Polysulfone
95% Ethanol	5 mo.	OK[1]	5 mo. membrane shrinking[2]
1:1 Acetone/Water	1 mo.	OK[1]	3 weeks membrane shrinking[2]
n-Butanol	1 mo.	OK[1]	3 weeks membrane shrinking[2]
Ethyl acetate	1 mo.	OK[1]	shrivels instantly
Tetrahydrofuran	1 mo.	OK[1]	dissolves instantly
Toluene	1 mo.	OK[1]	shrivels instantly
Chlorobenzene	1 mo.	OK[1]	dissolves instantly

1. No significant change in flux or in retention of Carbowax 20 M.
2. Membrane shrank ∿5% and could not be sealed in test cell adequately for testing.

Poly(vinyl alcohol) Process Studies

Purpose:

Following the demonstration of the high temperature stability of the KYNAR® membrane module for moderately long times, a series of process studies on a high temperature application of commercial interest was undertaken. There have been several studies (1-5) on the use of ultrafiltration for the recovery of textile sizing wastes at high temperature and at least two commercial plants employ this technology. Therefore it was decided to use poly(vinyl alcohol) [PVA] solutions as simulated textile sizing wastes for this study.

Our study had two basic purposes: 1) to determine the influence of flow rate, pressure, and temperature on the flux and retention of our modules and 2) to determine the ultimate stability of our modules at elevated temperatures under conditions similar to those in which they would be used in a commercial process.

Ultrafiltration Process Parameters:

A set of experiments was conducted in a "differential mode"; that is, the permeate and concentrate streams were returned to the feed tank in order to maintain a constant feed concentration. One module was run on each of the two test lines. All process variables (pressure, flow rate, temperature, and feed solution) were kept the same for each module on a given run, and, as a measure of reproducibility, the flux and retention of each module were determined independently. For each successive run one variable (pressure, flow rate, or temperature) was changed while the other two parameters were kept constant. Time-measured grab samples of the permeates were collected to determine flux and retention. Typical data are shown in Table 3 and Figure 1.

As expected, the flux is dependent on pressure at relatively low pressures, but as the pressure is increased, concentration polarization becomes the dominant factor and above ~30 psi increased pressure no longer has any effect on flux. Increasing the flow rate increases the mixing between the boundary layer at the membrane surface and the bulk of the solution and thus makes it easier for solvent molecules to reach the membrane surface. Therefore the flux increases with increased flow rate. Because polarization effects are only reduced, not eliminated, by increased flow rate, the flux vs. pressure relationship is similar for different flow rates. No significant variation in PVA retention with pressure or flow rate was found.

For maximum flux our modules should be operated at a pressure high enough to produce maximum polarization (i.e., above 30 psi) but not significantly higher than this because membrane compaction leading to flux declines may occur at very high pressures. The flow rate should also be high, but the optimum rate will depend on the economic balance between the higher

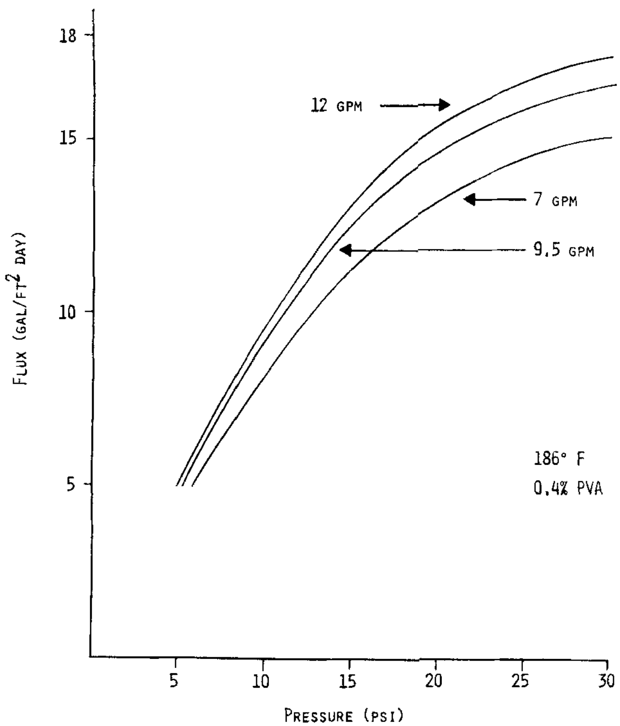

FIGURE 1. Differential study of flux and pressure, hot PVA.

fluxes that can be obtained at very high flow rates and the increased energy consumption required to produce high flow rates.

The flux increases with increasing temperature are due primarily to decreases in the viscosity of water and of the solution. Initially it appeared there was some decrease in retention at higher temperatures, but it became apparent later that the retention increased slightly as the run progressed, probably due to plugging of some of the larger pores in the membrane. The studies at 186°F were done first, followed by those at 155° and finally those at 125°. A repeat run at 186° after the completion of the other differential studies (bottom line of Table 3) demonstrates that retention does not vary significantly with temperature.

TABLE 3

Effect of Flow Rate and Temperature on Flux and Retention of KYNAR® Membranes

		Module 1		Module 2	
Temp.°F	Flow Rate gal/min	Flux gal/ft^{2}day	Retention %	Flux gal/ft^{2}day	Retention %
186	12.0	16.7	96	18.4	95
186	9.5	15.6	94	17.6	93
186	7.0	14.3	95	16.6	95
155	12.0	12.9	97	14.8	96
155	9.5	12.3	97	14.1	96
155	7.0	10.8	96	13.6	96
125	12.0	11.0	97	12.7	97
125	9.5	10.6	97	11.9	97
125	7.0	9.6	98	11.3	97
186	9.5	15.4	97	17.3	97

All data at 25 psi with a feed of 0.4% PVA.

The effect of solute concentration on the flux and retention of the modules was determined by a batch concentration experiment in which the permeate stream was continuously discarded. Ideally this experiment should have been run at the conditions that would give maximum flux. However, the experiment was run at 25 psi and 9.5 gal/min because long term automatic control by the system was better under these conditions. The temperature was maintained at 186°F. During the run, feed concentration increased from 0.4% to 4.6%. As expected the flux decreased linearly with the log of the concentration (Figure 2). PVA retention improved from 97 to 99% as the concentration increased.

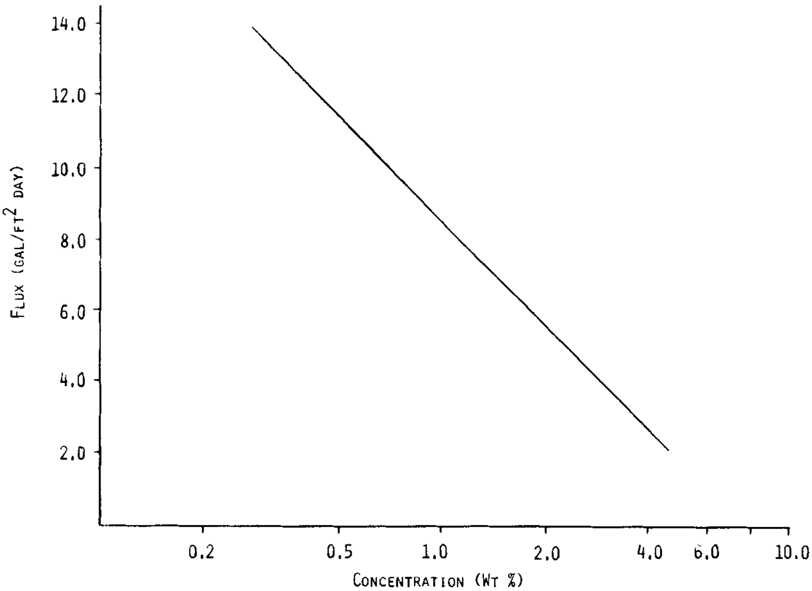

FIGURE 2. Flux vs concentration for hot PVA, batch experiment.

In all of these experiments replicate modules were subjected to identical conditions. As shown in Table 3, in all cases the results were closely duplicated. For simplicity the figures show only the data from module 1. The similarity of the data for the replicates confirms the reproducibility and quality control of the techniques used to produce the membranes and modules.

Long Term Studies:

Testing of the long term stability of KYNAR® modules at high temperature is still in progress. One module has been operating for 7 months in a 0.4% PVA solution at 186°F with a flow rate of 9.5-10 gal/min and pressure 20-25 psi. The flux of this module decreased from 11 to 7 gal/ft^2 day during the first two days of operation and has remained constant ever since. Retention has been constant at 97-98%. Another module

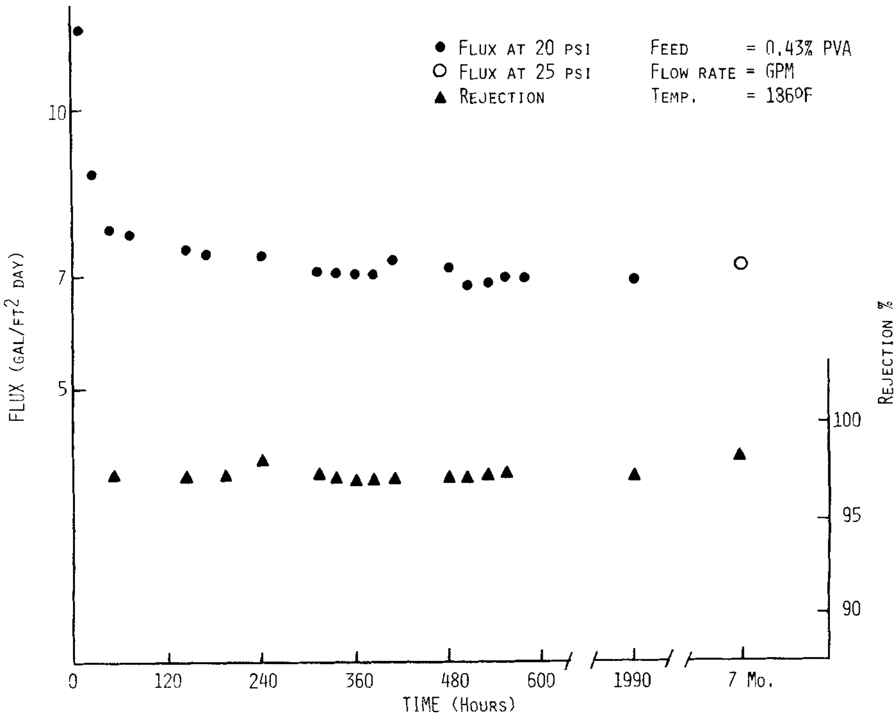

FIGURE 3. Long term stability of KYNAR module.

has been operating for over 4 months under the same conditions. Again, no change in retention has been observed.

No cleaning or flushing procedures have been used to increase the flux during these tests. However, on a number of occasions it has been necessary to shut the unit down for periods of one to several days because of maintenance work on the utilities in the building. During these shutdowns the modules have been removed and stored in containers of water at room temperature. Aside from these infrequent interruptions, testing is continuous.

CONCLUSIONS

KYNAR® membranes have excellent long term thermal stability and are superior to polysulfone membranes in resistance to many chemicals, especially strong oxidants and organic solvents. However, the KYNAR® membranes are degraded by extended exposure to high concentrations of caustic.

The resistance of the KYNAR® membranes to sterilants such as chlorine and hydrogen peroxide and the ability to withstand autoclaving are especially important if the membranes are to be used for food or medical applications. Shipment and storage of the KYNAR® membranes and modules are much easier because the membranes can be dried without addition of a surfactant or humectant. In the dry state the membranes should be incapable of supporting microbial growth.

The flux and retention of our modules in hot PVA solutions are comparable to the values reported for other membranes in various configurations. The changes in flux observed when pressure, flow rate, temperature, or feed concentration are changed are in agreement with theory. The stability of flux and retention during the 7 month run with the hot PVA solution provides assurance that commercial modules would have long lifetimes when operated at high temperature with industrial waste streams of similar composition. It should be noted that as yet no attempt has been made to optimize module or system design, and it is possible that, e.g., changes in spacer thickness or configuration could produce appreciable increases in flux.

The favorable properties of these membranes and modules should be advantageous for many ultrafiltration applications in which the modules must operate continuously at high temperature or in the presence of acids, oxidants, or solvents, or when they must be subjected frequently to harsh cleaning processes.

ACKNOWLEDGMENT

The authors thank J. M. deSimone, G. M. Hinde, and M. G. Toal for their valuable assistance in this work.

REFERENCES

1. G. L. Parsons, "Abstracts of Papers", 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1975; American Chemical Society: Washington, D. C., 1975; CELL 28.

2. G. L. Wright, presented at the Seminar on Industrial Applications of Membrane Separations, Clemson University, Aug.1975.

3. J. Trauter, and B. Ruess, Melliand Textilber. Int., 58 107(1977), ibid., 58, 711 (1977).

4. G. Wysochi, Melliand Textilber. Int., 58, 113 (1977).

5. C. R. Hoffman, R. Cadwalader, and M. H. Kleper, presented at the 4th Membrane Technology Seminar, Clemson University, March 1979.