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The Effect of Cleaning Agents on a Noncellulosic Ultrafiltration Membrane

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Abstract

Interactions of selected cleaning agents with clean Amicon PM-10 membranes were determined by water flux measurements. The membranes were contacted with the cleaning agents at various concentrations for 2.5-60 min. Modes of contact studied included the "static mode" (no overpressure) or ultrafiltration at 3.5 kg/cm^2 pressure. Several cleaning agents increased the membrane water flux, due to the apparent wetting effect exhibited by solutions above their critical micelle concentrations. Surface tension measurements indicated the persisting presence of these surfactants in the water permeate.

INTRODUCTION

Ultrafiltration (UF) is now an accepted unit operation in a variety of industries. Its operating principle is based on the use of anisotropic membranes for separation of components of differing molecular weights. The economy of UF is largely dependent on maximizing the permeation rate and the membrane life. The prevalent method for achieving these objectives is to remove membrane foulants by an in-place cleaning procedure followed by a sanitizing step. These procedures aim to restore the permeate flux to that value observed at the start of UF of a particular feed solution. In practice, some operators occasionally use the pure water flux as an indicator of the degree of cleaning during the actual cleaning process.

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While a study of membrane cleaning must ultimately deal with the interactions of cleaning agents with fouled membranes, it seems worthwhile nevertheless to conduct some investigation of the effect of cleaning agents on clean membranes as a control.

An implicit assumption of cleaning and sanitizing procedures is that the components of the formulations do not interact significantly with the membrane to affect rejection or flux characteristics. However, a study of the literature shows this assumption to be questionable.

In the case of a polyanionic-excess polyelectrolyte membrane such as the Amicon UM05, UF of a cationic surfactant solution resulted in extremely large, irreversible reductions in flux. Ultrafiltration of a 100-ppm solution of the anionic sodium dodecylbenzenesulfonate resulted in large, reversible flux reductions, while a 1000-ppm solution destroyed the membrane (*1*).

For noncellulosic membranes, contacting a DDS GR6P membrane with chlorine gave rise to increased water flux but decreased the whey flux (*2*). The membrane manufacturer (*3*) considers the use of a 1% Terg-a-zyme solution questionable with Amicon PM membranes whereas the detergent manufacturer recommends a working concentration of 0.75%. More intriguingly, a 0.002-*M* Triton X-100 solution is considered compatible with Amicon PM membranes, while a 0.001-*M* solution causes minor changes in flux or rejection (*3*).

It is apparent that the interaction of cleaning or sanitizing agents with UF membranes can have varying degrees of effect on membrane life and performance. Furthermore, the concentration of the agent used may be an important factor influencing consistency of performance of the cleaned membranes. To the best of our knowledge, there has been no study of the effects of commonly used cleaning agents on UF membrane performance. We report here on a study of the interaction of selected cleaning agents with Amicon PM-10 membranes as determined by water flux measurements.

EXPERIMENTAL

An Amicon 8400 stirred UF cell using 76 mm diameter PM-10 flat sheet membranes (Amicon Corp., Lexington, Massachusetts) was employed for most of the experimental work. Operating conditions were room temperature (18–23°C) and 3.5 kg/cm^2 pressure. Purified water, obtained by passing tap water through a Millipore Milli-Q water purification system (*RO*, carbon + ion exchange), was used throughout the study.

New membranes were "conditioned" by flushing in the cell with water until the flux reached an essentially constant value (typically 10–20% of the initial flux). Flux determinations were based on collection of permeate in tared beakers for 1 min. Results are reported in grams/minute rather than in normalized per unit area values to indicate the true magnitude of the flux changes.

The various cleaning solutions investigated were stirred in contact with a PM-10 membrane in the unpressurized cell for 15 min to simulate generally accepted clean-in-place procedures. After decanting the solution (300 mL used in all cases), the cell was quickly rinsed with 2 × 100 mL water, and water was flushed through the cell at 3.5 kg/cm^2. The flux and surface tension of the permeate were determined immediately after start-up and at appropriate intervals thereafter. Surface tension measurements were carried out with a Fisher Model 20 Surface Tensiometer (Fisher Scientific, Pittsburgh, Pennsylvania).

Membrane rejection was monitored by ultrafiltering a 0.1% solution of α-lactalbumin (200 mL) to give a permeate volume of 85 mL. The protein concentration of permeate and retentate was then determined by the method of Bradford (*4*).

Chemicals used were sodium dodecyl sulfate (Aldrich Chemical Co., Milwaukee, Wisconsin), cetyltrimethylammonium bromide (BDH Chemicals Ltd., Poole, England), Triton X-100 (J. T. Baker Chemical Co., Phillipsburg, New Jersey), and α-lactalbumin (Sigma Chemical Co., St. Louis, Missouri). Terg-a-zyme was obtained from Alconox Inc., New York, New York.

Selected experimental runs were also repeated with a DDS Lab-20 ultrafiltration module (De Danske Sukkerfabriker, Nakskow, Denmark) using GR6P membranes. Other procedures and materials were as described above.

RESULTS AND DISCUSSION

In New Zealand the cleaning agents for noncellulosic membranes which are used in commercial whey UF are nitric acid and sodium hydroxide-EDTA. When severe protein fouling occurs, enzyme-detergent formulations are used prior to the nitric acid and alkaline treatments (*5*). Accordingly, these reagents were studied as well as cationic, anionic, and nonionic surfactants, and a proprietary enzyme-detergent formulation, Terg-a-zyme. Table 1 summarizes the observed changes in water flux (ΔJ) after a membrane was contacted with the reagent. The ΔJ value

TABLE 1
Effect of Cleaning Agents on Water Flux of PM-10 Membranes[a]

Reagent	Water flux change (g/min)	
	Membrane A	Membrane B
1 *M* HNO_3	−7.1	−0.9
	0.8	4.5
	−1.6	6.4
	2.5	6.6
		23.6
1.2 *M* NaOH	25.3	36.5
	17.8	23.6
		39.1
0.1 *M* EDTA	1.2	−12.7
	5.9	2.5
		7.2
1.2 *M* NaOH + 0.1 *M* EDTA	0.4	20.8
	7.0	10.5
0.002 *M* Triton X-100	33.7	42.4
0.0001 *M* Triton X-100	−6.2	−0.1
	−3.0	−0.7
0.01 *M* SDS	21.5	36.3
		20.4
0.002 *M* SDS	7.0	18.5
		11.2
0.002 *M* CTAB	3.8	13.3
	22.6	18.4
0.0005 *M* CTAB	2.4	−2.8
	3.5	6.9
0.75% Terg-a-zyme	36.6	38.8
	52.0	27.4
0.075% Terg-a-zyme	11.5	7.5
	12.6	14.1

[a]Contact time between reagent and membrane: 15 min.

was calculated as the difference between the water flux immediately before treatment with the reagent and the flux immediately after treatment, rinsing, and start-up. From Table 1 it is apparent that individual membranes of the same type vary in their responses to the reagents tested, probably because of the slight batch-to-batch variations in the membrane manufacturing process. Furthermore, for a particular membrane, occasionally anomalous flux values were observed which cannot be readily explained; e.g., $\Delta J = 23.6$ and -0.9 mL/min for 1 *M* HNO_3. These anomalous fluctuations are unlikely to be due to experimental error (±4%) and may merit further investigation. Despite these

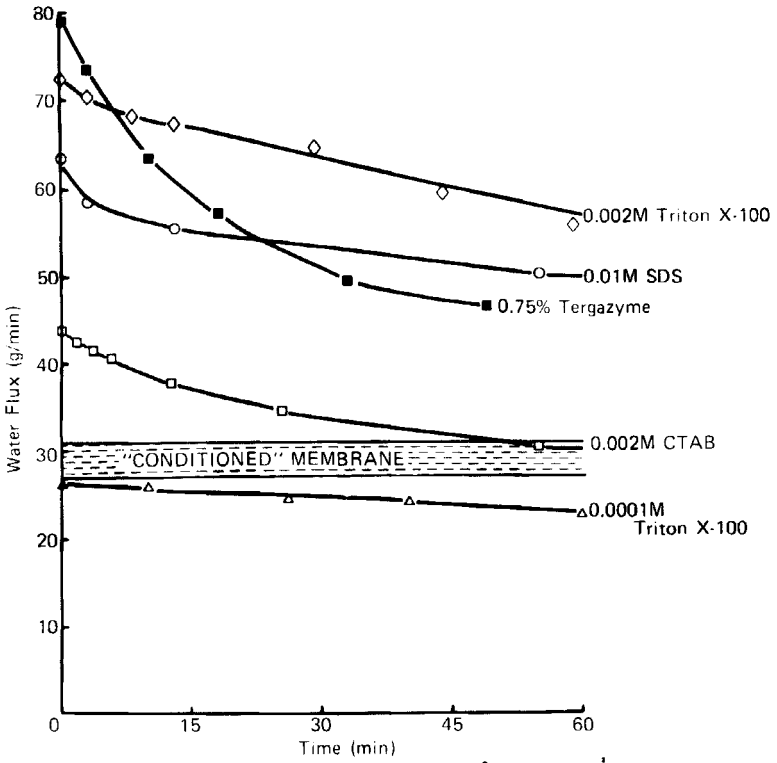

FIG. 1. Water flux vs time of ultrafiltration at 3.5 kg/cm^2 for a PM-10 membrane contacted for 15 min with various cleaning agents.

anomalies, certain trends may be discerned in the results, particularly for the surfactants.

Rather unexpectedly, all the reagents tested affect the water flux to some extent. Of the nonsurfactants, 0.1 *M* EDTA caused comparatively slight increases in flux, while a large flux increase was observed for 1.2 *M* NaOH. The difference in response of the two membranes precludes any definite conclusions about the effect of 1 *M* HNO_3 on water flux; to a lesser degree, the same inconclusiveness applies to the results from treatment of the two membranes with a mixture of 1.2 *M* NaOH and 0.1 *M* EDTA. A larger number of PM-10 membranes would need to be examined before a trend could be established. That contact with these simple chemicals would affect the water flux of clean membranes was not anticipated on the basis of current knowledge concerning interactions between polysulfones and the reagents in question.

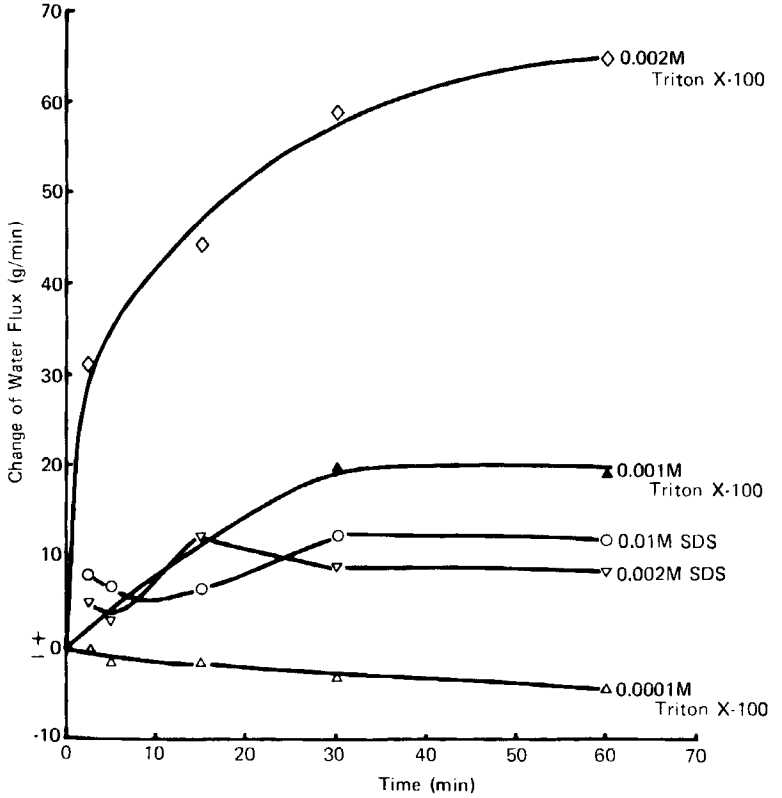

FIG. 2. Effect of contact time with solutions of Triton X-100 and sodium dodecyl sulfate on water flux of a PM-10 membrane measured immediately after rinsing.

The surfactant solutions of 0.002M Triton X-100, 0.01 *M* sodium dodecyl sulfate, and 0.75% Terg-a-zyme caused surprisingly large increases in water flux. These increases persisted for a significant time after the membrane was contacted with the reagent (Fig. 1). Thus, in the case of 0.002 *M* Triton X-100, water flux through the membrane at 3.5 kg/cm^2 was still 82% higher 1 h after flushing was commenced. For 0.75% Terg-a-zyme, the flux was 65% higher after 30 min. The cationic surfactant CTAB at 0.002 *M* concentration, on the other hand, caused only a slight flux increase. For 0.0001 *M* Triton X-100, a small but significant decrease in water flux was observed. This decrease was a persistent effect so that 30 min flushing with water did not restore the flux to its original value. The degree and persistence of this effect may have been confounded by membrane compaction, which has been shown to occur with changes in UF pressure (*6*).

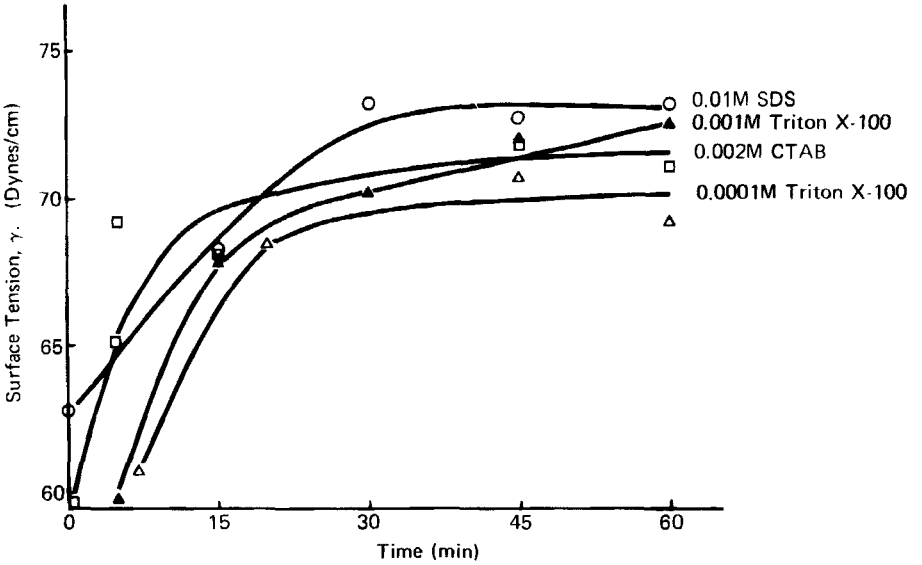

FIG. 3. Surface tension of permeate water ultrafiltered through a PM-10 membrane treated with various cleaning agents. (Initial surface tension measurements (dynes/centimeter ± standard deviation): Milli-Q water = 73 ± 0.5; 0.0001 *M* Triton X-100 = 41.8 ± 0.3; 0.001 *M* Triton X-100 = 33.0 ± 0.3; 0.002 *M* CTAB = 36.9 ± 0.2; 0.01 *M* SDS = 37.1 ± 0.3.)

The influence of the length of contact time between the membrane and the reagent on the change in water flux is shown in Fig. 2. A contact time of 2.5 min is sufficient for the effect to be observed: generally the longer the contact time, the longer the flux increase, although after 60 min a saturation effect is evident. The flux decreases observed with 0.0001 *M* Triton X-100 may be related to its critical micelle concentration which was reported as 0.0009 *M* (*7*). 0.0001 *M* Triton X-100 is below its critical micelle concentration, so that the surfactant will exist as discrete molecules in solutions. The surfactant molecules can then diffuse into the membrane "pores" (cut-off, 10,000 daltons) where they can form submicellar agglomerates which block the "pores," thereby reducing the water flux. We speculate that CTAB and sodium dodecyl sulfate did not cause a water flux reduction at concentrations below their critical micelle concentrations of 0.0001 *M* (*8*) and 0.0073 *M* (*9*), respectively, because charge repulsion may have caused a decrease in the rate of submicellar aggregation.

With regard to the persistent flux increases at concentrations greater than the critical micelle concentrations, we postulate a wetting effect which aids the convective water flow through the membrane pores. For

TABLE 2
Flux Changes in PM-10 Membranes Resulting from Ultrafiltration of 0.75% Terg-a-zyme and 0.002 *M* Triton X-100 at 3.5 kg/cm^2 Pressure

Detergent solution	Water flux before UF (g/min)	Detergent flux upon UF[a] (g/min)	Water flux after UF[b] (g/min)
0.75% Terg-a-zyme	37.2	16.4	98.0
0.002 *M* Triton X-100	54.0	13.9	65.7

[a]Average over 15 min UF period.
[b]All data are averages for two membranes.

0.002 *M* Triton X-100, the surfactant micelles are probably adsorbed on the membrane surface. On flushing the cell with water, the adsorbed micelles dissociate, dissolve, and are carried convectively into the "pores" where some readsorption can take place. The water flow prevents association into submicellar agglomerates, but the adsorbed surfactant effectively provides a wetted surface which facilitates the flux. With continued flushing, the adsorbed surfactant is eventually washed out and the flux returns to the starting value. Figure 3 shows the surface tension of water flushed through a treated membrane with various surfactants as a function of flushing time. In all cases it is evident that some surfactant is present even after 15 min of flushing.

Indirect evidence to support the wetting postulate comes from further experiments with Terg-a-zyme. The solid Terg-a-zyme was extracted with 10% ethanol to give a soluble organic fraction (25% by weight) and an insoluble inorganic fraction (75% by weight). The two fractions, when used separately at the concentrations corresponding to those in a 0.75% Terg-a-zyme solution, caused only moderate increases in the water flux of a PM-10 membrane. Thus, the organic fraction, which contains an anionic surfactant, increased the flux by 6.4 g/min while the inorganic component increased the flux by 4.9 g/min. However, a reconstituted solution corresponding to a 0.75% Terg-a-zyme solution gave a flux increase of 25.9 g/min, an effect that parallels the well-known synergism of detergency observed when an anionic surfactant acts in concert with an inorganic builder (*10*). The similarity between the two effects suggest that wetting is implicated in the observed water flux increase. That the membrane structure is not affected by the surfactant interaction was confirmed by measurements of the rejection of α-lactalbumin which was unchanged after treatment of a membrane with Terg-a-zyme.

Ultrafiltration of a 0.75% Terg-a-zyme solution and of 0.002 *M* Triton X-100 resulted in a lowering of the flux in comparison with water (Table 2).

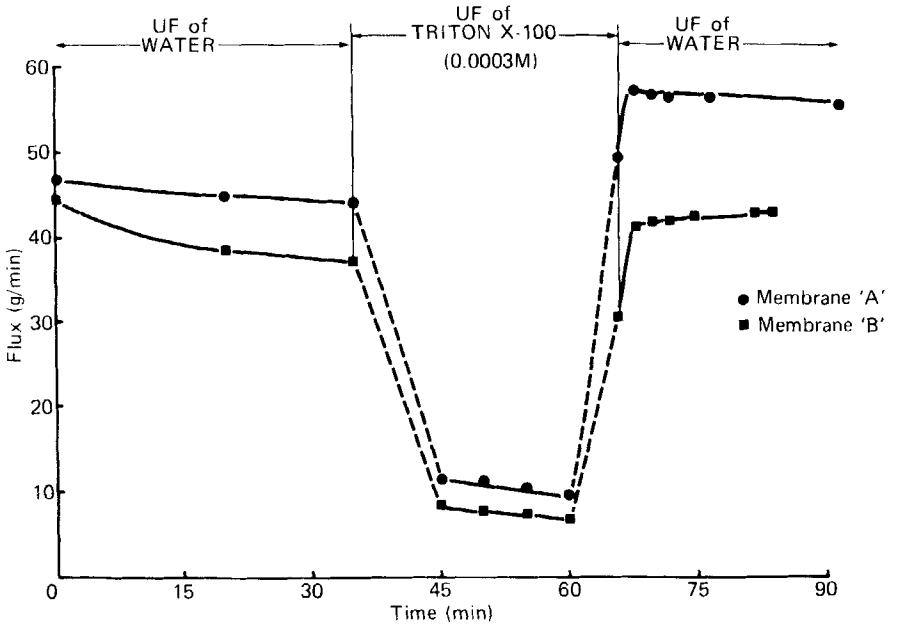

FIG. 4. Permeate flux change vs total time of ultrafiltration with two PM-10 membranes as affected by 0.0003 *M* Triton X-100.

However, on flushing with water at 3.5 kg/cm^2, the same flux increase was observed as when the membrane was contacted with these solutions in the unpressurized cell. Even when a 0.0003-*M* Triton X-100 solution, which is below the critical micelle concentration, was ultrafiltered and the cell subsequently flushed with water, instead of the expected decrease a slight increase in flux was observed (Fig. 4). This may be consistent with the remark of Bhattacharyya et al. (*11*) who, after ultrafiltering the same solution through an unspecified noncellulosic membrane, claims to have obtained complete flux recovery within 1 min of water flushing.

We interpret our seemingly paradoxical observation with 0.0003 *M* Triton X-100 solution (when compared with unpressurized contact with 0.0001 *M* solution) as follows: Ultrafiltration of the subcritical solution will give rise to concentration polarization at the membrane surface. A polarization modulus slightly greater than 3 will give rise to a local concentration of Triton X-100 at the membrane surface in excess of the critical micelle concentration, resulting in a situation similar to the static case when the membrane is contacted but not ultrafiltered with a solution whose concentration is above the critical micelle concentration. Hence, an increase in water flux would be expected and was indeed observed.

Only a slight flux increase was observed on contacting DDS GR6P membranes with 0.75% Terg-a-zyme solutions in a DDS Lab-20 Module. This may indicate that similar membranes from different manufacturers (polysulfone in this instance) may well have significantly different responses to cleaning agents. In instances when the pure water flux is used as an indicator of cleaning, these different responses can be misleading unless a control run has been previously carried out.

Another result which may have a practical implication, e.g., in food process applications, is the persistence of surfactants in permeates. Our findings suggest that the surfactants may not be completely flushed out by a short washing procedure.

CONCLUSIONS

Anionic, cationic, and nonionic surfactants unexpectedly give rise to increased water fluxes in clean PM-10 membranes. Triton X-100 is apparently absorbed strongly to PM-10 membranes and is only slowly desorbed by water flushing. Sodium hydroxide and EDTA, commonly used cleaning chemicals, also caused unexpected water flux increases in PM-10 membranes.

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