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REDUCED FOULING OF ULTRAFILTRATION MEMBRANES VIA SURFACE FLUORINATION

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ABSTRACT

The fouling resistance of a polysulfone membrane can be improved by fluorination. In the filtration of potato waste streams, fluorination of polysulfone membranes has improved both the initial flux and fouling rates of the treated membranes. Selectivities of the membranes as measured by COD and total organic nitrogen rejection were not affected by the fluorination process.

The fluorination process adds both fluorine and oxygen to the surface, and the increased oxygen and fluorine on the surface of the membrane increase the hydrophilic nature of the membrane. This increase of hydrophilicity reduces the rate of adsorption of hydrophobic foulants to the surface, decreasing the fouling rate. Increased hydrophilicity also decreases the capillary pressure and permits permeate flow through smaller pores.

INTRODUCTION

Fouling of ultrafiltration membranes is a critical problem in the food processing industry (1-5). Fouling of the membranes decreases flux and shortens their lifetime, making membranes less economical to food processors for concentrating process streams. Membranes foul with organic material (e.g., lipids during soy processing (6) and proteins from processing cheese whey (7)) and this results in a significant decline in flux. The fouling of the membranes may also be irreversible even with extensive cleaning, and as a result their lifetime is also decreased.

If fouling could be minimized, membrane separation would be a more economical and energy-saving method of concentrating the streams (1,2). Presently, the food processing industry consumes 2% of the total national energy usage (1). Most of the processes which consume this energy are thermally driven separations and concentrations where the process streams contain dilute solutions of organic matter. These process streams consist of recyclable organic material such as starch and protein. Present thermal concentration methods inherently use large amounts of energy to concentrate these process streams, due to the latent heat of vaporization of water.

Fouling of the membrane can be changed either by varying the hydrodynamics over the membrane or by varying the physico-chemical interaction between the foulant and the membrane (8-11). By varying hydrodynamics (i.e., increasing the crossflow velocity), foulant can be swept away from the membrane before adsorption can occur. This is illustrated in Figure 1. Alternatively, the adsorption of foulant may be reduced by decreasing the physico-chemical interaction between foulant and membrane, thus allowing the foulant to diffuse away and be swept from the surface.

This paper reports on an investigation of the effect of surface fluorination in reducing the fouling characteristics of membranes prepared from non-fluorinated polymers. Fluorination of the membrane chemically modifies the physico-chemical interaction between solution species and the membrane, and this modification can result in a decrease in fouling characteristics of the membranes. At the same time, fluorination should also help improve the lifetime of the membrane by providing an easier surface to clean during the cleaning cycle.

Spiral wound modules can be prepared more easily by use of surface fluorination on a non-fluorinated membrane than by the use of fluorinated polymers directly. Casting membranes using perfluorinated polymers is a difficult process (12). Further

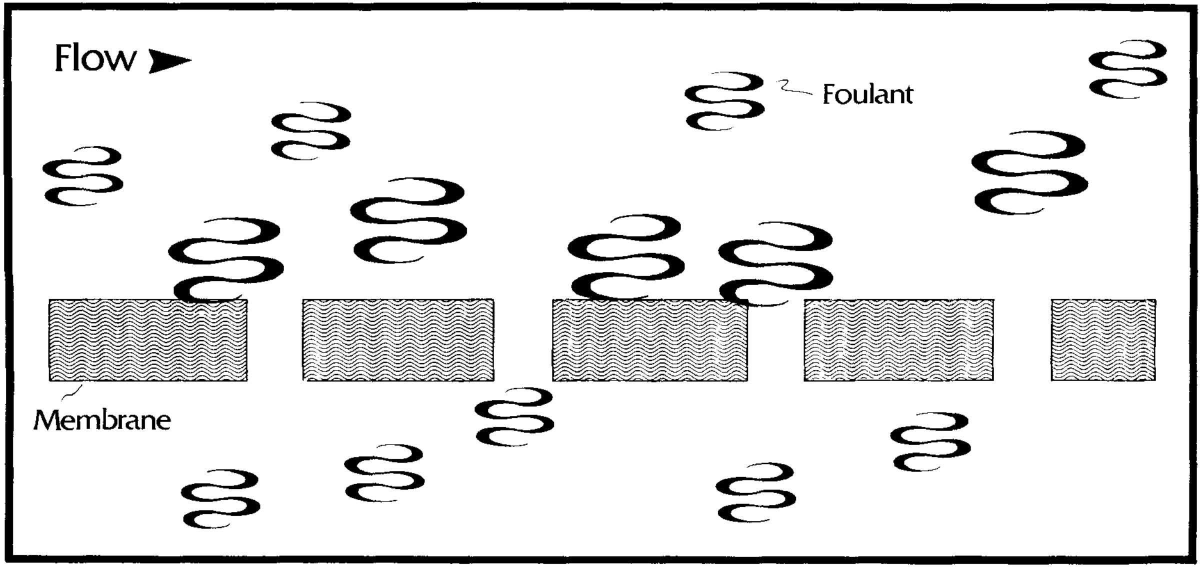

FIGURE 1. Schematic of ultrafiltration membrane separation of low M_w species from high M_w species via physical sieving.

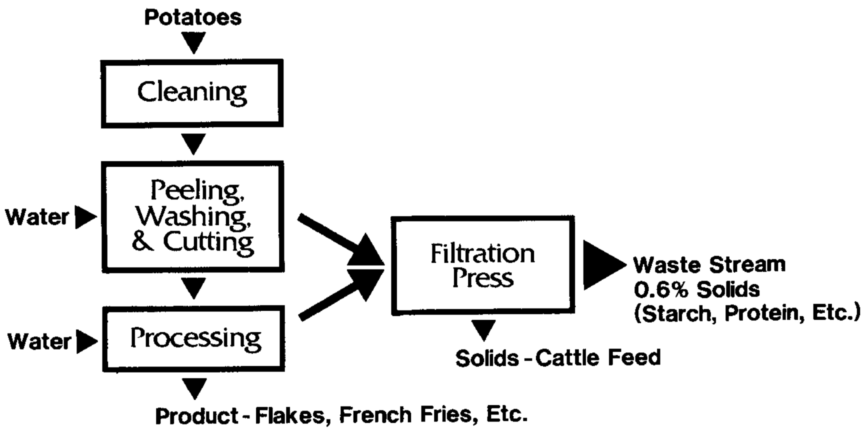

FIGURE 2. Schematic of a typical potato processor.

processing of fluorinated membranes into industrial type configurations is also difficult due to the non-wetting nature of the fluorinated polymer. Surface treatments are often necessary to allow adhesives to bond with these polymers in the construction of spiral modules (13). The fluorination process used in this work affects only the surface of a membrane without changing the bulk properties of the underlying polymer. Surface fluorination can be used to treat controlled areas, such that further processing is easily accomplished. The surface-fluorinated membranes investigated in this paper can easily be incorporated into currently available membrane modules if fluorination is introduced as a pre-treatment to the membranes before the construction of modules.

Ultrafiltration of potato-processing waste is a process where fouling has been noted. A schematic of the typical overall process is shown in Figure 2. The potato-processing industry produces 25 billion gallons of potato waste annually, and this aqueous waste stream contains about 0.6 % solids, mainly starch, protein and ash (1). A significant amount of energy would be needed to concentrate this dilute stream by thermal concentration. Presently, the waste is treated at a secondary waste-water treatment center or sprayed onto farm fields. With increased environmental concerns about biological oxygen demand (BOD) of waste products, waste streams must be pretreated before effluent can be released to any secondary waste-water treatment. Membrane concentration appears to be an energy-efficient way of concentrating potato-waste streams.

EXPERIMENTAL

Membrane Preparation

The ultrafiltration membranes studied were polysulfone membranes manufactured by Allied-Signal Fluid Systems (San Diego). Test membranes were cut from one large piece of asymmetric polysulfone membrane cast onto a polyester woven backing. The molecular weight cutoff of the prepared membrane was 100,000 daltons, as determined by the manufacturer via dextran rejection measurements. The membrane was stored wet. If it is allowed to dry, there is very little water flux through the membrane, even at applied trans-membrane pressures up to 2.76 MPa (400 psi).

The membranes were fluorinated at Allied-Signal's Morristown Laboratories by the Exploratory Research Group. The process used elemental fluorine in an inert gas. Oxygen was excluded from the reaction gas. The membranes were treated at various residence times from 0 to 60 minutes at a fluorine concentration of 0.025 vol% fluorine in nitrogen. After fluorination, the treated membrane was quickly exposed to air. One large sheet was treated at each set of fluorination conditions, and the same treated sheet was used for both ultrafiltration experiments and further surface analyses. Comparison of scanning electron micrographs of fluorinated and untreated membranes revealed no apparent surface damage due to the fluorination process.

Membrane Permeation System

Potato-waste filtration was carried out at room temperature in a standard closed-loop filtration system of three cells mounted in

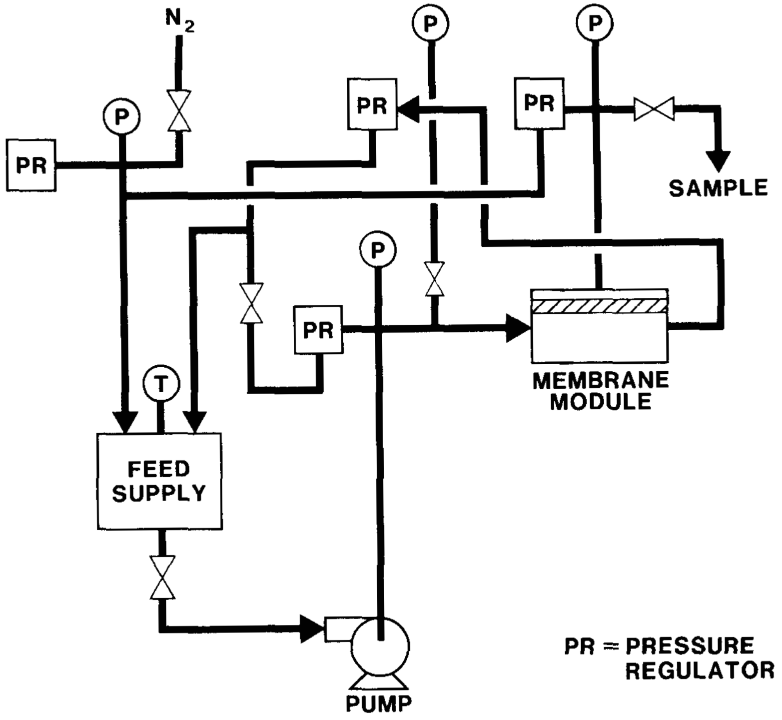

FIGURE 3. Schematic of an ultrafiltration system with a single cell.

series, each with an effective cross-sectional area of 19.4 cm^2 (3 in^2). A schematic of a related system containing one membrane module is shown in Figure 3. Filtrate and permeate were recycled to insure that feed composition remained constant. To reduce concentration polarization and minimize gel-layer formation (14), the unit was run in a cross-flow configuration with Reynolds number greater than 1600 for turbulent flow. The applied trans-membrane pressure was 0.69 MPa (100 psi).

Potato Waste Stream Feed

American Basic Foods (Blackfoot, ID) kindly provided an industrial potato-waste stream from water-gun slicing of potatoes.

The total solids of the waste stream was 1.1 wt %. The potato waste was kept in cold storage until the feed was to be tested. Even with cold storage, the potato waste degraded, resulting in a drop of pH from 6.7 to 3.9 for shipped waste and the feed used for this study, respectively. Before an experimental run, the waste water was treated with 200 ppm sodium benzoate as a preservative to prevent further degradation.

Analytical Procedures

COD measurements. Chemical oxygen demand (COD) measurements were made using a colorimetric method, following digestion with potassium dichromate. The COD measurement is an indirect analysis of the amount of organic carbon present in the retentate and permeate. The analysis was done with a commercially available HACH COD digestion reactor with the appropriate reagents for a particular COD range. COD results were read directly from a HACH DR 100 Colorimeter.

Total organic nitrogen. The total organic nitrogen of the permeate and feed streams was measured using a chemiluminescence technique (ASTM method D 4629-86). Total organic nitrogen is a direct measure of total protein for the feed used in this study.

Contact-angle measurements. Contact-angle measurements were taken with a comparator microscope fitted with a goniometer scale for measuring the angle directly. The contact-angle measurements were made on 2.54 cm by 2.54 cm (1" by 1") representative samples of membrane, using de-ionized water as the boundary liquid. The reported values are the average of at least six independent measurements on the membrane, where each contact-angle measurement was taken at three sites using both sides of the water drop. The measurements were taken within 2 minutes of placing the drop on the membrane surface. The contact angle provides a measure of the hydrophilicity of the membrane (15).

Surface composition. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface composition of the membranes. XPS has successfully been applied to the analysis of membrane properties (15-17). XPS data were recorded with an HP 5950 ESCA system. Small rectangular samples were covered with a gold-plated mask, containing a window 3 mm by 7 mm. Samples were introduced into the vacuum chamber and set to an angle of 38 degrees relative to the x-ray beam. This corresponds to an analysis depth of ca. 50 Å. The samples were flooded with electrons produced by a hot filament to minimize charge buildup. A survey scan of 0-1000 eV was taken to identify the elements on the membrane surface. Peak-fitting routines were used to obtain accurate area and binding-energy information for all peaks in the high-resolution windows. Adventitious carbon, seen on the samples exposed to air, has a binding energy equal to that of graphite or hydrocarbons. The binding energies reported have offset corrections to force adventitious carbon to 284.6 eV. The atomic percentages reported were corrected for the sensitivity of the instrument to the transition of each element and are presented as ratios with respect to the total number of carbon atoms. This procedure allows us to directly compare the atomic ratios of the various treated membranes by assuming that the number of carbons remains constant in the 50 Å layer that is being analyzed. Since no carbon is added to the surface and fluorination was done using dilute fluorine concentrations, this assumption is presumed to be valid.

RESULTS AND DISCUSSION

Membrane Performance

The effect of fluorination treatment time on membrane performances is illustrated in Figure 4 for three membranes. We observe that the initial fluxes of the treated membranes are higher than those of the untreated membrane. In general, initial flux increases with increased treatment time. We also note that treated membranes have lower fouling rates when compared to untreated

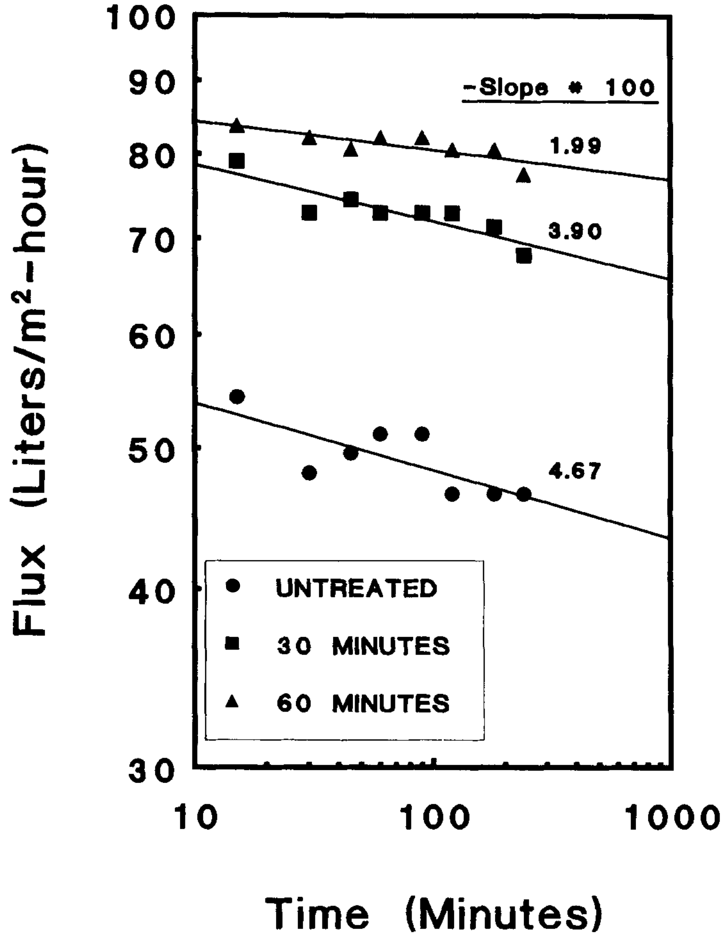

FIGURE 4. Changes in flux through untreated and fluorinated polysulfone membranes, using a potato-waste stream as feed.

TABLE 1. CONTACT-ANGLE MEASUREMENTS OF DEIONIZED WATER ON UNTREATED AND FLUORINATED POLYSULFONE MEMBRANES, TAKEN WITHIN 2 MINUTES AFTER DROP APPLICATION

Fluorination Time (Minutes)	Contact Angle (Deionized water)
0	90°
5	76°
10	69°
60	56°

membranes, as indicated by the decreasing slopes of the Log(Flux) versus Log(Time) plot of Figure 4. In general, the fouling rates of fluorinated membranes decrease with increasing treatment time. An ideal nonfouling membrane would have a slope of zero. Overall, fluorinated membranes exhibit better fouling resistance than the untreated polysulfone membrane.

COD and the total organic nitrogen were measured for both feed stream and permeate three hours into the experiment. The COD and total nitrogen of the feed stream were 8000 mg/l and 0.037 mass %, respectively. COD rejection through the membranes was 42 ± 1% and total organic nitrogen rejection was 78 ± 2%. The low rejection in COD is due to the large pore size of this polysulfone membrane. Rejections as measured by COD and total nitrogen were within one standard deviation of each other for fluorinated and untreated membranes, indicating that selectivity was not altered significantly by fluorination.

Contact-Angle Measurements

The contact angles measured for water on polysulfone and fluorinated polysulfone membranes are given in Table 1. The table illustrates the effect of fluorination treatment time on the contact angle of water on the membranes. The contact angle of water on treated polysulfone decreases with treatment time. Thus, a given

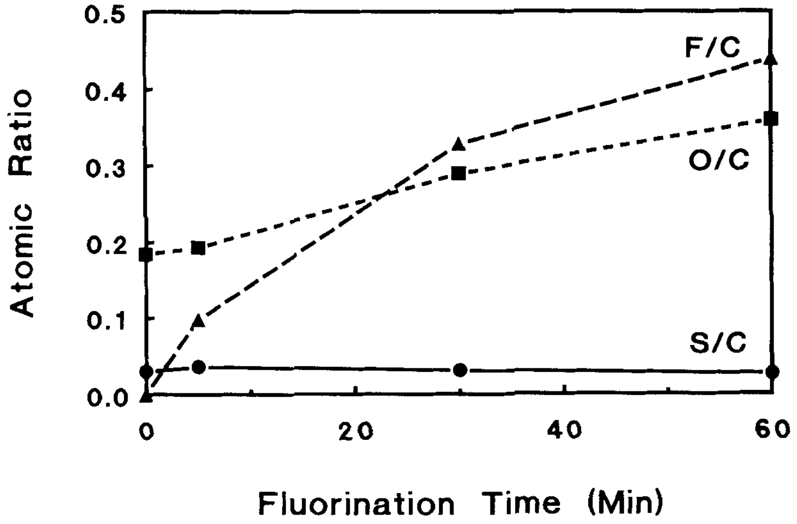

FIGURE 5. Selected atomic ratios for untreated and fluorinated polysulfone membranes, as determined by X-ray photoelectron spectroscopy.

membrane becomes more hydrophilic, not more hydrophobic, as would be expected if the membrane were perfluorinated.

Surface Composition

The effect of fluorination on the composition of membrane surfaces was analyzed by XPS. The results are shown in Figure 5. Assuming that the number of carbon atoms near the surface remains the same, atomic ratios with respect to carbon give a clear indication of chemistry that has occurred at the surface. The atomic ratio for sulfur/carbon remains relatively constant for all treatment times. We take this as an indication that fluorine does not cause significant C-S or C-C cleavage in the polysulfone backbone. The atomic ratios with respect to carbon show that fluorine content does increase as expected, with a atomic ratio of 0.44 F/C at 60 minutes. Note, however, that the figure also shows that the level of oxygen increases to an atomic ratio of 0.36 O/C after 60 minutes of fluorination. Since the reaction was carried out in an oxygen-free gas, the increase in oxygen must be a result of reaction with water or oxygen absorbed in the membrane prior to the start of the reaction, or reaction with atmospheric water or oxygen after removal of the sample from the fluorination reactor.

Based on our XPS results, we can advance two possible rationales for the increase in hydrophilicity we observe in the contact-angle experiments: polar interactions resulting from partial fluorination, and surface oxygenation. Fluorination can lower hydrophilicity as a surface becomes more like a perfluorinated polymer, but, at incomplete fluorination, it is reasonable that hydrophilicity might increase as a result of unbalanced dipole moments. The estimated Hildebrand interaction parameters (19) for a methyl group ($-CH_3$) and related fluorine-substituted methyl groups ($-CH_2F$, $-CHF_2$ and $-CF_3$) are 11.9, 16.4, 16.4 and 13.4 $MPa^{1/2}$, respectively. Thus, we could postulate that, with increasing fluorination, these methyl groups first become more hydrophilic, as revealed by the increase in the Hildebrand parameter, but eventually become more hydrophobic as the methyl group is perfluorinated.

Ring fluorination is expected to have a lesser effect on increasing the hydrophilicity of the surface. Thus, the Hildebrand interaction parameter for phenylene groups on the polysulfone molecule decreases on fluorination, which would have the effect of making a membrane more hydrophobic (i.e. 22.6 $MPa^{1/2}$ for the mono-substituted phenylene versus 24.7 $MPa^{1/2}$ for the phenylene group).

Surface oxygenation may also play a large role in increased hydrophilicity. Oxygenated species, such as acid fluorides, on a surface should greatly increase water wettability. Increase in hydrophilicity as a result of fluorination has been reported previously in the literature (21), with a minimum in contact angle observed at the maximum level of atomic oxygen on a fluorinated poly(ethylene) membrane for gas separation. However, at long treatment times, the membrane surface eventually became perfluorinated, and reached the maximum in contact angle. Of surface fluorination and oxygenation, we suspect that the hydrophilicity of the fluorinated membrane is mainly due to the increased oxygen level in the surface.

Thus, our results run in parallel to the results of Hayes and Dixon (20), which were obtained in a very different system. These authors investigated the effect of elemental fluorination on the surface energies of polyethylene. They measured the critical surface tensions using non-polar, polar and hydrogen bonding solvents and observed that fluorination lowered the critical surface tensions for non-polar and polar solvents, but increased the critical surface tension for hydrogen bonding solvents. Fluorine alone could not account for the large increase in hydrogen bonding energy since fluorine is a poor hydrogen bonder. They concluded that oxidation had occurred due to trace quantities of oxygen present at the polymer surface.

CONCLUSIONS

This study has shown that in the filtration of potato waste streams, permeate flux can be increased and the fouling rate of polysulfone membranes can be reduced by surface fluorination. Selectivities of the membranes, as judged by measurements of COD and total organic nitrogen, were not affected by fluorination.

We believe that the higher initial flux of the fluorinated membrane is due to increasing hydrophilicity of both the surface of the membrane and the surface inside the membrane pores. Increased hydrophilicity should decrease the capillary pressure necessary to initiate flow through the micropores of a membrane or, at a fixed trans-membrane pressure, the flow rate of permeate through a membrane should increase with increasing hydrophilicity. Increased hydrophilicity in the pores allows more smaller pores to participate in the separation process. Increased hydrophilicity also can explain the decrease in fouling rate shown in Figure 4. In other studies, the rate of adsorption of hydrophobic foulants (i.e., proteins) has been observed to decrease with the increase of hydrophilicity of a membrane surface (9,18). Pretreatment of a membrane with a hydrophilic polymer layer or hydrophilic surfactant layer evidently reduced the number of hydrophobic sites available for adsorption and deposition of protein to occur, thus reducing the observed fouling rate. In our study, we have seen that fluorination appears to similarly increase hydrophilicity and decrease fouling rate.

Surface analysis shows that the fluorination process adds both fluorine and oxygen to the surface. The increased oxygen and fluorine on the surface of the membrane are presumed to increase its hydrophilic nature.

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