MICROFILTRATION WITH RAPID BACKPULSING AND SURFACE-MODIFIED MEMBRANES

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1. Executive Summary

Novel water pretreatment systems consisting of foulant-resistant membranes and rapid backpulsing were explored. Work accomplished includes (i) development of methods to synthesize foulant-resistant membranes using polymer grafting, (ii) development and implementation of procedures for fouling characterization, and (iii) demonstration of rapid backpulsing for fouling control. Microporous membranes were first fabricated as originally proposed by photopolymerizing thin acrylate films with microcrystals which were subsequently dissolved. Although successful, the physical properties of these membranes are difficult to reproducibly control. New techniques, based upon grafting the desired functional groups on commercial polymer membranes as substrates, were also investigated and appear to have considerable promise.

Both one-step and two-step membrane surface modification techniques were studied. The one-step technique consists of the direct ultraviolet (UV) irradiation of membranes in the presence of benzophenone and monomer. This technique can be used when the hydrogen in the base membrane is significantly more reactive than the hydrogen in the monomer. The two-step technique includes the formation of surface photoinitiators induced by the irradiation of UV on the membranes in the presence of benzophenone and solvent, and the subsequent formation of a grafted layer induced by the irradiation of UV on the membranes with surface photoinitiators in the presence of monomer. Polypropylene and cellulose acetate membranes were modified with acrylic acid, methacrylic acid, poly(ethylene glycol 200) monomethacrylate, and 1H,1H-pentadecafluorooctyl acrylate. The effects of polymerization time, initiator concentration, monomer concentration, and solvent evaporation on the degree of grafting were examined. The results show for both one-step and two-step techniques that the degree of grafting increases with an increase in UV irradiation time and with benzophenone concentration. Significant homopolymerization occurred when the one-step technique was used, and when the monomer concentration was higher than 50 vol% in the two-step technique. These results indicate that polymerization conditions may be varied to adjust the degree of grafting.

The modified membranes were characterized with UV-vis spectrophotometry, Fourier transform infrared spectroscopy, and scanning electron microscopy. The results indicate that the monomers were bound to the membrane chains, the modified layer on the membrane surface was thin, and the layer did not extend into the interior of the membrane. Further, modified and unmodified membranes were evaluated using deadend and crossflow microfiltration devices to study fouling by bentonite and bacterial suspensions. These suspensions exhibited a combination of reversible and irreversible fouling, with irreversible fouling more severe for bacteria. Grafting was shown to reduce irreversible fouling.

Under optimized conditions, rapid backpulsing has yielded a 10-fold improvement in the net flux for bentonite suspensions with ceramic membranes, for which the fouling is mostly reversible. Tests with bacterial suspensions and commercial cellulose acetate membranes show severe fouling which is primarily irreversible. Nevertheless, two-fold and ten-fold improvements in the net flux were achieved with backpulsing under optimized conditions for unwashed and washed bacterial suspensions, respectively. Backpulsing also gave large flux improvements for oily water, but a long-term decline in performance was observed for unmodified ceramic and polymeric membranes. Preliminary backpulsing tests with bentonite suspensions and hydrophobic polypropylene membranes gave higher net fluxes when hydrophilic surface modification was made.

2. Introduction and Background

Small colloidal particles, microbes, viruses, and undissolved hydrocarbons are ubiquitous in both natural and industrial waters. Traditional technologies, such as gravity separators, air or gas flotation, chemical flocculation, and plate coalescers, are generally able to produce effluents containing as low as 30 ppm dispersed oil and particulates (Vandermuelen and Hrudey, 1987). However, these treatment technologies perform poorly on water streams containing very small (diameters less than 5-10 microns) particles and droplets, such as are typical in many desalting and pretreatment applications. The inability to fully treat water has led to tertiary treatment technologies, including hydrocyclones, centrifugation, carbon or other granular media adsorption, and membrane filtration. Hydrocyclones and centrifuges have high energy costs and are unable to remove drops and particles which are very small (diameters less than 5-10 microns, including most colloids, micelles, and microbes), or which have nearly the same density as water. The use of granular media, including filter aids, creates a significant disposal problem of the resulting solid wastes.

Membranes have been used successfully to treat wastewaters (e.g., Lahiere and Goodboy, 1993; Mueller *et al.*, 1997) and potable drinking water (e.g., Yoo *et al.*, 1995). Distinct advantages of membrane technology include low energy requirements, reduced sludge, and high quality of permeate. A recent study has shown that membrane processes may offer small facilities a less expensive alternative to conventional treatment for removal of particles and organic materials (Wiesner *et al.*, 1994). However, membrane technology can be relatively expensive for large volume applications. The high costs are due both to capital costs and to membrane costs. To reduce these costs, high permeate fluxes (volume processed per membrane area per time) are needed to reduce the membrane area and system size required. Unfortunately membranes experience a significant decline in performance due to fouling. Fouling results from the adsorption and accumulation of rejected hydrocarbons, suspended solids, microorganisms, and other components of the water stream on the membrane surfaces (external fouling) or in the membrane pores (internal fouling), as reviewed by Belfort *et al.* (1994). In general, membrane fouling may be *reversible* (physical deposition) or *irreversible* (chemical attachment).

A very promising technology for controlling fouling and improving permeate flux is crossflow filtration with rapid backpulsing (Rodgers and Sparks, 1992; Wenten, 1995; Redkar and Davis, 1995). In rapid backpulsing, the transmembrane pressure is reversed for approximately 0.1-1.0 s once every few seconds. This results in a hydraulic cleaning of the membrane by forcing permeate back through the membrane in the reverse direction; foulants are lifted off the membrane and swept to the filter exit by the crossflow. For nonadhesive foulants exhibiting reversible fouling, flux improvements of ten-fold or greater have been achieved with rapid backpulsing (Redkar and Davis, 1995; Redkar *et al.*, 1996); however, this technology is expected to be much less effective when the foulants are adhesive. For water treatment applications involving colloids, microbes, and undissolved hydrocarbons, the foulants are often adhesive and exhibit irreversible fouling, due to hydrophobic interactions, hydrogen bonding, van der Waals attractions, extracellular macromolecules, calcium bridging, and other effects.

Irreversible fouling can be reduced by changing the interactions between foulants and membranes. This can be carried out by modifying membrane surface chemistry, such as hydrophilicity, hydrophobicity, and surface charge or potential. Several membrane surface modification techniques have been developed. Kim *et al.* (1988, 1989) coated nonionic, water soluble polymers such as methylcellulose (MC), polyvinylalcohol (PVA), and polyvinylpyrrolidone (PVP) on poly-

sulfone ultrafiltration (UF) membranes by physical adsorption. Jonsson and Jonsson (1991) added different surface charge surfactants on commercial membranes of polysulfone (PS), poly(vinylidene fluoride) (PVDF), and cellulose acetate (CA) to improve the membrane performance. Kim *et al.* (1991) modified porous polyethylene (PE) microfiltration (MF) hollow fiber membranes with alcoholic hydroxyl or diol groups by electron beam irradiation-induced grafting of vinyl acetate or glycidyl methacrylate. A similar method was used by Keszler *et al.* (1991) to modify polyethersulfone with acrylic acid or acrylamide. Stengaard (1988) coated PVDF UF membranes with a hydrophilic cellulose polymer solution using heat curing. Hvid *et al.* (1990) modified polyethersulfone (PES) UF membranes with polyfunctional monomers using similar methods. Nystrom and Jarvinen (1991) modified PS membranes with dextrans using UV irradiation. Yan *et al.* (1988) grafted acrylamide on CA reverse osmosis (RO) membranes. Ulbricht *et al.* (1995, 1996a,b) reduced protein fouling by modifying UF polyacrylonitrile (PAN), PES and PS membranes using UV irradiation. Yamagishi *et al.* (1995a,b) modified poly(arylsulfone) UF membranes using a similar technique, and the membranes were used as both substrates and initiators to avoid homopolymerization in solution.

Photografting is a promising technology in membrane surface modification techniques due to its following advantages: mild reaction conditions, possible high selectivities by choosing suitable reactive groups and excitation wavelengths, and adjustable degree of polymerization and chain length of the grafts by controlling polymerization conditions. This technique was originally used to modify dense synthetic polymers in the 1950s by Oster and Shibata (1957). Wright (1967) reported surface photopolymerization of vinyl and diene monomers by UV radiation (200-350 nm) under vacuum conditions. Ang *et al.* (1980) studied photografting on polypropylene (PP) using benzoinethyl ether as a sensitizer. Ogiwara *et al.* (1981, 1982) developed two-stage processes where the polymer substrate was first coated with an initiator or sensitizer without UV light and then irradiated by UV in the presence of a vinyl monomer. Ranby and co-workers have performed research on the surface photografting of films using different processes, monomers, and initiators (Ranby *et al.*, 1988; Zhang and Ranby, 1990a,b,c; Yang and Ranby, 1996a,b,c).

3. Work Accomplished

This project was motivated by the goal of modifying membrane chemistry to reduce adhesion or irreversible fouling, in combination with the hydrodynamic techniques of backpulsing and crossflow to overcome nonadhesive or reversible membrane fouling. This novel, combined approach is expected to be effective against both physical deposition and chemical attachment. The project had three primary objectives or tasks: (i) membrane synthesis, (ii) fouling characterization, and (iii) development of rapid backpulsing. As detailed in the following sections, significant progress was made on all three tasks. Experiments were carried out primarily with bacterial suspensions and bentonite suspensions, and a few studies were also performed with oily waters.

3.1 Membrane Synthesis

Initial efforts on membrane synthesis were directed at photopolymerizing acrylate monomers to form dense films which were rendered microporous by dissolving fine crystals which had been incorporated during the polymerization. Powdered sugar was used for the dissolvable crystals, and microporous membranes were fabricated. However, these membranes are quite brittle, and their physical characteristics (such as pore size distribution and permeability) are difficult to

reproduce. Thus, an alternative strategy for the development of fouling-resistant membranes was pursued.

The alternative strategy uses commercially available microfiltration membrane materials which are then modified with polymer grafts of desired chemistries. A technique that involved one step using benzophenone (BP), a chosen monomer, and UV radiation was explored first. While this one-step technique provided favorable results, there are significant disadvantages inherent to the technique because of the reactivity of the monomer. To overcome these, we also developed a two-step process that involves the use of the same benzophenone initiator but two photoinduced reaction steps, with the first step including the initiator and a solvent and the second step including the desired monomer.

Commercially available porous polypropylene (PP) microfiltration disk membranes (M02WP04700), PP flat sheet membranes (M02WP00010), and cellulose acetate flat sheet membranes (A02SP00010) from MSI, Micron Separations Inc. were used for photochemical modification. Benzophenone was obtained from Aldrich (cat. no. B930-0). Poly(ethylene glycol 200) monomethacrylate (PEG200MA) (Polyscience, Inc., cat. no. 16712), acrylic acid (AA) (Aldrich, cat. no. 14,723-0), methacrylic acid (MAA) (Aldrich, cat. no. 15,572-1), and 1H,1H-pentadecafluorooctyl acrylate (FA) (Monomer-Polymer & Dajac Laboratories, Inc., cat no. 8932) were used as monomers to modify the PP and CA membranes. Benzene and deionized water were used as solvents. All chemicals were used without further purification.

Before performing membrane surface modification, it was necessary to examine if UV irradiation affects membrane pore sizes, and check the chemical compatibility of the membranes and solvents. To examine the effect of UV irradiation, the unmodified PP membranes were exposed to UV light, then water permeabilities were measured using a stirred cell microfiltration device. By comparing the fluxes of irradiated membranes with the flux of an unirradiated membrane, it was concluded that the UV irradiation did not affect the membranes. To test the chemical compatibility, membranes were weighed, soaked in benzene for 120 minutes, dried, and weighed again. Then, a stir-cell filtration device was used to measure the water flux. The flux for the membrane soaked in the solvent was the same as the flux for the unsoaked membrane, indicating that the solvent did not affect the membrane pores.

A UV-Vis spectrophotometer (model HP 8452A) was used to measure the absorbance of initiator, solvent, and monomers dissolved in ethanol. The UV spectra indicate that all these materials have an absorbance maximum at about 254 nm. The molar absorbance coefficients are listed in Table 1 for this short UV wavelength and at a long UV wavelength (365 nm).

Table 1: Absorbance coefficients

Species	**Absorbance coefficients (L/mole-cm)**	
	254 nm	365 nm
BP	5892	26.12
Benzene	61.31	0.011
AA	19.91	≈ 0
MAA	27.01	≈ 0
PEG200MA	8.087	≈ 0

One-Step Technique

The one-step technique (Figure 1), based on a recent method reported by Yang and Ranby (1996a), involves the use of short-wave UV radiation in the presence of benzophenone to generate reactive radicals on the surface of the membrane by hydrogen abstraction. In the presence of a monomer, these radicals propagate through the double bonds in the monomers to form polymer grafts that are covalently bonded to the membrane. The monomers react with the surface radicals preferentially because the benzophenone radical is much less reactive than the surface radical. The advantages of the one-step technique are that the rate of photografting polymerization can reach high values because both the monomer and initiator are reactants, which can shorten the irradiation time, and no solvent is needed. The disadvantage is that the hydrogen in the membrane must be more reactive than the hydrogen in the monomer. Otherwise, large amounts of homopolymerization will occur.

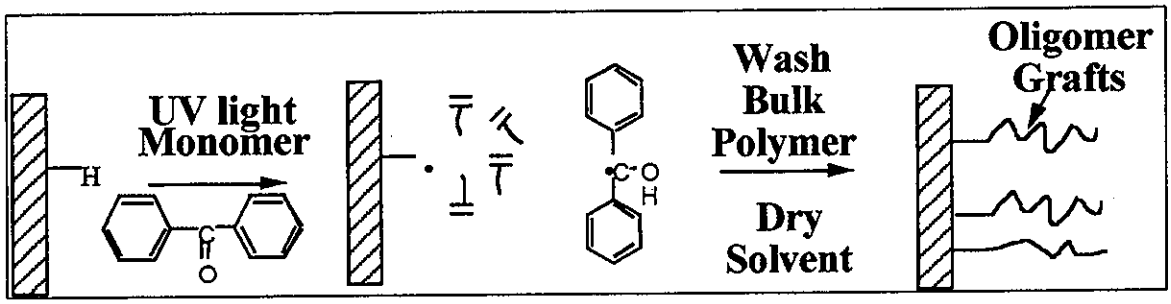


Figure 1. The one-step grafting technique.

For the one-step technique, the membrane presoaked in benzene was saturated with the BP and monomer solutions and then placed on a piece of plain glass, followed by placing a quartz on the upper side of the membrane to reduce oxygen inhibition and solvent evaporation. UV irradiations were carried out at room temperature with a short-wave UV lamp (254 nm, model R52G, UVP). Then, the residual unreacted solutions were removed by washing the membrane in deionized water and benzene, respectively. Finally, the membrane was dried at room temperature in air until constant weight.

Using this one-step technique, significant increases in pure water fluxes were found in very hydrophobic membranes such as polyethylene when acrylic acid (a very hydrophilic monomer) was grafted. The poly(AA) grafts increased the hydrophilicity of the membrane, thereby enhancing the flux of water through the membrane. Similar results were found with PP membranes, and with MAA and PEG200MA monomers.

Figure 2 illustrates the effects of polymerization conditions on the degree of grafting of AA on PP membranes. The degree of grafting increased with increasing UV irradiation time within the range studied. The results also show that the degree of grafting at a BP concentration of 5 wt% is higher than the weight gain at a BP concentration of 3 wt% under the same other conditions. However, the initiator concentration cannot be too high, as otherwise the initiator would absorb too much of the radiation before the radiation reached the membrane.

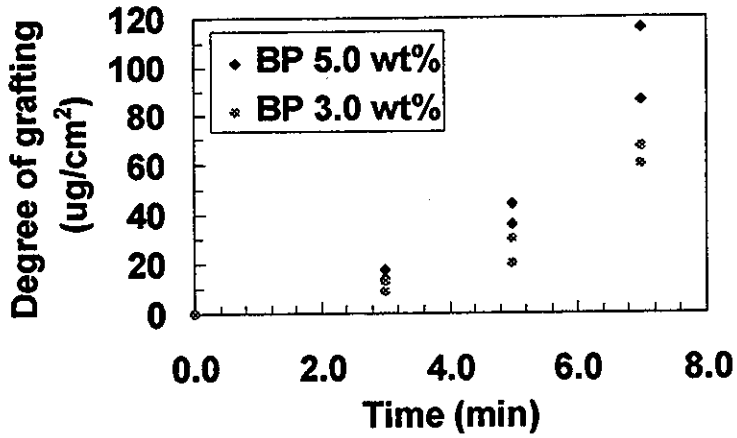


Figure 2. Photoinitiated grafting polymerization of AA onto 0.22 μm PP MF disk membranes.

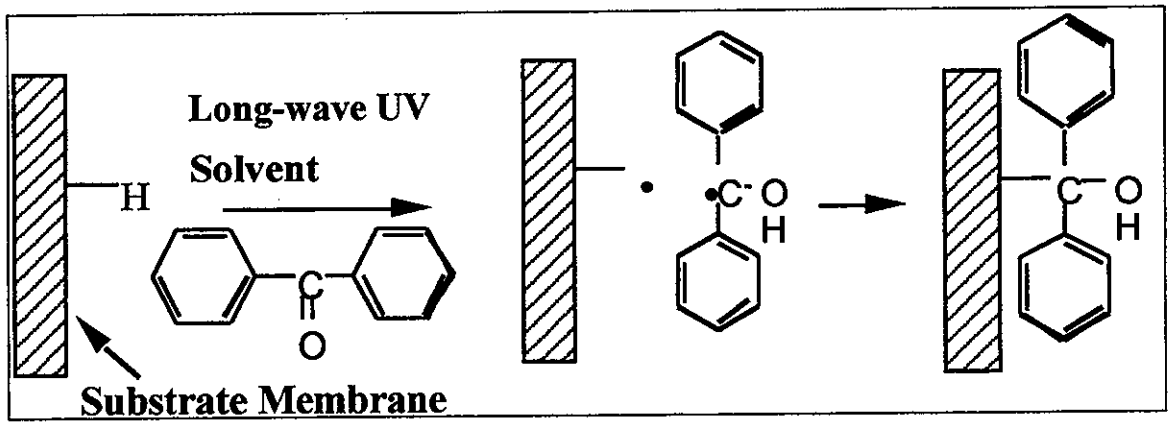
Because most monomers can also absorb light in the 200-300 nm wavelength range (see Table 1), there is a significant problem in using the hydrogen abstraction mechanism in the one-step technique. In the presence of the short-wave UV light, the monomers themselves can provide sites for hydrogen abstraction (*e.g.*, the hydrogens in the ethylene glycol chains of PEG200MA) and, as a result, form bulk polymer (as opposed to grafted polymer). In addition, as more than one hydrogen may be abstracted from a growing chain, a crosslinked network structure may evolve. Such a crosslinked polymer does not dissolve readily and fills the pores of the membrane. Thus, the flux through the membrane decreases significantly with large amounts of grafting.

Two-step Technique

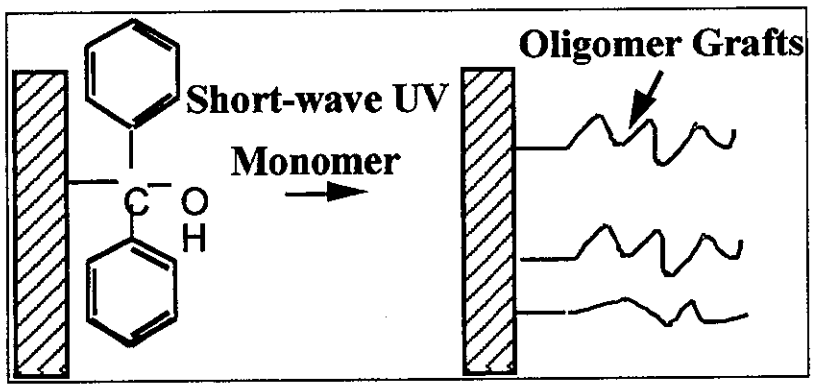
To circumvent some of the problems associated with the one-step technique, another method to perform polymer grafting was developed. As illustrated in Figure 3, this method is a two-step process that involves (1) the synthesis of a surface initiator, *i.e.*, a polymer substrate or membrane with the benzophenone initiator covalently bonded to the surface, and (2) the grafting of a desired monomer.

In step 1, a solution of benzophenone in a solvent (a solvent is chosen which does not degrade or dissolve the membrane) is applied on the membrane to be modified. This membrane is exposed to long-wave UV radiation (365 nm). The benzophenone absorbs this radiation, and facilitates the abstraction of hydrogen atoms from the surface of the membrane. Surface photoinitiators are formed by the recombination of the radicals generated from benzophenone and the radicals created on the membrane surface. Short-wave radiation is not used in this step because the solvent (benzene) absorbs too much short-wave UV radiation (see Table 1).

Because there is no monomer in this first step, the recombination of the radicals generated from benzophenone and the radicals created on the surface takes place readily. By repeated coats of the benzophenone/solvent mixture and exposure to short-wave UV light, a surface initiator is formed. Excess benzophenone that is unattached to the polymer substrate is then washed away using a solvent and the membrane is dried.



Step 1



Step 2

Figure 3. The two-step grafting technique.

In step 2, the membrane with initiator groups grafted on its surface is exposed to short-wave UV radiation (254 nm) in the presence of the monomer to be grafted. Although the monomers absorb in the short-wave UV region (see Table 1), the problem of benzophenone abstracting hydrogen from the monomers is prevalent only when benzophenone is free in solution and not when it has been grafted on the surface. By diluting the monomers with water in step 2, the problems associated with homopolymerization and light absorption by the monomers may be eliminated. The UV light cleaves the carbon-carbon bond of the surface initiator species to form surface radicals and benzophenone radicals. The monomer reacts with the surface radicals preferentially because of steric effects. Thus, the desired oligomer chains or low molecular weight polymer chains can be grafted on the membrane.

For the two-step technique, the procedures in the first step were the same as those in the one-step technique, except that the membranes were saturated with BP and benzene solutions instead of BP and monomer solutions. The residual unreacted solutions were removed by washing the membrane in benzene, and then the membrane was dried at room temperature in air until constant weight. In the second step, the procedures in the first step were repeated, except that monomer solutions were used instead of BP solutions and a long-wave ultracure UV lamp (365 nm, 100 ss

Plus) was used. Then, membranes were soaked in deionized water for 10 hours, washed and dried. Finally, the membranes were washed in benzene and dried.

Benzene was chosen as a solvent for the present research because it wets the membranes used but does not dissolve them, it does not have easily extractable hydrogen, and it is easily removed after step 1. Benzene is a poor hydrogen donor due to the high carbon-hydrogen bond energy and low hydrogen abstraction reaction rate constant (Turro, 1967; Gilbert and Baggott, 1991).

Figure 4 shows the effect of BP concentration on the degree of grafting for step 1. The degree of grafting increased quickly with increasing BP concentration at first, then increased more slowly. This is because the BP in the solution layer absorbed more UV light when the BP concentration was higher, and less UV light then reached the membrane surface.

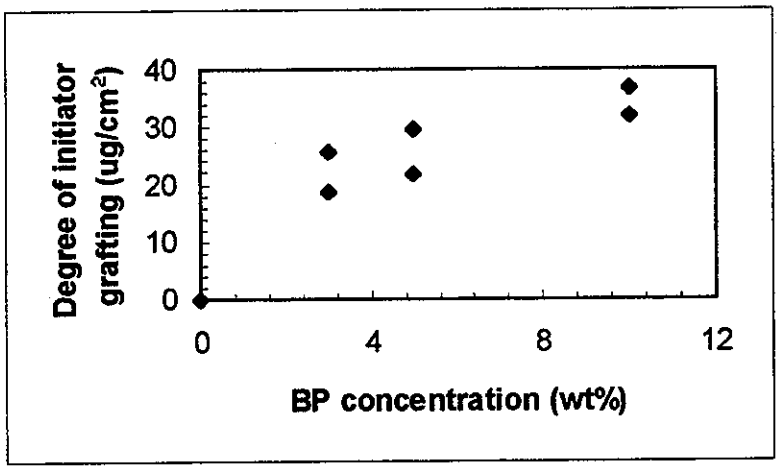


Figure 4. Photoreduction of BP onto 0.22 μm PP MF disk membranes; data are shown for two experiments performed for each BP concentration with the same conditions.

Table 2 shows that the degree of grafting of photoinitiator in step 1 increased with increasing irradiation time. Additional grafting occurred when the initiator solution was added and irradiated multiple times (the bottom three entries in Table 2), indicating the initiation becomes depleted and/or the solvent evaporates after long irradiation times. The number of active sites of surface photoinitiator formed was calculated from the measured weight gain and the molecular weight of benzophenone. If it is assumed that each active site can photoinitiate one polymer chain, then the number of grafting polymer chains can be controlled by adjusting the photoreduction reaction conditions.

In Step 2, the desired polymerization takes place on the membrane surface because of the surface photoinitiator. However, significant homopolymerization also occurred in the grafting process because AA and other monomers are very sensitive to the short-wave UV light. To solve this problem, monomer solutions were diluted with deionized water. The degree of homopolymerization was reduced substantially when the monomer concentration was no more than 50 vol%. The effect of polymerization time and monomer concentration on the degree of monomer grafting is shown in Table 3. The degree of monomer grafting increased with increasing polymeri-

Table 2. Grafting of photoinitiator on polypropylene 0.22 μm disk membranes using 5 wt% benzophenone in benzene.

Irradiation Time (min)	Degree of grafting ($\mu g/cm^2$)	Number of active sites ($10^{16}/cm^2$)
15	13	4.3
30	23	7.6
60	28	9.4
90	33	10.9
15 × 2	26	8.5
30 × 2	39	12.9
30 × 3	57	18.7

Table 3. Effect of monomer concentration and irradiation time on the grafting of acrylic acid on 0.22 μm polypropylene disk membranes.

monomer concentration (vol%)	irradiation time (min)	degree of grafting ($\mu g/cm^2$)	average chain length (repeat units/chain)
33	30	0	0
33	60	6.6	5
33	90	23.7	20
33	120	31.6	26
33	150	44.7	37
50	10	0	0
50	90	28.0	23
50	120	36.8	31
50	150	49.3	41
67	> 7	homopolymer	n/a
75	> 7	homopolymer	n/a
100	> 7	homopolymer	n/a

zation time. The average chain length was calculated from the weight gain and the monomer molecular weight. The average chain length of formed polymer can be controlled by adjusting the polymerization time.

Both PP and CA flat-sheet membranes used for crossflow microfiltration were also modified with AA, PEG200MA, and FA. The results are illustrated in Table 4.

Table 4. Modification of 0.22 μm flat-sheet membranes by the two-step method.

Membrane	Monomer	Degree of grafting ($\mu g/cm^2$)
PP	AA	50
PP	PEG200MA	56
PP	FA	130
CA	AA	3300
CA	FA	37

Characterization of modified membranes:

The modified membranes were characterized by Fourier transform infrared spectroscopy (FTIR), UV spectroscopy, and scanning electron microscopy (SEM). FTIR and UV spectroscopy was used to identify the functional groups. SEM was used to examine the morphology of membranes.

Representative FTIR data for AA-modified and unmodified PP membranes are shown in Figure 5. The absorbance around 1000-700 cm^{-1} represents the aromatic functional group. Its presence indicates that BP was bound to the membranes by chemical bonds; otherwise, BP would have been washed off in the solvent. The absorbance around 1725-1700 cm^{-1} represents the carbonyl (C=O) functional group, which indicates that the monomers were grafted on the membranes. These results suggest that the termination reaction of the grafting system is mainly by a combination of growing chain radicals and semipinacol radicals. This is the same conclusion as Yang and Ranby (1996a) made from kinetic studies.

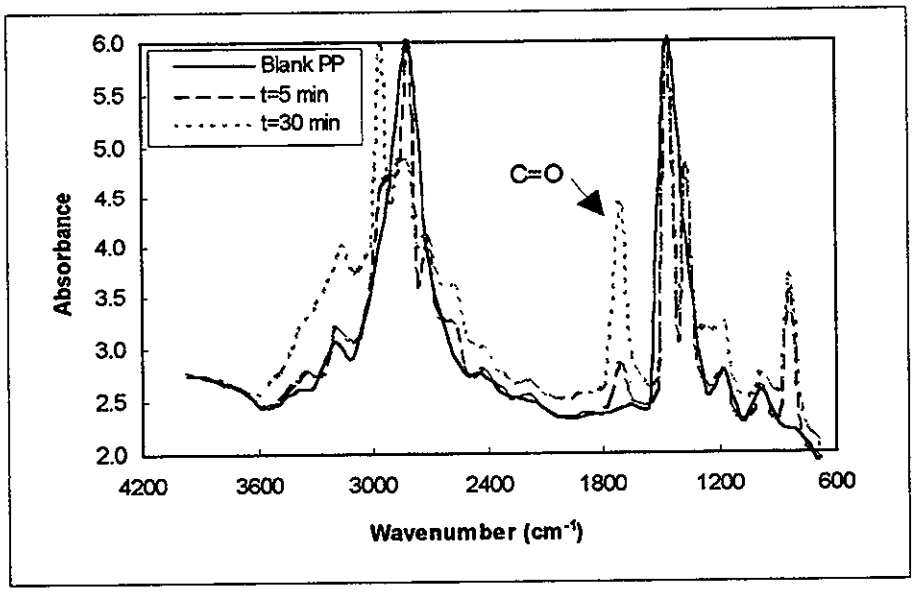


Figure 5. FTIR spectra of unmodified PP MF membrane and PP MF membranes modified with AA the using one-step technique with irradiation times of 5 min and 30 min, and a BP concentration of 5.0 wt%.

Figure 6 shows the UV spectra of PP membranes unmodified and modified with MAA using the one-step technique. The membranes were first melted to obtain UV spectra with less light scattering. The absorbance of the modified membrane at 200-300 nm suggests that the monomers were grafted on the membrane. However, the UV absorbance is too high. Further effort is needed to find a suitable solvent for dissolving the membrane to get suitable UV spectra.

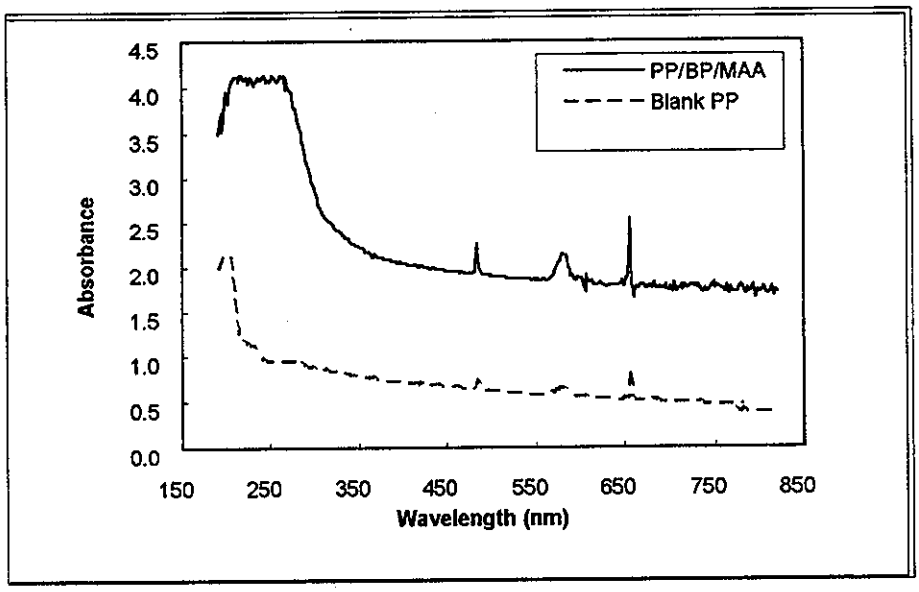


Figure 6. The UV spectra of a melted unmodified PP membrane and a PP membrane modified with MAA using the one-step technique with 5.0 wt% BP at 30 min irradiation.

To examine the morphology of the membranes, several scanning electron micrographs were recorded. All samples were gold coated, and then cross sections were obtained by fracturing in liquid nitrogen. Figures 7 and 8 show a cross-section scan of unmodified and modified polypropylene membranes, respectively. The modified PP membrane consists of fibrous strands, and the nonfibrous part of the modified membrane is considered to be grafted polymer. The results confirm omers were grafted on the membrane surface, and indicate grafts did not extend to the interior of membranes.

3.2 Fouling Characterization

Membrane fouling may be analyzed by direct or analytical characterization, and by indirect or physical characterization. The analytical characterization involves determining the identities and amounts of foulants, whereas physical characterization involves determining the effects of foulants on membrane performance.

With respect to analytical characterization of fouling, initial studies were performed to examine the qualitative and quantitative aspects of how different substances adsorb differently to different surfaces. A technique utilizing Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) was developed and calibrated such that it could be used to quantify the amount of foulant adsorbed onto a surface under a variety of conditions.

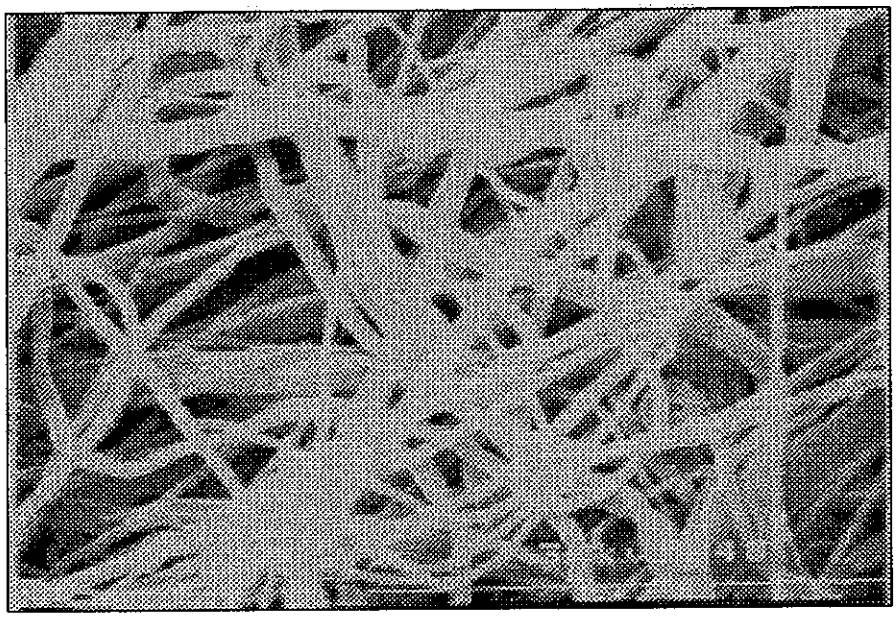


Figure 7. SEM image of an unmodified PP membranes (Magnification 0.75 KX).

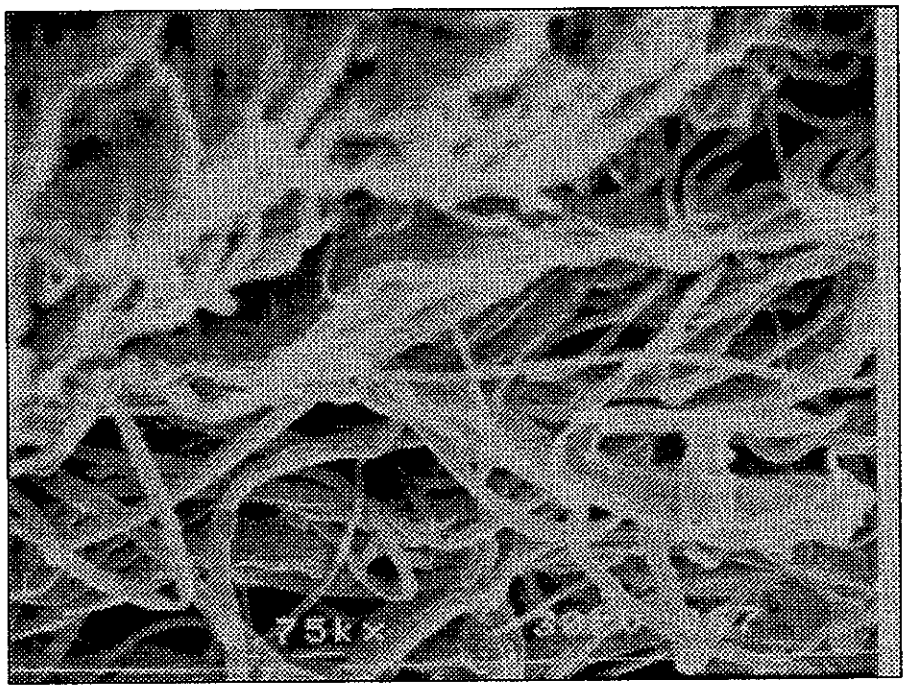


Figure 8. SEM image of a PP membrane modified with AA using the one-step technique with an irradiation time of 10 min and a BP concentration of 5.0 wt% (Magnificaton 0.75 KX).

For physical characterization of fouling, standardized procedures have been developed to characterize three primary features of fouling: (i) mechanism (external or internal), (ii) degree (amount of flux loss), and (iii) type (reversible or irreversible). The fouling mechanism is identified using the method described previously by Tracey and Davis (1994) in which the resistance (which is inversely proportional to the permeate flux) is plotted versus time for normal membrane filtration without backpulsing. A concave down resistance-versus-time curve indicates external fouling, whereas a concave up resistance-versus-time curve indicates internal fouling. An example is shown in Figure 9 for a bentonite suspension which clearly exhibits external fouling (as expected, since the average diameter of the bentonite particles is about five times the nominal pore size of the 0.8 μm ceramic membrane).

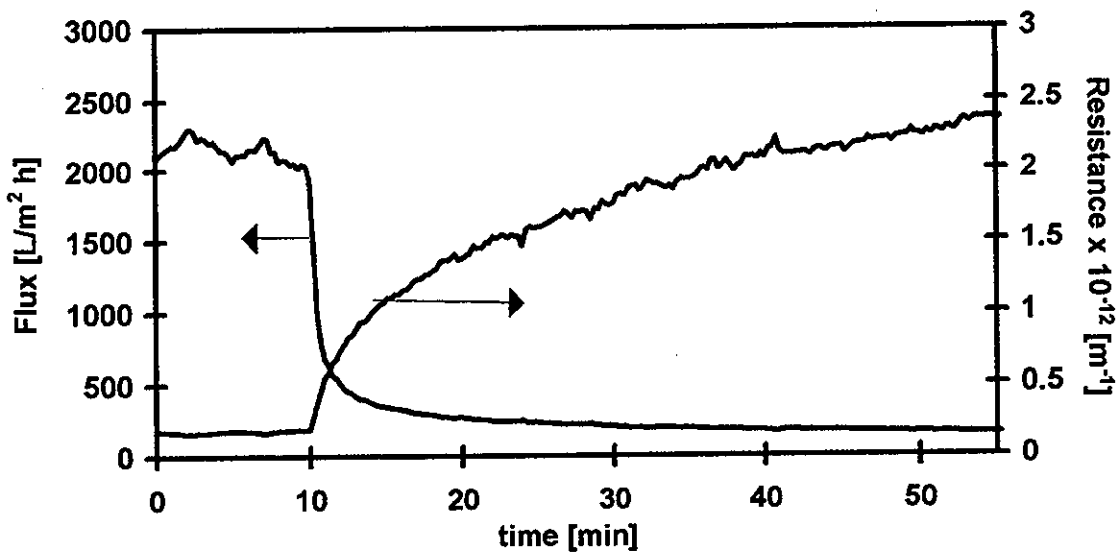


Figure 9. Flux and resistance versus time for a 0.2 g/L bentonite suspension filtered through a 0.8 μm tubular ceramic membrane under crossflow conditions at 25°C, with a transmembrane pressure of 15 psi (103 kPa) and an average feed velocity of 2.6 m/s.

The degree of fouling is determined by a simple fouling index, defined by

$$\text{F.I.} = 1 - J_s / J_o \quad , \tag{1}$$

where J_o is the initial or clean membrane flux and J_s is the long-term or steady flux for the fouled membrane after filtering a suspension for a specified interval. For the bentonite suspension of Figure 9, F.I. = 1 - 150/2000 = 0.93, indicating that the permeability of the fouled membrane is only 7% of that for the clean membrane. For bacterial suspensions, the fouling is even more severe, with measured fouling indices as high as 0.999 obtained.

The type of fouling is characterized by a cleaning index, defined by

$$\text{C.I.} = J_c / J_o \quad , \tag{2}$$

where J_c is the water flux of the fouled membrane after it has been cleaned. The value of the cleaning index represents the fractional flux recovery as a result of the cleaning process and so is a measure of the fraction of the fouling which is reversible (under the prescribed cleaning procedure). Since the current focus is on *in situ* cleaning by backpulsing (passing of water or permeate in the reverse direction through the membrane), the cleaning procedure adopted is to backwash the membrane with water after cessation of filtration to remove reversibly-bound foulants. For cellulose acetate membranes fouled by bacterial suspensions under normal crossflow filtration without backpulsing, the cleaning index value, C.I. = 0.002, is close to zero (irreversible fouling). In contrast, a value closer to unity (C.I. = 0.56, partially reversible fouling) was obtained for ceramic membranes fouled by bentonite suspensions.

A rapid and simple method for determining the fouling and cleaning indices has been developed. Using a deadend filtration cell which holds a flat, 47 mm circular membrane (Figure 10), water is passed through a commercial or surface-modified membrane to determine the water flux (J_o). A suspension is then filtered through the membrane to foul it. Unless the foulant concentration is very low, the fouling is severe ($J_s \approx 0$) and F.I. $\approx$ 1. The membrane is then cleaned by backwashing with water for varying amounts of time (typically 30 or 60 seconds), after which the water flux through the fouled membrane after cleaning (J_c) is measured.

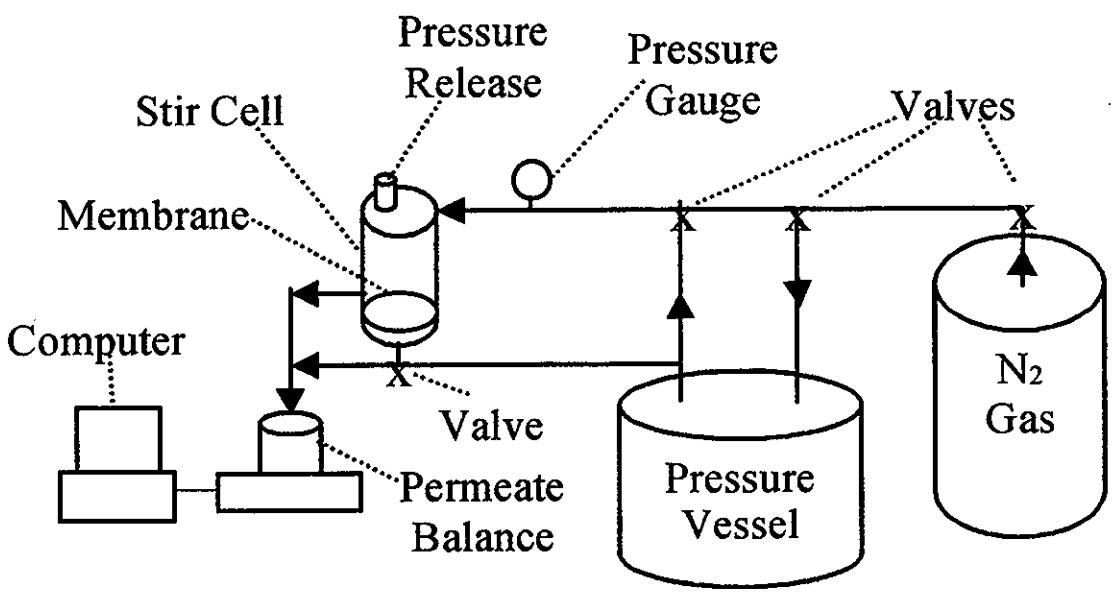


Figure 10. Schematic of the deadend filtration cell, which was operated without stirring. During forward filtration, pressure was applied directly from the N_2 gas cylinder to the stir cell and the permeate was collected on a microbalance interfaced to a computer for automated data recording. During backwashing, pressure was applied to the pressurized tank and water was run through the cell in the opposite direction.

Figure 11 shows the fouling of commercial (unmodified) CA (pore size = 0.22 μm), PP (pore size = 0.22 and 0.45 μm), and PS (pore size = 0.22 μm) membranes. The foulant was 0.2 g/L suspension of bentonite clay in water and the transmembrane pressure was 5 psi. In all cases, two

runs were done with plain water, then one with the clay. The membranes were than backwashed for 30 seconds, after which two forward runs were done with plain water. The water moved most quickly through the 0.45 μm PP membranes, with 60 g passing in roughly 10 seconds. Though PP is hydrophobic and thus passes water with more difficulty, the greater pore size of 0.45 μm caused the water flux to be much higher. Water passed much more easily through hydrophilic CA (60 g in 35 s) and the 0.22 μm PP (60 g in 40 s, after prewetting with ethanol) than through PS (60 g in 75 s). Furthermore, the flux recovery after fouling was poorest for the PS, indicating that it was the most irreversibly fouled. PS is naturally hydrophobic, although the manufacturer indicated its surface was modified to be hydrophilic (this is often done using a surfactant which is not covalently bound to the surface).

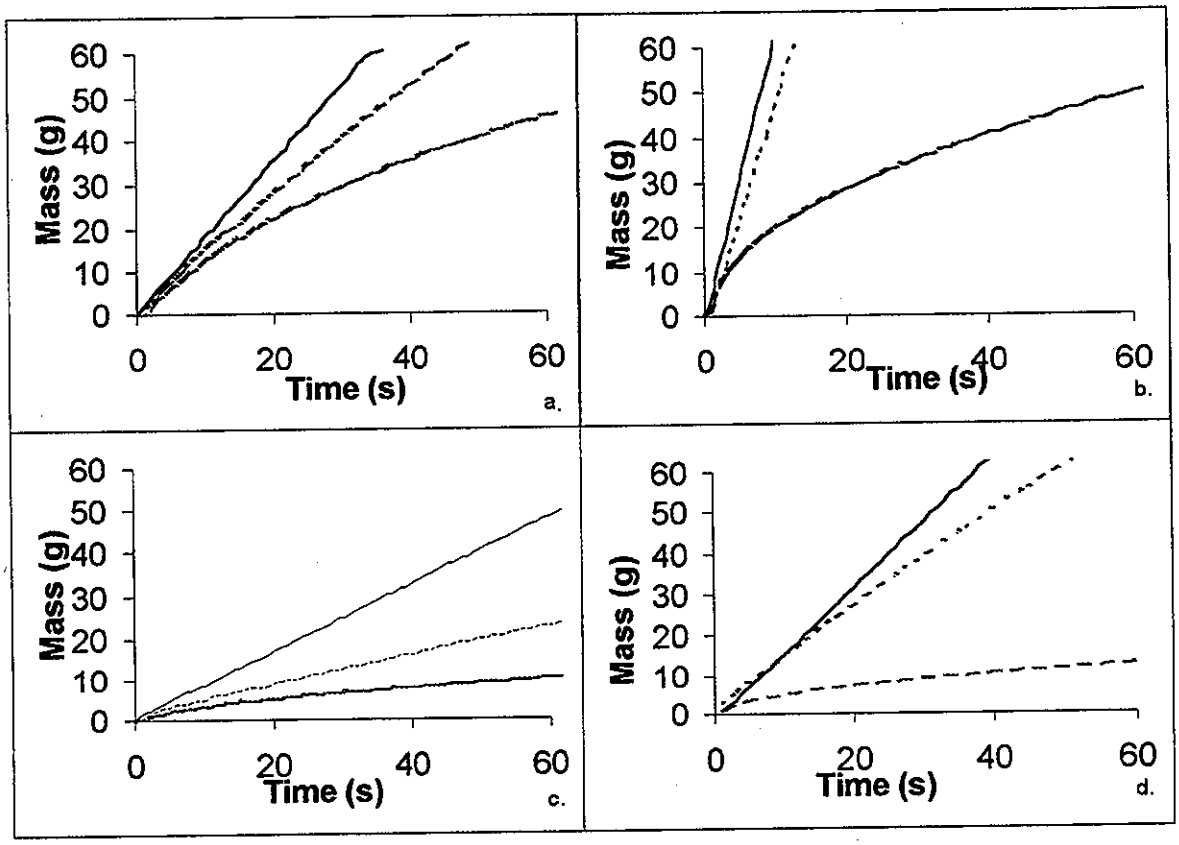


Figure 11. Permeate mass versus time for the deadend filtration cell at 25°C and a transmembrane pressure of 5 psi using water, followed by a 0.2 g/L bentonite suspension, and then water again after 30 seconds of backwashing; (a) 0.22 μm CA membrane, (b) 0.45 μm PP membrane, (c) 0.22 μm PS membrane, (d) 0.22 μm PP membrane. In each plot, the top curve is the initial water run, the bottom curve is the run with bentonite suspension, and the middle curve is the second water run after backpulsing.

The results of preliminary fouling studies for 0.45 μm PP membranes modified with MAA by the one-step method are shown in Figure 12 and Table 5. With 4.6% and 7.8% weight gains due to grafting, there is an increase in the water flux, presumably due to the MAA rendering the

membranes hydrophilic. At the higher weight gain of 13.2%, the water flux is reduced; this is likely the result of the grafted polymer constricting or plugging the membrane pores. In general, the recovery of the water flux after fouling by bentonite and subsequent backwashing to remove the fouling layer improved with grafting. An exception occurred for the grafted membrane with 4.6% weight gain, for which the nonlinear nature of the water flux curve after backwashing indicates that foulant may have remained in the device. Also, the nonlinear nature of the water flux curves for the new membrane with 2.8% grafting indicate possible fouling by residual clay from a previous experiment. Unfortunately, our early grafting procedures did not give sufficient reproducibility to repeat these data and check these anomalies.

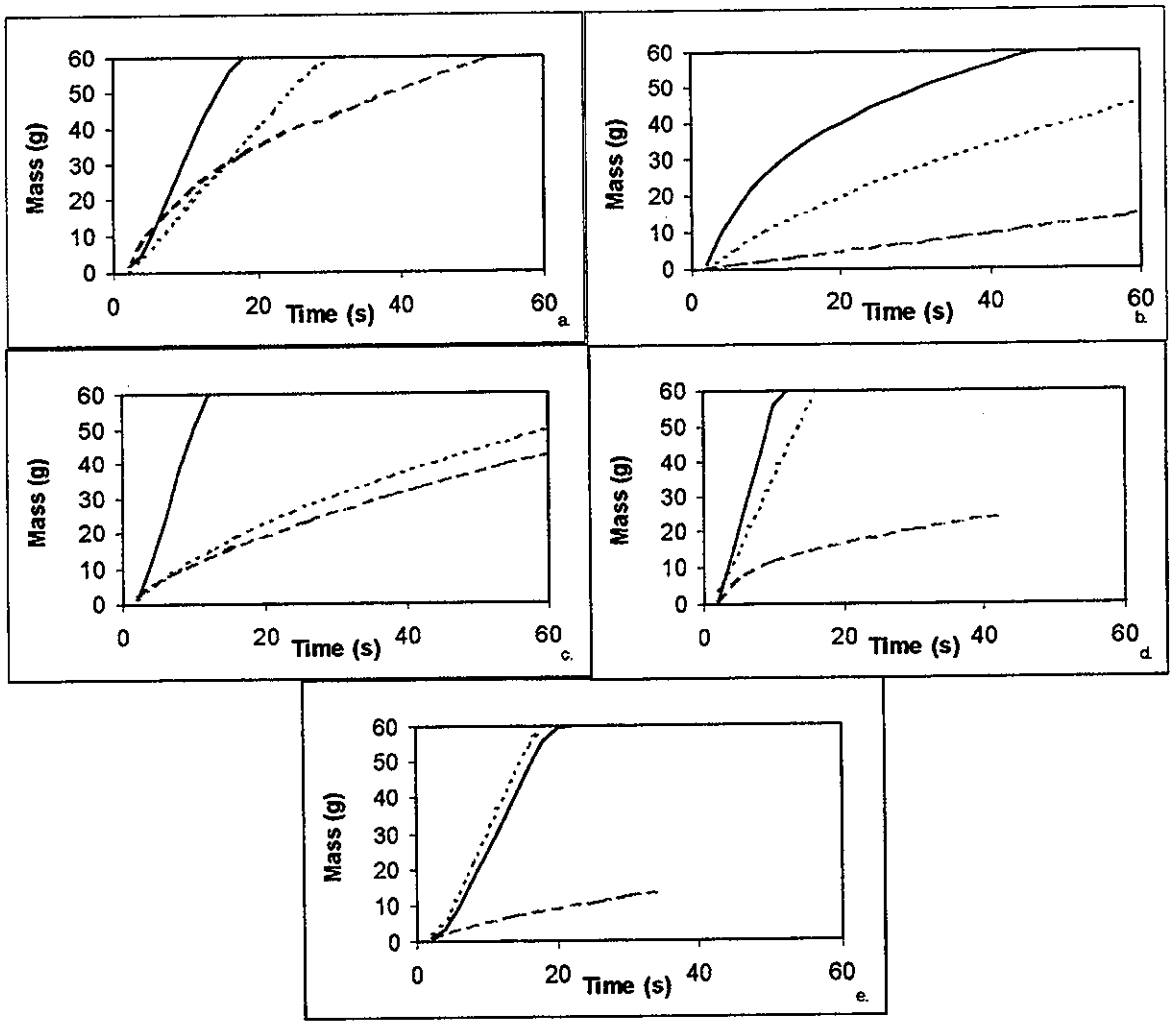


Figure 12. Mass versus time for the deadend filtration cell at 25° C and a transmembrane pressure of 5 psi using water, followed by a 0.2 g/L bentonite suspension, and then water again after 1 minute of backwashing, filtered through a 0.45 μm PP membrane grafted by the one-step method with 5 wt % BP and (a) 0%, (b) 2.8%, (c) 4.6%, (d) 7.8%, and (e) 13.2% weight gain of MAA. The solid curves are the initial water runs, the dashed curves are runs with bentonite, and the dotted curves are the second water runs after backwashing.

Table 5. Flux values and cleaning indices for unmodified and modified 0.45 μm PP membranes tested in a stir cell with fouling by a 0.2 g/L bentonite suspension; modification was by the one-step method with MAA (Note: 1 L/m^2-h (LMH) = 0.59 gal/ft^2-day (GFD) = 2.8×10^{-5} cm/s).

Membrane	Modification	J_o (LMH)	J_c (LMH)	C.I.
PP, 0.45 μm	None	10100	5120	0.51
PP, 045 μm	2.8 wt % (260 μg/cm^2) MAA	3350	1550	0.45
PP, 0.45 μm	4.6 wt % (420 μg/cm^2) MAA	14800	17010	0.12
PP, 0.45 μm	7.8 wt % (720 μg/cm^2) MAA	16200	9240	0.57
PP, 0.45 μm	13.2 wt % (1220 μg/cm^2) MAA	8880	8880	1.00

After the preliminary studies, a decision was made to switch to 0.22 μm PP membranes, because of their tighter pore size and more uniform properties. The effects of grafting AA on 0.22 μm PP membranes by the one-step method are given in Table 6. The PP membranes were all prewetted with ethanol. This was done to improve the consistency of the water flux through the unmodified, hydrophobic PP membranes. The results indicate that the cleaning indices are close to unity for both the unmodified PP membranes and the PP membranes modified with small amounts of AA, indicating little irreversible fouling by bentonite. However, the clean water flux decreases with both relatively small and large amounts of grafting, in agreement with the results given in Table 5 for the 0.45 μm PP membranes. The weight percent grafts used for the 0.22 μm PP membranes are considerably lower than those used in the 0.45 μm PP membranes, because of the much smaller pore sizes of the 0.22 μm PP membranes.

Table 6. Flux values and cleaning indices for unmodified and modified 0.22 μm PP membranes tested in a deadend stir cell with fouling by a 0.2 g/L bentonite suspension; modification was by the one-step method with AA. The transmembrane pressure was 5 psi for water fluxes and backwashing, and 10 psi for fouling by bentonite. For the unmodified membrane, plus and minus one standard deviation for 6-9 repeats are shown.

Membrane	Modification	J_o (LMH)	J_c (LMH)	C.I.
PP	None	3000 ± 400	2700 ± 500	0.9 ± 0.2
PP	0.35 wt% (13.8 μg/cm^2) AA	3050	2460	0.81
PP	0.45 wt % (17.8 μg/cm^2) AA	2660	2510	0.94
PP	2.22 wt % (86.2 μg/cm^2) AA	510	200	0.40

3.3 Rapid Backpulsing

As shown in Figure 13, particles which are reversibly deposited on the membrane during forward filtration are lifted off the membrane by the backpulse fluid and swept out of the filter by the crossflow during reverse filtration. Irreversibly deposited foulants will remain adsorbed to the membrane.

In order to account for both reversible and irreversible fouling, the backpulsing model developed previously (Redkar and Davis, 1995) was modified to give the following prediction of the net flux per cycle:

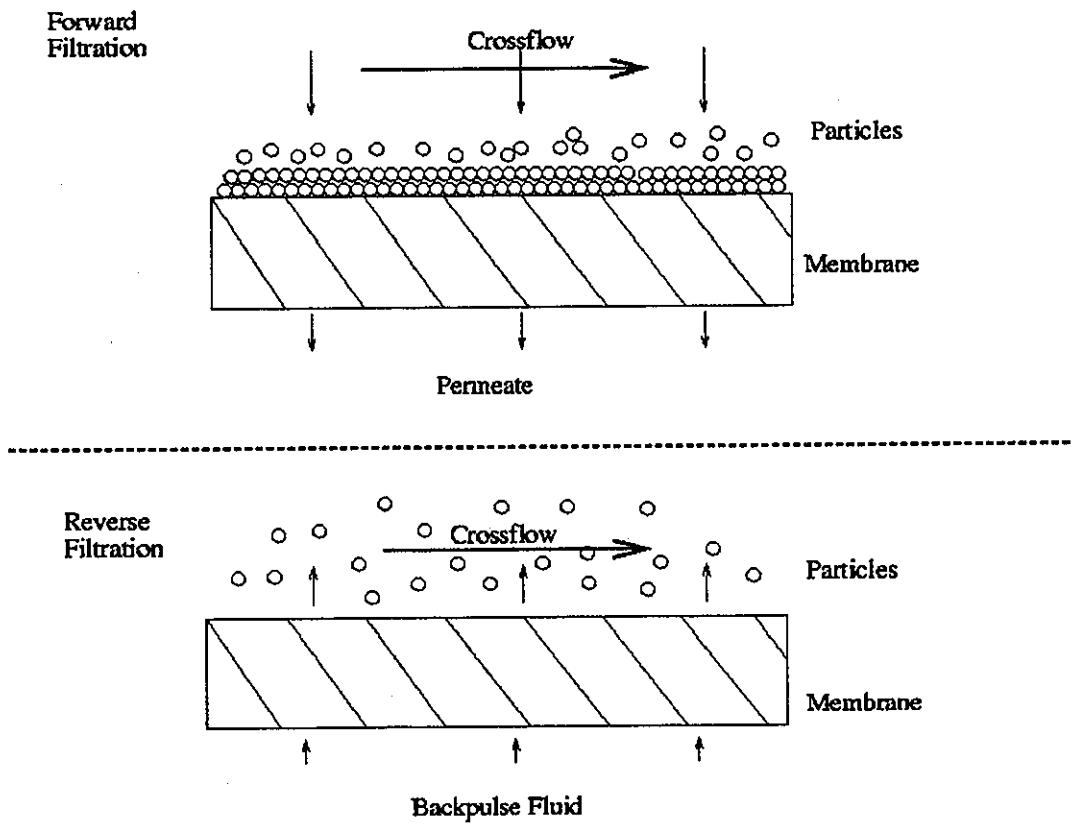


Figure 13. Schematic of forward and reverse filtration during backpulse operation.

$$\langle J \rangle = \beta J_o \left(\frac{2\tau\left[\left(1+t_f/\tau\right)^{1/2}-1\right]-\alpha t_b}{t_f+t_b} \right) + (1-\beta) J_s \left(\frac{t_f-\alpha t_b}{t_f+t_b} \right) \quad , \tag{3}$$

where t_f and t_b are the durations of forward and reverse filtration, respectively, τ is the time constant for cake growth during forward filtration, α is the ratio of the magnitudes of the reverse and forward transmembrane pressures, and β is the cleaning efficiency (representing the fraction of the fouled membrane which is cleaned with each backpulse cycle). The cleaning efficiency (β) is expected to be close to the cleaning index (C.I.) for slow backflushing (large t_f and t_b) but not for rapid backpulsing (small t_f and t_b), as shown below.

We performed extensive backpulsing tests with commercially available, unmodified membranes, and then preliminary experiments with modified membranes. The initial backpulsing experiments were performed with unmodified cellulose acetate membranes and bacterial suspensions, since these exhibit substantial irreversible fouling. Figure 14 shows net flux data obtained previously for a 1.2 g/L (dry cell weight) suspension of washed *E. coli* bacterial cells in water as a function of the duration of forward filtration between backpulses of fixed duration t_b = 1 sec. The

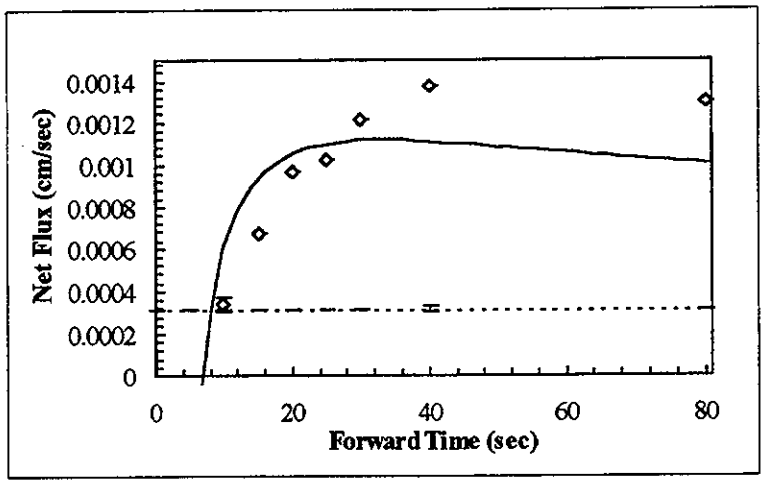


Figure 14. Net flux versus forward filtration time for backpulsing experiments (t_b = 1 sec) done with a 0.2 μm flat-sheet cellulose acetate membrane and 1.2 g/L washed bacterial suspension. The solid line is the theoretical prediction with $\beta = 0.18$, and the dashed line is the long-term flux without backpulsing. Error bars represent plus and minus one standard deviation for 2-4 repeats.

data are fit according to equation (3), with $\beta = 0.18$ obtained by least-squares regression. This cleaning efficiency is much larger than the measured cleaning index (C.I. ≈ 0.002), which demonstrates that backpulsing reduces the tendency of the cake of rejected bacterial cells to consolidate and irreversibly adhere to the membrane surface.

Both theory and experiment show an optimum duration of forward filtration, t_f, or an optimum backpulsing frequency, $1/(t_f + t_b)$, which maximizes the net flux. Higher frequencies yield a greater loss of permeate due to the frequent backpulses, whereas lower frequencies lead to greater flux loss due to fouling during the long periods of forward filtration.

Figure 15 shows results for the same system as Figure 14 but with a shorter backpulse duration of $t_b = 0.1$ sec. For forward filtration durations of $t_f > 1$ sec, the best-fit value of the cleaning efficiency is $\beta = 0.03$, indicating that the shorter backpulses are less effective in removing the fouling deposits. However, for shorter durations of forward filtration, the net flux is much higher than predicted by the theory with $\beta = 0.03$; a value of $\beta = 0.08$ provides a better fit of these data. Evidently, very short periods of forward filtration allow for relatively less irreversible fouling.

Additional experiments were performed with more concentrated bacterial suspensions. Figure 16 is for washed bacterial cells, and Figure 17 is for diluted bacterial fermentation broth, both at 10 g/L dry cell weight. The concentrated suspension of washed cells behaves very similar to the more dilute suspension of washed cells but with lower flux (compare Figures 15 and 16). However, the behavior of the fermentation broth is quite different, with two local maxima in the net flux versus forward filtration time curve, and less flux enhancement due to backpulsing. The differences are due to the presence of extracellular macromolecules in the fermentation broth which irreversibly foul the membrane, presumably with different fouling mechanisms and time scales than for the bacterial cells. A plot of resistance versus time in the absence of backpulsing (not shown) revealed a combination of internal and external fouling for the fermentation broth.

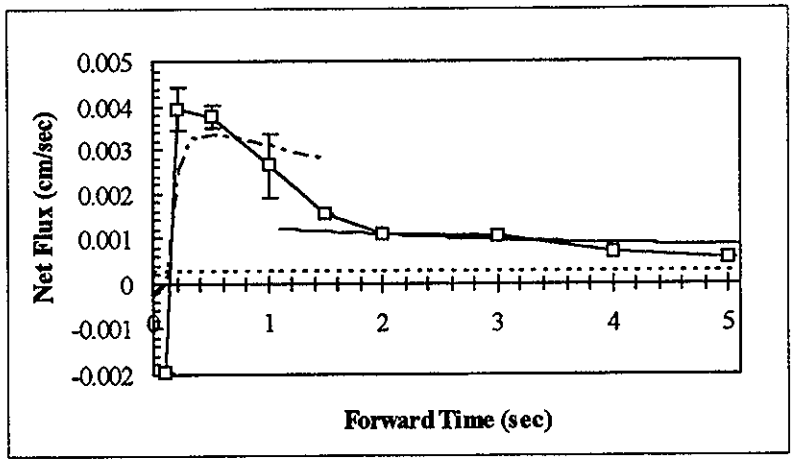


Figure 15. Net flux versus forward filtration time for backpulsing experiments (t_b = 0.1 sec) done with a 0.2 μm flat-sheet cellulose acetate membrane and 1.2 g/L washed bacterial suspension. The dashed line is the theoretical prediction with $\beta = 0.03$, the dashed-dotted line is the theoretical prediction with $\beta = 0.08$, and the dotted line is the long-term flux without backpulsing. Error bars represent plus and minus one standard deviation for 2-4 repeats.

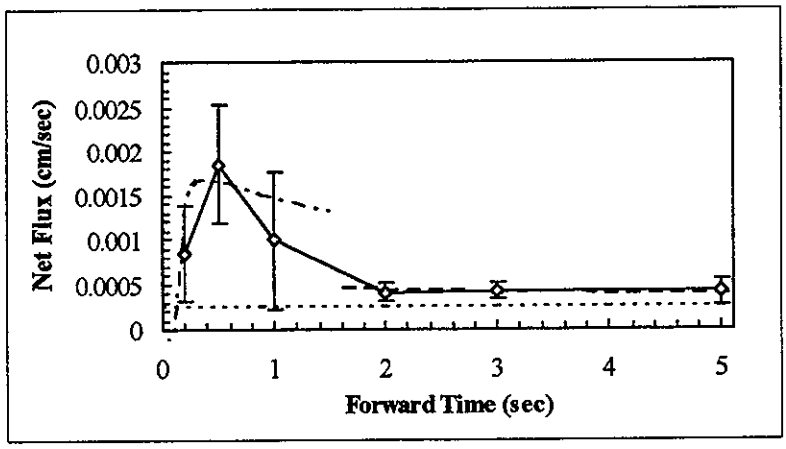


Figure 16. Net flux versus forward filtration time for backpulsing experiments (t_b = 0.1 sec) done with a 0.2 μm flat-sheet cellulose acetate membrane and 10 g/L washed bacterial suspension. The dashed line is the theoretical predication with $\beta = 0.02$, the dashed-dotted line is the theoretical prediction with $\beta = 0.09$, and the dotted line is the long-term flux without backpulsing. Error bars represent plus and minus one standard deviation for 2-4 repeats.

The results of backpulsing experiments with the unmodified cellulose acetate membrane and bacterial suspensions are summarized in Table 7. In the absence of backpulsing, the flux declines by a factor of 400 (F.I. = 0.996) for the most dilute suspension, and by a factor of 1000 (F.I. = 0.999) for the most concentrated suspension. Even though the flux recovery is essentially zero (C.I. = 0.002) from backwashing after filtration in the absence of backpulsing (indicating irreversible fouling), backpulsing is able to partially prevent irreversible fouling and lead to ten-fold flux enhancement for washed bacterial suspensions, and two-fold flux enhancement for unwashed bacterial suspensions (fermentation broth).

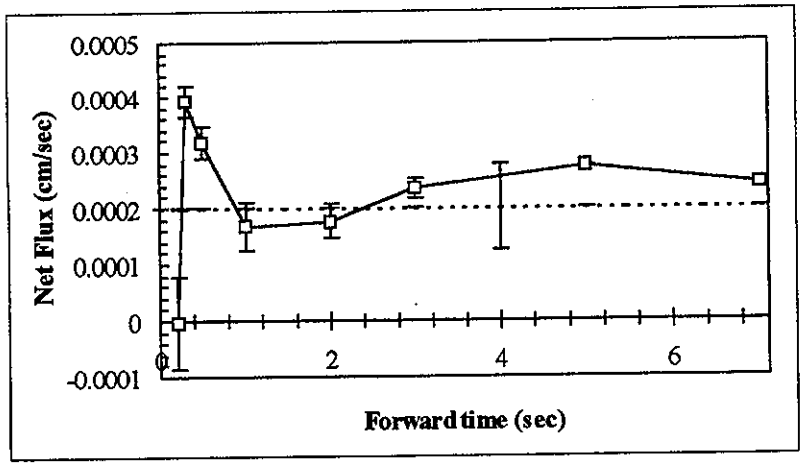


Figure 17. Net flux versus forward filtration time for backpulsing experiments (t_b = 0.1 sec) done with a 0.2 μm flat-sheet cellulose acetate membrane and 10 g/L bacterial fermentation broth. The dashed line is the long-term flux without backpulsing. Error bars represent plus and minus one standard deviation for 2-4 repeats.

Table 7. Clean membrane flux (J_o), long-term flux without backpulsing (J_s), and maximum net flux with backpulsing ($\langle J \rangle^{max}$), plus and minus one standard deviation for 2-4 repeats, for bacterial suspensions filtered through an unmodified 0.2 μm flat-sheet cellulose acetate membrane (note: 1 L/m^2-h (LMH) = 0.59 gal/ft^2-day (GFD) = 2.8×10^{-5} cm/s)

Bacterial Suspension	J_o (LMH)	J_s (LMH)	t_b(s)	t_f^{max} (s)	$\langle J \rangle^{max}$ (LMH)	$\langle J \rangle^{max}/J_s$
1.2 g/L washed	4600 ± 700	11.3 ± 0.4	1.0	40	50	4.3 ± 0.1
1.2 g/L washed	4600 ± 700	11.3 ± 0.4	0.2	2.0	32 ± 4	2.8 ± 0.4
1.2 g/L washed	4600 ± 700	11.3 ± 0.4	0.1	0.2	140 ± 20	12 ± 2
10 g/L washed	4600 ± 700	9 ±3	0.1	0.5	70 ± 20	7 ± 4
10 g/L unwashed	4600 ± 700	7 ± 3	0.1	0.3	14 ± 1	2.0 ± 0.7
45 g/L unwashed	4600 ± 700	4.4 ±0.1	0.1	3.0	8 ± 1	1.9 ± 0.3

Figure 18 shows net flux data obtained for a 0.2 g/L bentonite suspension using a ceramic tubular membrane with 0.8 μm nominal pore size. The data fit according to the model proposed, Equation (3), yielding a best-fit value of β = 0.82 for the cleaning efficiency. This cleaning efficiency is larger than the cleaning index (C.I. = 0.56), which supports the expectation that rapid backpulsing reduces the degree of irreversible adherence of the bentonite particles to the membrane surface.

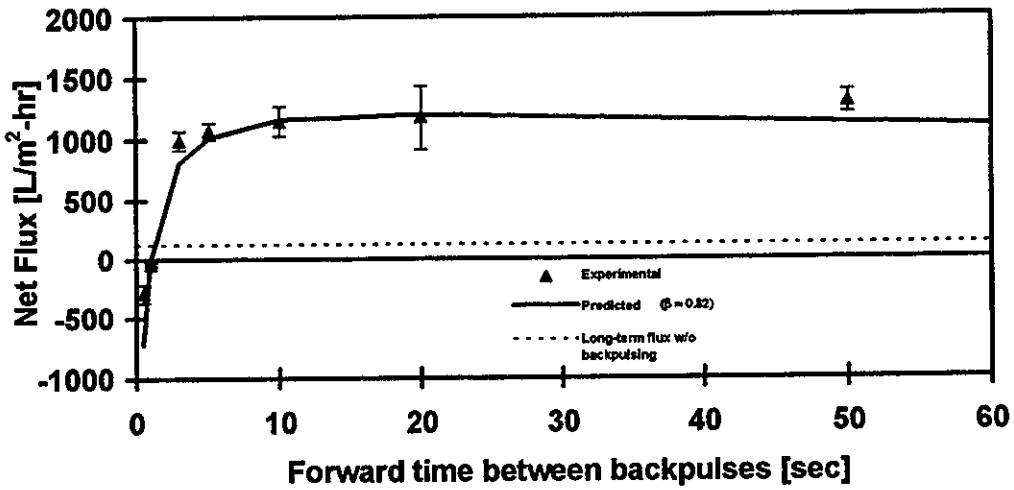


Figure 18. Net flux versus filtration time for backpulsing experiments (t_b = 0.5 sec) done with a 0.8 μm tubular ceramic membrane and 0.2 g/L bentonite suspension. The solid line is the theoretical predication with $\beta = 0.82$, and the dashed line is the long-term flux without backpulsing. Error bars represent plus and minus one standard deviation for 2-4 repeats.

Cross-flow experiments with backpulsing were continued on both hollow-fiber PS and α-alumina tubular ceramic membranes, using both bentonite suspensions and oil-in-water emulsions. Figure 19 shows net flux data obtained for a 2 g/L bentonite suspension using a 0.45 μm nominal-pore size hollow fiber cartridge. The clean water flux observed was J_o = 2070 L/m^2-hr at 20 Psi (138 kPa) transmembrane pressure, while the long-term membrane flux for operation with back-pulsing was J_s = 200 L/m^2-hr. The best fit using the non-uniform cleaning model yields a value of $\beta = 0.29$ for the cleaning efficiency. The cleaning efficiency with rapid backpulsing in this case is lower than the cleaning index for long backwashing (C.I. = 0.80). This could be attributed in part to the flow configuration of the hollow fiber cartridge; for example, those lumen fibers which are packed together very tightly may not experience the same degree of restoration in flux as those lumens which are loosely packed. At this higher feed concentration, the net flux with backpulsing is increased three-fold over the long-term flux without backpulsing, compared to the ten-fold enhancement seen in Figure 18 for the more dilute bentonite feed.

Experiments with dilute oil-in-water emulsions were performed with both hollow-fiber PS membranes and tubular α-alumina membranes of nominal pore diameters of 0.2 μm. A gradual decline in the clean membrane pure water flux (J_o) was observed with subsequent use of the membranes, which in turn results in lower net average fluxes when backpulsing is employed. Figure 20 shows the results of experiments with a 50 ppm oil-in-water emulsion when a backpulse duration of 0.5 sec was employed for the two membranes tested. Two curves are presented for each of the membranes used, the higher curve for experiments when the membranes were being used for the first time and the lower curves for experiments performed later in the life of the membrane. The degradation in performance occurs much more rapidly for the hollow-fiber module (over approximately 20 hrs of cumulative time of operation), probably due to the high hydrophobicity of the PS membrane material. The degradation in flux of the ceramic membrane occurs

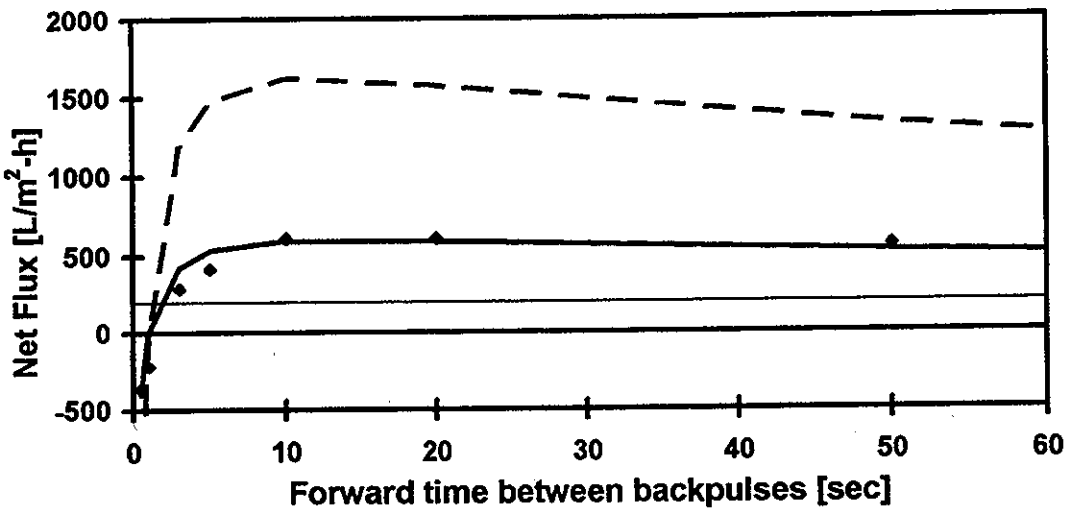


Figure 19. Net flux versus filtration time for backpulsing experiments (t_b = 0.5 s) for a 0.45 μm hollow-fiber polysulfone (unmodified surface) membrane and a 2 g/L bentonite suspension. The solid curve is the theoretical prediction with $\beta = 0.29$, and then dashed curve is the net flux prediction assuming complete membrane cleaning ($\beta = 1$) occurs with each backpulse. Error bars represent plus and minus one standard deviation for 2-4 repeats. The horizontal solid line is the long-term flux without backpulsing.

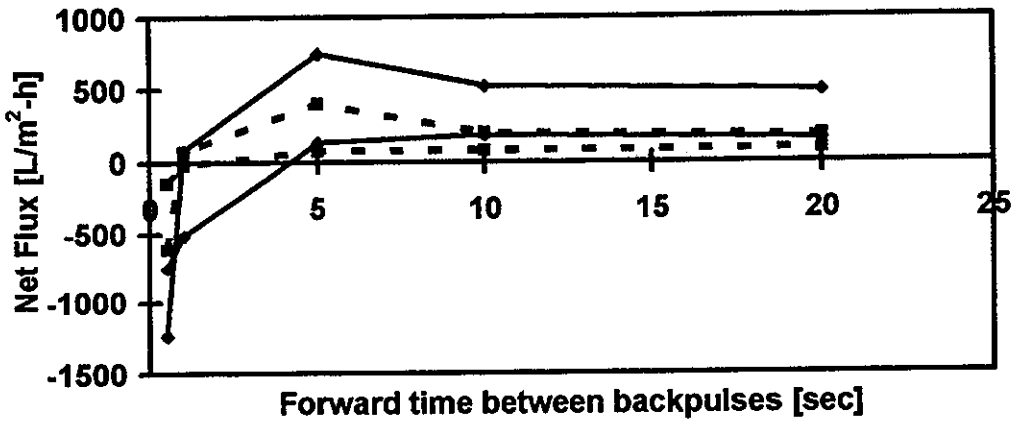


Figure 20. Net flux versus forward filtration time for backpulsing experiments (t_b = 0.5 s) done with new and used 0.2 μm unmodified polysulfone hollow-fiber membrane (upper and lower dashed curves, respectively) and new and used 0.2 μm α-alumina tubular membrane (upper and lower solid curves, respectively). Oil content in feed was 50 ppm and the cross-flow velocity was 3.5 m/s. The clean membrane pure water fluxes for the unused membranes were J_o = 1740 L/m^2-hr and J_o = 1950 L/m^2-hr for the hollow-fiber and ceramic membranes, respectively. The degraded membrane pure water fluxes corresponding to the lower curves were J_o = 90 L/m^2-hr and J_o = 250 L/m^2-hr for the hollow-fiber and ceramic membranes, respectively. The long-term fluxes without backpulsing were 80 L/m^2-hr for the hollow-fiber membrane and 30 L/m^2-hr for the ceramic membrane.

over a much longer time period (approximately 200 hrs of cumulative time of operation), consonant with the fact that the α-alumina matrix is hydrophilic and presents a resistance to wetting by the organic phase. The gradual flux degradation could be due to microscopic particulates naturally present in the crude oil phase which gradually deposit within the membrane pores, or due to the gradual irreversible coating of the membranes with hydrophobic material. It is hoped that this degradation would be significantly reduced with grafted membranes.

Crossflow experiments with backpulsing were also done on unmodified flat-sheet PS, PES, CA, and PP membranes (all of 0.2 μm pore size) using bentonite clay as the foulant and a flow rate of 360 ml/min. The PS and PP membranes recovered the least amount of flux when backpulsed for one second after each 10 seconds of forward filtration, while the PES and CA membranes recovered the most (Table 8). The difference may be due to the hydrophobic nature of unmodified PP and PS, indicating the possibility of improvement by surface modification.

Table 8. Clean membrane flux (J_o), long-term flux without backpulsing (J_s), and net flux with backpulsing ($\langle J \rangle$), plus and minus one standard deviation for 2-6 repeats, for 0.2 g/L bentonite suspensions filtered at 25°C through various unmodified 0.2 μm flat-sheet membranes. The backpulse transmembrane pressure was 10 psi and the forward transmembrane pressure was 10 psi for all runs.

Membrane	Conc (g/L)	J_o (LMH)	J_s (LMH)	t_b (s)	t_f (s)	$\langle J \rangle$ (LMH)	$\langle J \rangle / J_s$
PS	0.2	6960 ± 70	320 ± 20	1	10	540 ± 70	1.7 ± 0.1
PES	0.2	7500	425	1	10	2060 ± 10	4.85 ± 0.03
CA	0.2	4900 ± 500	270 ± 40	1	10	1100 ± 100	4.2 ± 0.6
PP	0.2	7100 ± 200	370 ± 20	1	10	580	1.6 ± 0.2

Figure 21 for the unmodified PP membrane and Table 9 for the unmodified PS membrane indicate that varying the backpulse frequency and duration, respectively, had little effect on improving the net flux for these hydrophobic membranes. However, it appears that the backpulse pressure may be optimized (Table 10), as backpulsing which is too weak does not adequately lift the fouling layer off whereas backpulsing which is too strong causes considerable permeate loss. The flux also declined with increasing concentration.

PP membranes modified with AA and FA using the two-step method were tested in the crossflow device with backpulsing (Table 11). Experiments were run with a backpulse transmembrane pressure of 1 psi because pressures greater than this tore the modified membranes. The concentration of bentonite was 1.0 g/L, the forward filtration time was 20 sec, and the backpulse time was 1 sec. Two of the membranes were patterned (denoted as "P" in Table 11); for these, three of the nine 3.5 cm^2 sections of the membrane were grafted, while the other six were left unmodified. The other two grafted membranes were modified in their entirety.

The hydrophobic FA graft gave no improvement, whereas the hydrophilic AA graft gave small improvements in the flux with backpulsing over that of the hydrophobic unmodified PP membrane. While encouraging, these results are preliminary, as repetitions and optimization of the backpulsing conditions are needed once a large number of membranes are grafted.

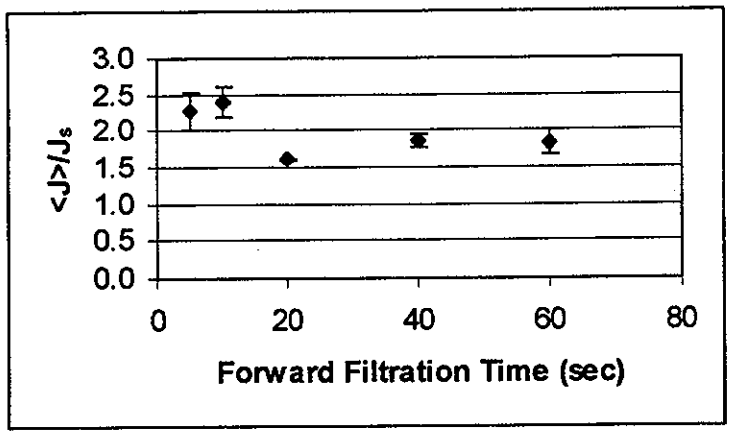


Figure 21. The ratio of flux with backpulsing to flux without backpulsing plotted versus forward filtration time. Data are for unmodified 0.2 μm PP membranes at 25°C with 1 g/L bentonite suspensions using a backpulse transmembrane pressure of 1 psi and a forward transmembrane pressure of 10 psi.

Table 9. Clean membrane flux (J_o), long-term flux without backpulsing (J_s), and net flux with backpulsing ($\langle J \rangle$) of various durations, plus and minus one standard deviation for 2-3 repeats, for bentonite suspensions filtered through unmodified 0.2 μm flat-sheet PS membranes. The backpulse transmembrane pressure was 10 psi and the forward transmembrane pressure was 10 psi for all runs.

Membrane	Conc (g/L)	J_o (LMH)	J_s (LMH)	t_b (s)	t_f (s)	$\langle J \rangle$ (LMH)	$\langle J \rangle / J_s$
PS	0.2	6960 ± 70	320 ± 20	0.1	20	460	1.4 ± 0.1
PS	0.2	6960 ± 70	320 ± 20	0.5	20	620	1.9 ± 0.1
PS	0.2	6960 ± 70	320 ± 20	1	20	740 ± 20	2.3 ± 0.2
PS	0.2	6960 ± 70	320 ± 20	2	20	639	2.0 ± 0.1

Table 10. Clean membrane flux (J_o), long-term flux without backpulsing (J_s), and net flux with backpulsing ($\langle J \rangle$), plus and minus one standard deviation for 2-6 repeats, for bentonite suspensions filtered through unmodified 0.2 μm flat-sheet PP membranes. The backpulse time was t_b = 1 sec and the forward filtration time was t_f = 20 sec for all runs.

Membrane	Conc (g/L)	ΔP_f	ΔP_b	J_o (LMH)	J_s (LMH)	$\langle J \rangle$ (LMH)	$\langle J \rangle / J_s$
PP	0.2	10	1	7100 ± 200	370 ± 20	1010	2.7 ± 0.1
PP	1.0	10	1	7100 ± 200	242 ± 1	391 ± 3	1.62 ± 0.01
PP	0.2	10	5	7100 ± 200	370 ± 20	1228	3.3 ± 0.2
PP	1.0	10	5	7100 ±200	242 ± 1	594	2.45 ± 0.01

Table 11. Clean membrane flux (J_o), long-term flux without backpulsing (J_o), and net flux with backpulsing (<J>), plus and minus one standard deviation for 2-6 repeats, for 1 g/L bentonite suspensions filtered through modified and unmodified 0.2 μm flat-sheet PP membranes. The backpulse transmembrane pressure was 1 psi and the forward transmembrane pressure was 10 psi for all runs. "P" stands for patterned.

Membrane	Modification	J_o (LMH)	J_s (LMH)	t_b (s)	t_f (s)	<J> (LMH)
PP	None	7100 ± 200	242 ± 1	1	20	391± 3
PP	11 μg/cm^2 P - AA	n/a	n/a	1	20	503
PP	48 μg/cm^2 AA	n/a	n/a	1	20	456
PP	50 μg/cm^2 AA	n/a	n/a	1	20	450
PP	128 μg/cm^2 P - FA	n/a	n/a	1	20	387

4. Conclusions and Recommendations

The original objectives of developing a method for producing fouling-resistance membranes for water pretreatment, characterizing the fouling behavior of these membranes, and testing them in a crossflow microfiltration device with rapid backpulsing to reduce both reversible and irreversible fouling were met. Considerable extra effort was required for developing a suitable method for membrane modification, however, and so most of the fouling characterization and backpulsing studies were performed with the unmodified, base membranes, with only preliminary results obtained for modified membranes. Specific conclusions from these studies include:

(i) Microporous membranes may be formed as originally proposed by photopolymerizing dense films in the presence of microcrystals which are later dissolved, but it is difficult to reproducibly obtain the necessary physical properties.

(ii) A one-step method for grafting various monomers on the surface of polymeric membranes using ultraviolet radiation in the presence of benzophenone to form reactive surface radicals results in desired surface modification but also yields undesired homopolymerization if the monomer also has reactive hydrogen atoms.

(iii) A two-step method, in which benzophenone is used to form a surface photoinitiator in the first step, which then reacts with monomer in the second step, successfully forms grafted membranes and avoids homopolymerization, when proper solvents and radiation wavelengths are used.

(iv) The degree or amount of grafting is easily controlled by grafting conditions such as initiator concentration and irradiation time.

(v) Small amounts of an hydrophilic graft on an hydrophobic base membrane increase the water flux by improving the wettability of the membrane, whereas too much graft can block the membrane pores and reduce the water flux.

(vi) Hydrophilic grafts on an hydrophobic base membrane reduce irreversible fouling by bentonite and lead to improved membrane cleaning with backwashing.

(vii) Rapid backpulsing yields approximately 10-fold improvement in the net flux for relatively nonadhesive foulants such as bentonite and washed bacteria, and two-fold improvement in the net flux for relatively adhesive foulants such as unwashed bacteria, when optimal backpulsing frequency and duration are used.

(viii) Preliminary backpulsing experiments with hydrophobic polymer membranes show modest (10-20%) improvements in the net flux for bentonite suspensions when the membrane surface was modified by grafting of an hydrophilic moiety, with some weakening of the membranes.

Crossflow microfiltration with rapid backpulsing is a commercially viable process and is now used in the biotechnology industry. It has also been shown to be economically viable for water treatment and pretreatment when the foulants are primarily nonadhesive (Davis, 1996). For adhesive foulants, permanent surface modification is required to make the fouling reversible or nonadhesive. The photografting technique developed in this project shows considerable promise, but additional development and testing are needed. Specific recommendations include:

(ix) Obtain photopolymerization equipment which will provide uniform irradiation over membrane surface areas used in laboratory-scale crossflow microfiltration devices, and use this equipment to find the best grafting conditions.

(x) Test a variety of base membrane materials (PP, CA, PS, PES), surface grafts (AA, MAA, FA, PEG200MA), and foulants (colloidal clay, bacteria, hydrocarbons) to identify the most promising surface modifications for fouling reduction.

(xi) Study long-term performance of photografted membranes with backpulsing.

(xii) Obtain basic understanding of the chemistry and physics of foulant deposition and removal, to guide choices of material and operating conditions.

(xiii) Seek a patent on the process and a company interested in commercializing it.

ACRONYMS AND NOMENCLATURE

AA	-	acrylic acid (monomer)
ATR	-	attenuated total reflectance
BP	-	benzophenone (initiator)
CA	-	cellulose acetate (membrane)
C.I.	-	cleaning index (equation 2)
FA	-	1H,1H-pentadecafluorooctyl acrylate (monomer)
F.I.	-	fouling index (equation 1)
FTIR	-	Fourier-transform infrared (spectroscopy)
$\langle J \rangle$	-	net flux with backpulsing (cm/s)
$\langle J \rangle^{max}$	-	maximum net flux with backpulsing (cm/s)
J_c	-	water flux after fouling and cleaning (cm/s)
J_o	-	water flux for unfouled membrane (cm/s)
J_s	-	long-term flux for fouled membrane (cm/s)
MAA	-	methacrylic acid (monomer)
MC	-	methylcellulose (monomer)
MF	-	microfiltration
PAN	-	polyacrylonitrile (membrane)
PE	-	polyethylene (membrane)
PEG200MA	-	polyethylene glycol (200) monomethacrylate (monomer)
PP	-	polypropylene (membrane)
PS	-	polysulfone (membrane)
PVA	-	Polyvinylalcohol (membrane)
PVDF	-	poly(vinylidene fluoride) (membrane)
PVP	-	polyvinylpyrrolidone (PVP)
RO	-	reverse osmosis
SEM	-	scanning electron microscopy
t_b	-	backpulse duration (s)
t_f	-	duration of forward filtration between backpulses (s)
t_f^{max}	-	duration of forward filtration which maximizes net flux (s)
UF	-	ultrafiltration
UV	-	ultraviolet
α	-	ratio of backpulse and forward transmembrane pressures
β	-	cleaning efficiency
τ	-	time constant for cake growth (s)

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DATA APPENDIX

A. Data for Figure 2.

Name of Membranes	BP Concentration (wt %)	Irradiation Time (min)	Initial Weight of Membranes (g)	Weight Gain of Modified Membranes (wt)%	Degree of Graft-ing (ug/cm2)
PP/AA148	4.96	3	0.05892	0.4582	17.76
PP/AA149	4.96	3	0.05916	0.3550	13.82
PP/AA150	4.96	5	0.05891	1.1373	44.08
PP/AA151	4.96	5	0.05948	0.9079	35.53
PP/AA141	4.96	7	0.05899	2.2207	86.18
PP/AA142	4.96	7	0.05865	3.0009	115.79
PP/AA159	2.96	3	0.0589	0.2207	8.55
PP/AA160	2.96	3	0.05914	0.3382	13.16
PP/AA161	2.96	5	0.05902	0.5083	19.74
PP/AA162	2.96	5	0.05878	0.7656	29.61
PP/AA163	2.96	7	0.05933	1.7023	66.45
PP/AA164	2.96	7	0.05921	1.5369	59.87

B. Data for Figure 4

Name of Membranes	BP Concentration (wt%)	Irradiation Time (min)	Initial Weight of Membranes (g)	Weight Gain of Modified Membranes (wt%)	Degree of Grafting (ug/cm^2)
PP/Bz/AA181	3.02	30.0	0.05964	0.65	25.7
PP/Bz/AA182	3.02	30.0	0.05895	0.47	18.4
PP/Bz/AA177	4.96	30.0	0.05938	0.56	21.7
PP/Bz/AA178	4.96	30.0	0.05962	0.75	29.6
PP/Bz/AA183	10.03	30.0	0.05907	0.83	32.2
PP/Bz/AA184	10.03	30.0	0.05947	0.94	36.8

C. Data for Figures 14 and 15

E. coli Suspen-sion	DCW = 1.2 g/L

Backpulsing	Experiments	
Forward Time (sec)	Backpulse Time (sec)	Net Flux (cm/sec)
0.1	0.1	-0.001944646
0.2	0.1	0.004657971
0.2	0.1	0.00375843
0.2	0.1	0.003492361
0.2	0.1	0.003826453
0.5	0.1	0.003558876
0.5	0.1	0.003670931
0.5	0.1	0.004075717
1	0.1	0.003433038
1	0.1	0.001970881
1	0.1	0.002527844
1.5	0.1	0.001561972
2	0.1	0.001085277
3	0.1	0.001071476
4	0.1	0.000715826
5	0.1	0.000559276
5	1	-0.000550055
10	1	0.000315264
10	1	0.000322099
10	1	0.000374867
15	1	0.000673973
20	1	0.000964104
25	1	0.001026893
30	1	0.001216155
30	1	0.000596316
40	1	0.00137184
80	1	0.00130014

Normal	Crossflow	Experiments
Date	Flux (cm/sec)	
3/6/96	0.000331	
3/6/96	0.000307	
7/23/96	0.000309	

D. Data for Figure 16

E. coli Suspen-sion	DCW = 10 g/L

Backpulsing	Experiments	
Forward Time (sec)	Backpulse Time (sec)	Net Flux (cm/sec)
0.2	0.1	0.000260914
0.2	0.1	0.00095491
0.2	0.1	0.001302993
0.5	0.1	0.002639414
0.5	0.1	0.001431597
0.5	0.1	0.001495346
1	0.1	0.000447923
1	0.1	0.001536134
2	0.1	0.000338886
2	0.1	0.000478697
3	0.1	0.00035748
3	0.1	0.000484838
5	0.1	0.000311545
5	0.1	0.000521995

Normal	Crossflow	Experiments
Date	Flux (cm/sec)	
9/27/96	0.000195	
10/11/96	0.000327	

E. Data for Figure 17

Diluted Fermentation	Broth, DCW = 10g/L

Backpulsing	Experiments	
Forward Time (sec)	Backpulse Time (sec)	Net Flux (cm/sec)
0.2	0.1	-6.04113E-05
0.2	0.1	5.60776E-05
0.3	0.1	0.000412939
0.3	0.1	0.000373656
0.5	0.1	0.000298759
0.5	0.1	0.00033829
1	0.1	0.000158035
1	0.1	0.00021413
1	0.1	0.000129115
2	0.1	0.000154107
2	0.1	0.000198118
3	0.1	0.000222838
3	0.1	0.000247212
5	0.1	0.000275488
7	0.1	0.000242059

Normal	Crossflow	Experiments
Date	Flux (cm/sec)	
9/11/96	0.000256	
10/11/96	0.000147	

F. Data for Figure 18

t_f (sec)	Net Flux (L/m2-h)
0.5	-291±76
1	-40±13
3	990±76
5	1067±70
10	1145±121
20	1176±257
50	1296±95

G. Data for Figure 19

t_f (sec)	Net Flux (L/m^2-h)
0.5	-361±36
1	-220±29
3	292±26
5	416±20
10	607±21
20	607±2
50	561±1

H. Data for Figure 20

t_f (sec)	Net Flux (L/m^2h) – unused membrane	Net Flux (L/m^2h) – used membrane
0.5	-1235	-753
1	80	-508
5	748	135
10	525	184
20	489	159

t_f (sec)	Net Flux (L/m^2h) – unused membrane	Net Flux (L/m^2h) – used membrane
0.5	-609	-139
1	76	-15
5	405	76
10	202	83
20	187	92

I. Data for Figure 21

Membrane	Conc. (g/L)	ΔP_b (psi)	t_f (s)	t_b (s)	J_{net} (LMH)
PP, 0.22	1	n/a	n/a	n/a	241
PP, 0.22	1	n/a	n/a	n/a	242
PP, 0.22	1	1	5	1	500
PP, 0.22	1	1	5	1	600
PP, 0.22	1	1	5	1	530
PP, 0.22	1	1	10	1	550
PP, 0.22	1	1	10	1	610
PP, 0.22	1	1	20	1	393
PP, 0.22	1	1	20	1	389
PP, 0.22	1	1	40	1	430
PP, 0.22	1	1	40	1	460
PP, 0.22	1	1	60	1	450
PP, 0.22	1	1	60	1	410