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MEMBRANE SURFACE MODIFICATION AND BACKPULSING FOR WASTEWATER TREATMENT

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ABSTRACT

Using a novel photoinduced grafting method, hydrophobic polypropylene (PP) membranes were rendered hydrophilic by grafting monomers of poly(ethylene glycol 200) monomethacrylate (PEG200MA), dimethyl aminoethyl methacrylate (DMAEMA), or acrylic acid (AA), to produce a neutral, positive, or negative charge, respectively, on the membrane surface. Using both unmodified and modified PP membranes, as well as a hydrophilic cellulose acetate (CA) membrane, the effects of backpulsing and surface chemistries on membrane fouling were investigated for crossflow microfiltration of bentonite clay suspensions and crude oil emulsions. Without backpulsing, the permeate volumes collected over 60 min were not strongly dependent on membrane surface chemistry and morphology for the filtration of either clay or oil. With backpulsing, however, 5-fold and 6-fold permeate enhancements were obtained by backpulsing alone and by a

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combination of backpulsing and surface modification, respectively, for clay filtration. The recovered water fluxes after backwashing the PP membranes fouled without backpulsing were approximately 80% of the initial water flux, showing that bentonite fouling is primarily nonadhesive. However, the recovered fluxes with backpulsing were slightly less than those without backpulsing, due to internal fouling after each backpulse. For the filtration of crude oil, 1.3-fold and 2.7-fold permeate volume enhancements were obtained by backpulsing alone and by a combination of backpulsing and surface modification, respectively. More than a 3-fold permeate volume enhancement was obtained upon adding an anionic or cationic surfactant to the oil mixture when the modified membrane was similarly charged. The recovered flux after backwashing the unmodified PP membrane fouled without backpulsing or surfactant was only about 30% of the initial water flux, indicating adhesive primarily fouled by oil, but the recovered flux doubled when the membranes were rendered hydrophilic by surface modification.

Key Words: Backpulsing; Surface modification; Membranes; Microfiltration; Wastewater; Bentonite clay; Oil; Fouling.

INTRODUCTION

Small colloidal particles, microbes, and undissolved hydrocarbons are ubiquitous in both natural and industrial waters. Membrane technology holds much promise for wastewater treatment (1–5) and can compete with traditional technologies, such as gravity separation, air or gas flotation, chemical flocculation, and plate coalescers, due to its advantages of low energy utilization and high quality of permeate. However, a major problem with membrane processes lies in the dramatic flux decline resulting from fouling. Membrane replacement due to fouling is the single largest operating cost when membranes are used in water treatment applications (6). 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. (7). Generally, two distinct types of fouling phenomena are considered (8): (i) macrosolute adsorption, which refers to the specific intermolecular interactions between the macrosolute and the membrane that occur even in the absence of filtration, and (ii) filtration-induced macrosolute or particulate deposition, which is over and above that observed in a static (nonflowing) system. A variety of methods has been reported to

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reduce either nonadhesive fouling or adhesive fouling, as summarized by Ma et al. (9), who demonstrated a combined method of backpulsing and surface modification for fouling reduction during filtration of bacterial wastewater in a crossflow membrane system.

As described by Mores et al. (10), rapid backpulsing in crossflow filtration involves reversing the transmembrane pressure for approximately 0.1–1.0 s once every few seconds. This reversal results in hydraulic cleaning of the membrane by forcing permeate back through the membrane in the reverse direction; foulants are lifted off the membrane by the backpulses and then swept to the filter exit by the crossflow. Crossflow filtration with rapid backpulsing has been studied extensively by a number of groups in various membrane/foulant systems, and it has been reported as an effective technology for controlling fouling and improving permeate flux for nonadhesive foulants exhibiting reversible fouling (11–16). Unfortunately, rapid backpulsing is much less effective in reducing adhesive fouling (17–19).

Several methods with the potential for reducing or eliminating adhesive fouling by changing the membrane surface chemistry have been reported (20–30). A novel photografting technique was designed and developed in our previous work (31). This technique significantly reduces undesired homopolymer and crosslinked polymer in many cases, preferentially forms linear grafted polymer chains, and facilitates independent control of the grafting density and graft polymer chain length.

In the current study, commercial PP membranes were modified using the novel photografting method (31), and the membranes were evaluated in a crossflow microfiltration system with and without backpulsing in the presence of clay suspensions and oil emulsions. The foulant-surface interactions were investigated under various conditions, and suitable conditions to reduce both adhesive and nonadhesive fouling and to maximize membrane performance were determined.

MATERIALS AND METHODS

There were two types of base PP membranes used in these experiments: (i) commercial, porous-disk microfiltration membranes with a diameter of 47 mm, thickness of approximately 110 μm, porosity of 40%, and nominal pore diameter of 0.22 μm (Micron Separations, Inc.), and (ii) cellulose acetate microfiltration membranes with a diameter of 47 mm, thickness of approximately 120 μm, and nominal pore diameter of 0.22 μm (Sartorius). Acrylic acid (AA) (Aldrich), poly(ethylene glycol 200) monomethacrylate (PEG200MA) (Polyscience, Inc.), and dimethyl aminoethyl methacrylate (DMAEMA) (Aldrich) were used as the monomers. All three monomers are hydrophilic; AA is negatively charged, DMAEMA is positively charged, and PEG200MA is neutral. Unmodified PP and

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CA membranes are hydrophobic and hydrophilic, respectively, and they are both nearly neutral. Benzophenone (BP) (Aldrich) was used as the initiator. Benzene, acetone, and deionized water were used as solvents. All chemicals were used without purification.

The surface modification procedures and the proposed grafting mechanism for the modification of PP membranes are described in our previous paper (31). In brief, the grafting is a two-step process. In the first step, benzophenone abstracts hydrogen from the substrate to generate surface radicals and semipinacol radicals, which combine to form surface photoinitiators in the absence of monomer solutions. The unreacted benzophenone is then washed off with a good solvent. In the subsequent step, the monomer solution is added onto the active substrate, and the surface initiators initiate the graft polymerization upon exposure to UV irradiation.

The clay suspension was prepared by combining the desired amount of bentonite clay (Aldrich Cat. No. 28,533-4, density 2.1 g/cm^3) with 2 L of tap water at 25°C and agitating it vigorously in a beaker. The resulting suspension exhibited a number-averaged particle diameter of 4.6 μm (indicating the presence of clustered aggregates of colloidal particles, since bentonite has mixed charges) and a standard deviation of 1.7 μm, as determined by analysis with a Coulter Multisizer (3). The sedimentation velocity of clay particles of the average size is about 1×10^{-3} cm/s, and a settling of the clay particles within the filter is expected to be negligible for all but the largest particles.

The oil emulsions were prepared by adding heavy crude oil (API 12 weight, density 0.97 g/cm^3, supplied by UNOCAL from the Hueneme field in California) to tap water at a concentration of 50 mg/L. For certain experiments, 50 mg/L of an ionic surfactant was also added to the mixture. A blender (Osterizer Model 890-28M) was used to mix the oil, surfactant, and water at a high setting for approximately 2 min. The anionic surfactant was provided by the Navy Research Laboratory and is made of nonylphenoxypolyethoxyethanol, liquid Tide™ (without bleach), and Stoddard solvent (32). The cationic surfactant is cetytrimethylammonium bromide from Aldrich. An Horiba (model OCMA-220) oil-content analyzer was used to determine the total oil content in the feed and the permeate. Oil-droplet size distributions for the feed emulsions were determined using a Coulter Multisizer. A hemacytometer slide and optical microscope were also used to confirm these measurements. Most of the droplets in the feed were 1–8 μm in diameter, with settling velocities less than 1×10^{-4} cm/s.

A schematic of the experimental apparatus is presented in Fig. 1. The crossflow module was fabricated in our instrument shop. A disk membrane with a diameter of 47 mm was used. The filtration area was 30 mm wide by 23 mm long, and the thickness of the silicon gaskets between the membrane and the top plate of the module was 0.4 mm. All experiments were performed at room temperature (22–25°C), with an average crossflow velocity of 24 cm/s. The PP membranes

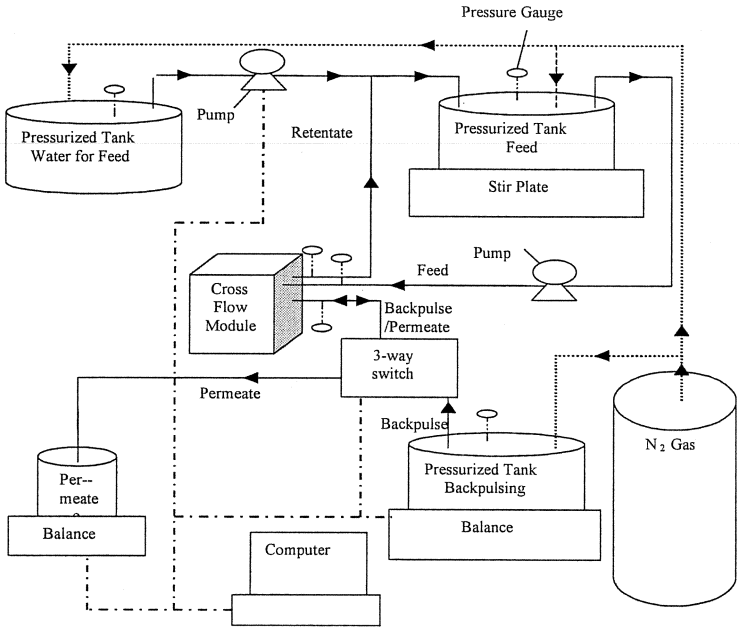

Figure 1. Schematic diagram of the crossflow filtration system. The solid lines depict liquid flows, the dotted lines depict gas flows, and the dashed-dotted lines depict electronic connections from the computer to a pump, the solenoid valve, and two balances (from 10).

were wetted using ethanol just before each filtration experiment. The water flux was determined with tap water at a forward transmembrane pressure of 5.0 psi (34 kPa) for 5 min. Then, filtration of suspensions/emulsions with or without backpulsing was performed for 1 h. A new membrane was used for each experiment. Crossflow filtration with backpulsing was performed at a backward transmembrane pressure of 3.0 psi (21 kPa) for 0.2 s after every 4 s of forward filtration at a transmembrane pressure of 5.0 psi. After obtaining the average net flux (over the 1-h filtration period) and the long-term net flux (over the last 5 min of filtration, during which the flux remained steady), backpulsing was stopped and the system was immediately backwashed for at least 5 min (which we found to be sufficient for removing all reversible foulants) at a reverse transmembrane pressure of 3.0 psi, while still running water over the membrane. Finally, tap water was passed through the membrane at 5.0 psi forward transmembrane pressure for five minutes to determine the recovered permeate flux.

For crossflow filtration without backpulsing, forward filtration was performed at a transmembrane pressure of 5.0 psi for 1 h. The long-term flux was

measured over the last 5 min of the filtration process (during which the flux remained steady). The backwashing process and recovered flux measurements were performed the same as those done after filtration with backpulsing.

RESULTS AND DISCUSSION

Water Flux for Clean Membranes

The water fluxes for clean membranes were measured first. The average water fluxes for unmodified PP and unmodified CA membranes are 1100 ± 100 L/m^2 h and 3000 ± 200 L/m^2 h, respectively, where 1 L/m^2 h = 2.8 × 10^{-5} cm/s and the uncertainties are expressed as plus or minus one standard deviation for 20 repeats. The higher water flux for CA membranes as compared to PP membranes primarily reflected the difference in membrane morphologies. The average water flux for PP membranes modified with PEG (20 repeats, weight gain 4.0 ± 0.3 wt%), AA (9 repeats; weight gain 4.0 ± 0.4 wt%) and DMAEMA (12 repeats; weight gain 4.0 ± 0.8 wt%) are, respectively, 1200 ± 100 L/m^2 h, 1100 ± 100 L/m^2 h and 1200 ± 100 L/m^2 h. The water fluxes were nearly the same for unmodified and modified PP membranes, which suggests that the bulk structure of PP membranes was not greatly altered by the surface modification process in the weight gain range (3–5 wt%) used in the experiments. These results are similar to those reported in our previous work (9).

Filtration of Clay Suspensions

An unmodified PP membrane, a modified PP membrane with weight gain of 4.1% PEG200MA, and an unmodified CA membrane were tested with the clay suspension in the crossflow filtration system without backpulsing. Figure 2 shows that the flux declines rapidly during the initial stage of filtration and then nearly reaches a steady state after approximately 10 min. The performance for PP membranes modified with AA and DMAEMA is similar to that reported in Fig. 2. Although the CA membrane has an initial flux that is more than twice that of the PP membranes, its flux drops the most rapidly and becomes comparable to that of the other membranes within 1–2 min. For all membranes, the long-term flux after 60 min without backpulsing is only approximately 80 L/m^2 h. It is expected that the fouling is primarily due to physical deposition of the bentonite particles on the membrane surfaces, which is not strongly dependent on the membrane surface chemistry.

Figure 3 shows the results for filtration of clay using different membranes with backpulsing, and using an unmodified PP membrane without backpulsing.

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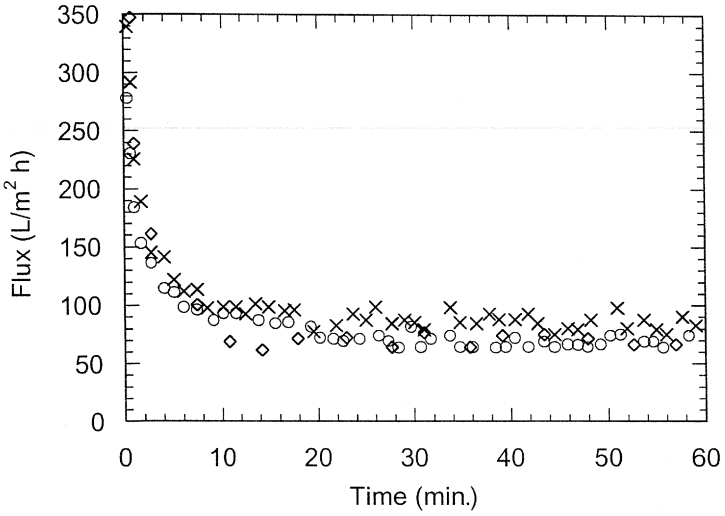

Figure 2. Permeate flux versus filtration time for crossflow filtration of a 0.5 g/L bentonite suspension: (○) unmodified PP membrane; (×) modified PP membrane with weight gain of 4.1 wt% PEG200MA graft; (◇) unmodified CA membrane. The experiments were performed at a forward transmembrane pressure of 5.0 psi.

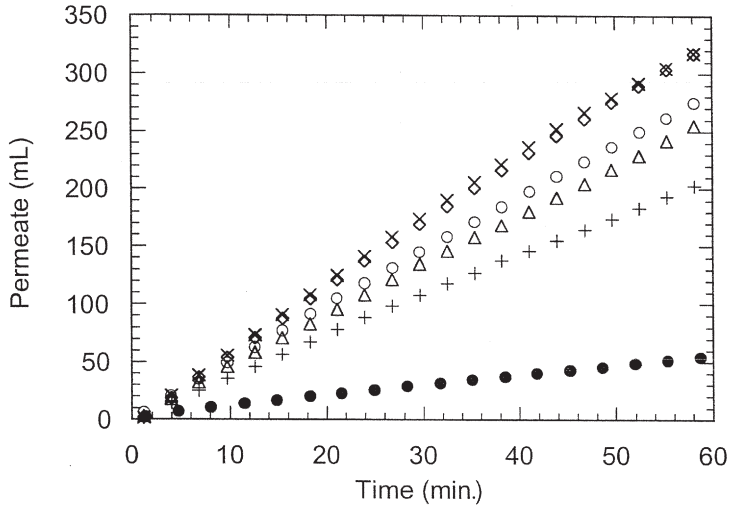

Figure 3. Permeate volume versus filtration time for crossflow filtration of a 0.5 g/L bentonite suspension: (○), (●) unmodified PP membranes with and without backpulsing, respectively; (×), (+), (Δ) backpulsing results for PP membranes modified with weight gains of 4.2 wt% PEG200MA graft, 4.3 wt% AA graft, and 3.9 wt% DMAEMA graft, respectively; (◇) unmodified CA membranes with backpulsing. Backpulsing experiments were performed at a backward transmembrane pressure of 3.0 psi for 0.2 s after every 4 s of forward filtration at a transmembrane pressure of 5.0 psi.

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Comparing the results for unmodified PP membranes with and without backpulsing, we see that a 5-fold enhancement in permeate collection was obtained by backpulsing, indicating that backpulsing is an effective method to reduce bentonite fouling by periodically lifting a substantial portion of the cake off the membrane. The rapid flux decline in the first 5 min due to fouling without backpulsing (see Fig. 2) did not occur with backpulsing. A 6-fold permeate enhancement was achieved with backpulsing for a PP membrane modified with 4.2 wt% PEG200MA, demonstrating that bentonite fouling is reduced even further by an appropriate combination of backpulsing and membrane surface modification. The permeate collections for the PP membranes modified with AA (hydrophilic, negatively charged) and DMAEMA (hydrophilic, positively charged) are less than that of the unmodified PP membrane (hydrophobic, neutral). Since bentonite has both negatively and positively charged surface groups, it is not surprising that the neutral, hydrophilic membrane surfaces (CA, and PP with PEG200MA) were the most effective in reducing bentonite fouling. The charged surfaces interacted strongly with the bentonite particles, and thus, backpulsing less effectively removed the foulants from the charged surfaces. The permeate volume for the unmodified CA membrane is nearly the same as that of the PP membrane modified with PEG200MA, which indicates that membrane morphology was of less importance for this case.

As demonstrated in Table 1, the long-term flux for filtration of clay without backpulsing does not vary greatly between the different membranes, with a typi-

Table 1. Effect of Membrane Surface Chemistry and Backpulsing on Long-Term Flux and Recovered Flux after Backwashing for Filtration of Bentonite Suspensions[a]

	Without Backpulsing		With Backpulsing		
Membrane	Long-term Flux (L/m^2 h)	Recovered Flux (L/m^2 h)	Long-term Net Flux (L/m^2 h)	Recovered Flux (L/m^2 h)	Clean Water Flux (L/m^2 h)
Unmodified PP	70 ± 10	900 ± 100	390 ± 60	760 ± 50	1100 ± 100
Unmodified CA	70 ± 4	2210 ± 170	420 ± 90	930 ± 210	3000 ± 200
PP + 3.8 wt% PEG200MA	80 ± 10	1040 ± 20	400 ± 100	900 ± 90	1200 ± 100
PP + 4.2 wt% AA	68 ± 3	760 ± 20	300 ± 50	670 ± 80	1100 ± 100
PP + 3.8 wt% DMAEMA	67 ± 1	950 ± 40	370 ± 20	800 ± 150	1200 ± 100

[a] Shown are the averages, plus and minus one standard deviation for 3 or 4 repeats. For comparison, the average water fluxes, plus and minus one standard deviation for 9–20 repeats, are shown for the clean membranes.

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cal value of 70 L/m^2 h. The long-term net fluxes with backpulsing are not significantly different for the different membranes, except for the PP membrane modified with AA (which has the lowest long-term net flux). The long-term net flux values with backpulsing are approximately 5-fold greater than those without backpulsing for all of the membranes. These results provide further evidence that bentonite fouling is primarily nonadhesive and that backpulsing is an effective method for reducing this fouling.

As listed in Table 1, the recovered flux due to a 5-min backwash after 1 h of clay filtration with or without backpulsing did not vary significantly with surface modification, except for the PP membrane modified with AA (which has the lowest recovered flux). The recovered flux for the unmodified CA membrane is more than twice that of the other membranes, indicating that the membrane morphology greatly affected the recovered flux when backpulsing was not used. In all cases, however, the recovered flux due to a 5-min backwash after 1 h of filtration with backpulsing is lower than that when backpulsing was not used. As reported previously (9,19), backpulses repeatedly expose portions of the membrane, which then experience additional internal fouling by small particles that would have been screened by the external cake layer in the absence of backpulsing.

Filtration of Oil Emulsions

An unmodified PP membrane, a modified PP membrane with weight gain of 3.9% PEG200MA, and an unmodified CA membrane were tested with oil wastewater in a crossflow filtration system without backpulsing. As shown in Fig. 4, the flux declined rapidly during the initial stage of filtration (approximately 5 min), and then declined slowly until reaching a value of 90 L/m^2 h at the end of 1 h. A similar performance was observed for the PP membranes modified with AA or DMAEMA, and during the filtration of oil emulsions in the presence of an anionic surfactant for all of the membranes. These results indicate that membrane surface chemistry and morphology, as well as the presence of the surfactant, do not significantly affect the average flux and long-term flux for filtration of oil emulsions without backpulsing. Physical deposition of the oil droplets on the membrane surfaces is the dominant fouling mechanism.

A very different result can be observed with backpulsing, however, as shown in Fig. 5. For the unmodified PP membrane (which is hydrophobic and neutral), the total permeate volume after 60 min of filtration with backpulsing but no surfactant is only 1.3 times that obtained without backpulsing, indicating that oil fouling of the hydrophobic surface was primarily adhesive. In contrast, the total mass of the permeate after 60 min of filtration with backpulsing using the PP membrane modified with AA (hydrophilic and negatively charged), PEG200MA (hydrophilic and neutral), and DMAEMA (hydrophilic and positively charged) is

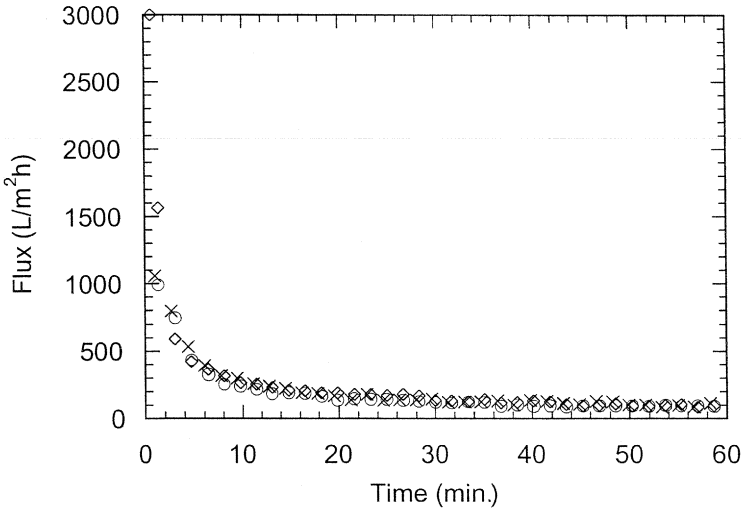

Figure 4. Permeate flux versus filtration time for crossflow filtration of a 50 PPM oil emulsion: (○) unmodified PP membrane; (×) modified PP membrane with weight gain of 3.9 wt% PEG200MA graft; (◇) unmodified CA membrane. The experiments were performed at a forward transmembrane pressure of 5.0 psi.

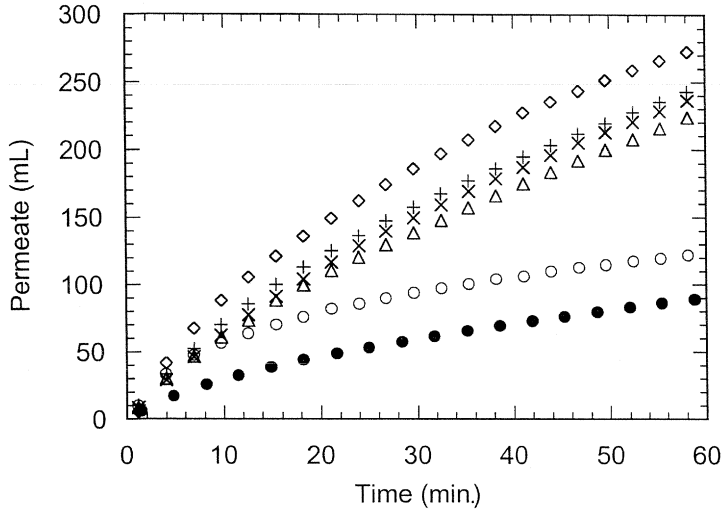

Figure 5. Permeate volume versus filtration time for crossflow filtration of a 50 PPM oil emulsion: (○), (●) unmodified PP membranes with and without backpulsing, respectively; (×), (+), (Δ) backpulsing results for PP membranes modified with weight gains of 4.0 wt% PEG200MA graft, 4.2 wt% AA graft, and 4.0 wt% DMAEMA graft, respectively; (◇) unmodified CA membranes with backpulsing. Backpulsing experiments were performed at a backward transmembrane pressure of 3.0 psi for 0.2 s after every 4 s of forward filtration at a transmembrane pressure of 5.0 psi.

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more than 2.5 times that obtained without modification and backpulsing. The flux enhancement obtained for the modified PP membranes with backpulsing demonstrates that membrane fouling can be reduced further by an effective combination of backpulsing and surface modification. Even higher permeate volume enhancement (3-fold) was observed for the unmodified CA membrane with backpulsing over that for the unmodified PP membrane without backpulsing, due to the differences in both hydrophilicity and membrane morphology. It is not surprising that the unmodified PP membrane provided the least permeate volume, since the crude oil is hydrophobic.

Upon addition of an anionic surfactant, the oil-droplet surfaces become negatively charged. As shown in Fig. 6, the permeate volume enhancement obtained in this case for the PP membrane modified with negatively charged AA increased 3.1-fold, due to the anionic repulsion between the membrane surface and the oil droplets. In contrast, the permeate volume collected with backpulsing for the PP membranes modified with positively charged DMAEMA was enhanced to only 1.7-fold over that of the unmodified PP membrane without backpulsing. The permeate collection for the neutral membrane was not strongly influenced by the

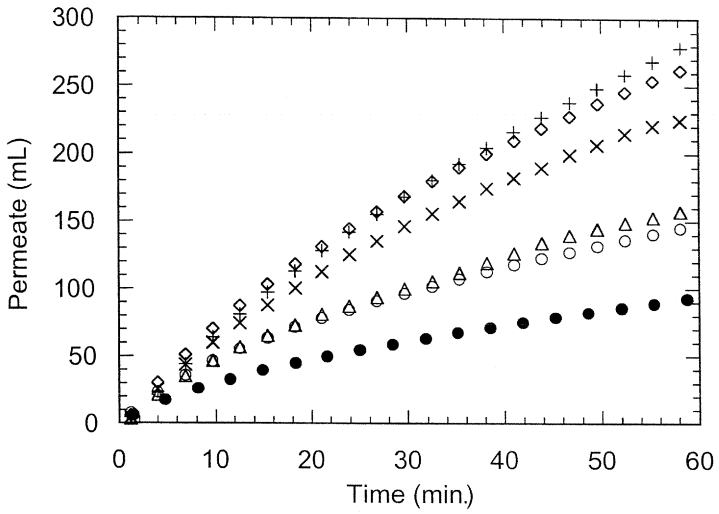

Figure 6. Permeate volume versus filtration time for crossflow filtration of a 50 PPM oil emulsion with an anionic surfactant: (○), (●) unmodified PP membranes with and without backpulsing, respectively; (×), (+), (Δ) backpulsing results for PP membranes modified with weight gains of 3.8 wt% PEG200MA graft, 4.1 wt% AA graft, and 3.9 wt% DMAEMA graft, respectively; (◇) unmodified CA membranes with backpulsing. Backpulsing experiments were performed at a backward transmembrane pressure of 3.0 psi for 0.2 s after every 4 s of forward filtration at a transmembrane pressure of 5.0 psi.

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presence of the anionic surfactant. With a cationic surfactant, the greatest permeate volume enhancement (3.2-fold) was obtained for the PP membrane modified with positively charged DMAEMA, and the least permeate volume was obtained for the PP membrane modified with negatively charged AA. The performance of the neutral membranes was again similar to that in the absence of surfactant.

As shown in Table 2, the long-term flux values without backpulsing are nearly the same for the different membranes (with or without surfactant), providing further evidence that the physical deposition of crude oil on the membranes during filtration is the dominant fouling mechanism and that the membrane surface chemistry and morphology are less important without backpulsing. In the absence of surfactant, the long-term net flux for the unmodified PP membrane with backpulsing was essentially the same as that without backpulsing, due to the strong hydrophobic interactions between the membrane surfaces and the oil droplets. For the PP membranes modified with PEG200MA, AA, and DMAEMA, the long-term net fluxes with backpulsing but no surfactant are, respectively, 2.7, 2.9, and 2.7 times that of the unmodified PP membrane without backpulsing, indicating that the oil layer is more easily lifted off the modified (hydrophilic) membrane surfaces than off the unmodified (hydrophobic) membrane during each backpulse.

For the nearly neutral membranes (unmodified PP, unmodified CA, and PP modified with PEG200MA), the long-term net flux with backpulsing was not significantly affected by surfactants. Apparently, the adsorption of surfactant onto the neutral membranes (which would yield a repulsive surface charge with respect to the oil droplets) did not provide a significant effect. In contrast, the positively charged DMAEMA-modified membrane gave a slightly higher flux with a cationic surfactant, whereas the opposite trend was observed for the negatively

Table 2. Long-Term Fluxes (L/m^2 h) at Different Conditions for Filtration of 50 PPM Crude Oil[a]

	Without Backpulsing		With Backpulsing			
Membrane	No Surfactant	Anionic Surfactant	No Surfactant	Anionic Surfactant	Cationic Surfactant	Clean Water Flux
Unmodified PP	90 ± 14	90 ± 10	90 ± 20	110 ± 25	110 ± 20	1100 ± 100
Unmodified CA	90 ± 20	90 ± 15	300 ± 50	280 ± 30	270 ± 40	3000 ± 200
PP + 5.0 wt% PEG200MA	90 ± 15	80 ± 14	240 ± 30	210 ± 50	220 ± 40	1200 ± 100
PP + 4.2 wt% AA	90 ± 20	80 ± 8	250 ± 60	290 ± 60	140 ± 20	1100 ± 100
PP + 3.8 wt% DMAEMA	80 ± 20	80 ± 15	240 ± 25	130 ± 15	300 ± 60	1200 ± 100

[a] Shown are the averages plus and minus one standard deviation for 2–8 repeats. For comparison, the average water fluxes, plus and minus one standard deviation for 9–20 repeats, are shown for the clean membranes.

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Table 3. Recovered Fluxes (L/m^2 h) at Different Conditions for Filtration of 50 PPM Crude Oil

	Without Backpulsing		With Backpulsing			
Membrane	No Surfactant	Anionic Surfactant	No Surfactant	Anionic Surfactant	Cationic Surfactant	Clean Water Flux
Unmodified PP	330 ± 60	400 ± 100	250 ± 40	310 ± 80	300 ± 70	1100 ± 100
Unmodified CA	1200 ± 130	1300 ± 200	650 ± 80	600 ± 70	600 ± 90	3000 ± 200
PP + 5.0 wt% PEG200MA	600 ± 20	600 ± 80	420 ± 90	420 ± 80	410 ± 70	1200 ± 100
PP + 4.2 wt% AA	680 ± 60	700 ± 50	430 ± 100	500 ± 60	350 ± 50	1100 ± 100
PP + 3.8 wt% DMAEMA	600 ± 30	570 ± 80	400 ± 70	370 ± 40	500 ± 100	1200 ± 100

[a] Shown are the averages plus and minus one standard deviation for 2–8 repeats. For comparison, the average water fluxes, plus and minus one standard deviation for 9–20 repeats, are shown for the clean membranes.

charged AA-modified membrane. As expected, the highest long-term net flux enhancements (about 3.3-fold) with backpulsing were obtained when the membrane surface and the surfactant had like charges.

The recovered fluxes obtained under various conditions are listed in Table 3. In the following discussion, the recovered flux (J_c) following a 5-min backwash after 1 h of oil filtration without backpulsing or surfactant using the unmodified PP membrane is taken as the baseline value. Without backpulsing or surfactant, the recovered fluxes for the PP membranes modified with PEG200MA, AA, and DMAEMA, respectively, are 1.8, 2.1, and 1.8 times J_c. These results demonstrate that the hydrophobic oil layer is more readily lifted off hydrophilic membrane surfaces than off the unmodified hydrophobic surface. Without backpulsing but with an anionic surfactant, the recovered flux for unmodified PP is 1.2 times J_c, likely due to the reduced hydrophobicity of the oil droplets and/or the adsorption of surfactant on the membrane surface, although this difference in recovered flux is not statistically significant at the 90% confidence level. The anionic surfactant also did not significantly affect the recovered fluxes after backwashing the other membranes fouled without backpulsing.

With backpulsing but without surfactant, the recovered flux for the unmodified PP membrane is only 0.76 times J_c, which may be due to internal fouling, as discussed previously for clay filtration. Similarly, the recovered flux for each modified PP membrane is approximately 0.7 times that of the corresponding membrane without backpulsing. With backpulsing and an anionic surfactant, the recovered flux for the unmodified PP membrane is 0.94 times J_c. The small improvement made by adding the surfactant is thought to be due to the reduced

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hydrophobicity of the oil droplets, which is possibly due to the adsorption of surfactant on the membrane. This may allow the drops to be more easily lifted off the otherwise hydrophobic and neutral membrane surface during the backwash. For the modified PP membranes and the unmodified CA membranes, the recovered fluxes following a 5-min backwash after filtration with backpulsing are always lower than those after filtration without backpulsing. Surfactants do not appear to affect the recovered fluxes for the neutral, hydrophilic membranes, but a surfactant of like charge gives a slight improvement in flux recovery with the charged membranes.

CONCLUSIONS

The effects of membrane surface chemistry and backpulsing on fouling reduction have been demonstrated for crossflow filtration of bentonite clay suspensions and crude oil emulsions. Without backpulsing, both clay and oil fouling appear to be dominated by physical deposition of foulants, and so membrane surface characteristics and morphology are of less importance in this case. It was found that bentonite exhibits primarily nonadhesive fouling, and so membrane surface modification is not as effective as backpulsing in reducing membrane fouling. For example, 5-fold and 6-fold enhancements in the permeate volumes collected over 1 h were obtained for neutral PP membranes filtering 0.5 g/L bentonite using backpulsing alone and in combination with surface modification, respectively, whereas no improvement due to surface modification was observed without backpulsing. On the other hand, both positively and negatively charged membranes yielded lower permeate collection than did neutral membranes with backpulsing, presumably due to the attraction of bentonite (which has mixed charges) to the surfaces of the charged membranes.

In contrast, crude oil demonstrated substantial adhesive fouling. Therefore, both membrane surface chemistry and surfactants play important roles in the filter performance. It was demonstrated that neither surface modification nor backpulsing alone is very effective in reducing crude oil fouling of PP membranes. Instead, a combination of appropriate membrane surface modification and backpulsing provides significant permeate volume enhancement. For instance, with backpulsing, the permeate volumes collected in 1 h are 1.3 and 2.7 times those found without backpulsing for the unmodified (hydrophobic) and modified (hydrophilic) PP membranes, respectively. Moreover, by adding an anionic or a cationic surfactant, an approximately 3-fold permeate volume enhancement was obtained with backpulsing when the membrane and the surfactant had charges of the same sign. The performance was much poorer when the surfactant and membrane had opposite charges, apparently due to the attraction of the emulsified oil to the membrane surface. The unmodified (hydrophilic) CA membrane performed approximately as well as the best modified PP membrane in each case.

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The recovered fluxes after a long backwash of the fouled membranes also support the differences between clay and oil fouling. For bentonite clay, the water fluxes for both modified and unmodified PP membranes were recovered with backwashing to approximately 80% of the initial water flux. In contrast, crude oil exhibited more adhesive fouling, which was reduced by surface modification; the flux recovery is only about 30% for the unmodified, hydrophobic PP membrane, while it improved to about 60% for the modified, hydrophilic PP membranes. For both foulants, the flux recovered from a long backwash after fouling with backpulsing, is lower than that after fouling without backpulsing, apparently due to the membranes' exposure to internal fouling after each backpulse.

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