

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Microfiltration of Activated Sludge Using Modified PVC Membranes: Effect of Pulsing on Flux Recovery

Dae Sik Kim^a; Jong Seok Kang^a; Young Moo Lee^a

^a National Research Laboratory for Membrane, School of Chemical Engineering, College of Engineering, Hanyang University, Seoul, South Korea

Online publication date: 20 February 2003

To cite this Article Kim, Dae Sik , Kang, Jong Seok and Lee, Young Moo(2003) 'Microfiltration of Activated Sludge Using Modified PVC Membranes: Effect of Pulsing on Flux Recovery', *Separation Science and Technology*, 38: 3, 591 – 612

To link to this Article: DOI: 10.1081/SS-120016653

URL: <http://dx.doi.org/10.1081/SS-120016653>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.



Microfiltration of Activated Sludge Using Modified PVC Membranes: Effect of Pulsing on Flux Recovery

Dae Sik Kim, Jong Seok Kang, and Young Moo Lee*

National Research Laboratory for Membrane, School of Chemical Engineering, College of Engineering, Hanyang University, Seongdong-KU, Seoul, South Korea

ABSTRACT

A combined effect of backpulsing, crosspulsing, and membrane-surface modification was investigated for the reduction of membrane fouling and the recovery of flux for crossflow filtration. The hydrophobic poly(vinyl chloride) (PVC) membranes were subjected to the surface modification with N-vinyl-2-pyrrolidinone (NVP) monomer by the ultraviolet-assisted graft polymerization to increase the surface wettability and to decrease the adsorptive fouling. The flux was dependent on the membrane-surface properties. The flux of the modified membrane was higher than that of the unmodified membrane due to the increase of hydrophilicity on the membrane surface and the more or less dilution of protein concentration

*Correspondence: Young Moo Lee, National Research Laboratory for Membrane, School of Chemical Engineering, College of Engineering, Hanyang University, Seongdong-KU, Seoul 133-179, South Korea; Fax: 82-2-2291-5982; E-mail: ymlee@hanyang.ac.kr.



in the sludge solution at NVP layer. The recovered fluxes of modified and unmodified membranes, after the removal of the foulants from the membrane surface, were about 61% and 34% of the initial flux, respectively. These results suggest that the adhesive interactions of the mixed liquor-suspended solid (MLSS) with the hydrophilic membrane surfaces are weaker than those with a hydrophobic surface. To clean foulants, backpulsing and crosspulsing were carried out. 3.6-fold and 5.6-fold enhancements of modified membranes in the average permeate flux, in comparison with unmodified membranes, were obtained for filtering MLSS using backpulsing alone and a combination of backpulsing and surface modification, respectively. The average permeate flux of surface modified membrane with backpulsing (5.6-fold) was higher than with crosspulsing (2.8-fold), indicating that the deposition of MLSS in the interior of the membrane pore was the dominant fouling mechanism. The transmembrane pressure (TMP) of modified membranes was lower than that of unmodified membrane.

Key Words: Microporous membrane; Poly(vinylchloride); N-vinyl-2-pyrrolidinone (NVP); Sludge; Crossflow filtration; Backpulsing.

INTRODUCTION

Membrane systems have become increasingly important to the water treatment in, for instance, the pharmaceutical, biotechnology, and food and beverage industries. A major obstacle to further incorporation of membrane process in industrial operation is flux decline resulting from fouling through the adsorption of a solute within pores. In water treatment applications involving colloids, microbes, and undissolved hydrocarbons, the foulants are often adhesive and exhibit fouling due to hydrophobic interaction, hydrogen bonding, van der Waals attraction, extracellular macromolecular interactions, and other effects. Fouling can occur as accumulation of cells, cell debris, or other rejected particles on the top surface of the membrane (external fouling), or as deposition and adsorption of small particles or macromolecules (internal fouling).

Many of the commercially available synthetic membranes in the field of microfiltration and ultrafiltration are made of hydrophobic polymers such as polyvinylchloride (PVC), polysulfone (PSf), polypropylene (PP), and so on, because of their good mechanical property. However, the hydrophobic membranes are very susceptible to protein fouling by adsorption in the feed, giving rise to a fast flux decrease and an increasing demand for frequent cleaning cycles. Particularly, in the filtration of biological solutions,



the membrane fouling due to pore plugging, pore narrowing, and cake formation by a protein is a considerable restriction in application.

A variety of methods have been reported to reduce this type of fouling for a range of different application. The first method is the addition of coagulants to form larger particles that are readily lifted off the membrane surfaces.^[1] The second case is the introduction of the instability of flow by low-frequency axial pressure and velocity pulsing or by injecting air into the feed stream.^[2] The third way of reducing fouling is the crosspulsing by periodically stopping the permeate flow and forward rinsing with a rinse solution such as pure water.^[3] The final method is the backpulsing using fluid or gas.^[4] During filtration, particles accumulate on the membrane surface, forming a cake or gel layer. Foulants are lifted off the membrane by the backpulsing and then swept to the filter exit by the crossflow.^[5,6] This results in a hydraulic cleaning of the membrane by forcing permeates back through the membrane in the reverse direction.

Membrane surface properties are important because the interactions between the polymers and their environments occur chiefly at their surfaces. Several methods have been reported with the potential to reduce or eliminate adhesive fouling by changing the membrane surface chemistry: (a) physical coating of the charged surfactants onto the membrane surface for temporary surface modification^[7] has been suggested, (b) coating hydrophilic polymers on the membrane,^[8] and (c) photografting of functional monomers on the surface of the membrane using light sources were also supported for effective reduction of membrane fouling.^[9,10] To reduce the membrane fouling, the conventional grafting polymerization technique has required chemically reactive groups on the surface as well as on the membrane pore wall. For this reason, a series of prefunctionalization steps are necessary for covalent grafting. The surface prefunctionalization techniques such as UV, γ -ray irradiation, plasma, ion beam, or chemical initiators has been suggested.^[9,10] Among these techniques, the radiation grafting method is one of the preferable methods because of the uniform and rapid creation of active radical sites without a catalytic contamination in grafting sample. Many researchers have reported the reduction of protein (BSA) fouling by membrane-surface modification using photografting methods.^[9,11]

N-vinyl-2-pyrrolidinone (NVP) is known as a hydrophilic graft monomer for radiation grafting on various trunk polymers, and it has been described as useful not only for the preparation of membranes, but also for the preparation of a biocompatible polymer.^[12–14] The water-absorption capacity of modified membranes is directly related with the degree of grafting, which itself depends greatly on the irradiation dose.



The objective of this study is to investigate the effect of the combination of surface modification and pulsing to recover flux or to decrease membrane fouling. At first, the PVC membranes for the microfiltration were prepared according to our previous study.^[15] To improve the membrane performance, grafting NVP on the surface of PVC membrane by UV irradiation changed the surface hydrophilicity of a membrane. To confirm the effect of the membrane grafting on the filtration performance, the unmodified and the modified PVC membranes were compared with respect to their deionized-water permeation. To further investigate the effect of the pulsing for the recovery of flux, both unmodified and modified PVC membranes were tested in a crossflow microfiltration system with and without crosspulsing or backpulsing in the presence of activated sludge suspensions.

EXPERIMENTAL

Materials

Poly(vinyl chloride) (PVC) (LG Chem Ltd. Seoul, Korea, Grade:PB1752, DP:1700) was obtained and used as a base polymer. Tetrahydrofuran (THF, Milwaukee, WI) and *n*-butyl alcohol (n-BA, Junsei Co., Tokyo, Japan) were used as a good solvent and a nonsolvent additive, respectively. N-vinyl-2-pyrrolidinone (NVP, Aldrich Chemical Co., Milwaukee, WI) was vacuum-distilled to remove an inhibitor before use and dissolved in methanol and then used as a grafting monomer. Methanol (J. T. Baker, Paris, KY) was used with a reagent grade. Deionized water was produced by an ultra-pure water system (Milli-Q plus, Millipore, MA).

Surface Modification of PVC Membranes

Cosolvent, which consisted of 70 wt.% THF and 30 wt.% *n*-butyl alcohol, was utilized in the preparation of polymer solution while the total concentration of PVC in the solution was maintained to be 9 wt.%. The membranes were prepared inside a glove box (JEIO Tech. Model SK-G001, Seoul, Korea) capable of controlling both the relative humidity (RH) and temperature in the accuracy limit of $\pm 2\%$. The dope solution was cast on a polyester fabric with the casting knife of 150 μm thickness inside the glove box, keeping the humidity range of 80% at $25 \pm 0.5^\circ\text{C}$. In this study, for UV irradiation and grafting experiments, PVC membranes were first dipped in 20 wt.% aqueous NVP solution for 2 hr prior to mounting in the glass vessel. Then, PVC membranes were placed at a distance of 10 cm from UV source



and irradiated in air with an unfocused medium-pressure mercury UV lamp (450W power, Ace Glass Co., NJ) having mixed wavelengths of 303, 313, 348, and 363 nm (λ_{main}) to graft the NVP monomer on the surface of the PVC membrane. After grafting the reaction for 5 min, the grafted membrane was taken out from the glass vessel and washed in the flask filled with deionized water at a shaking water bath at 65°C for 1 day to remove the unreacted monomer (NVP) and homopolymer remaining on the membrane. Deionized water was exchanged five times. After washing, all prepared membranes were dried completely in the vacuum oven. The graft yield was obtained gravimetrically by the following equation:

$$\text{Graft yield } (\mu\text{g}/\text{cm}^2) = \frac{w_g - w_0}{A}$$

where w_0 and w_g are the weight of a membrane before and after NVP grafting, respectively. A is the effective area of membrane surface

Membrane Characterization

Pore Size and Distribution

In order to investigate the change of pore size and distribution between the unmodified and the modified PVC membranes, a capillary-flow porometer (CFP-1200-AEL, PMI Co.,) was used. The membrane is first wetted with a liquid (Porewick®) having a low surface tension ($\gamma = 16*10^{-3}$ N/m). The wetted membrane is subjected to increasing pressure by a compressed clean and dry air source. As the air pressure increases, it will reach a point where it can overcome the surface tension of the liquid in the largest pores and will push the liquid out. Increasing the pressure still further allows the air to flow through smaller pores, according to Cantor's equation.^[16]

Contact-Angle Measurements

The sessile-drop method was used to determine the polarity of the unmodified and the modified PVC membranes. 0.1 μL of deionized water with a microsyringe was dropped onto a dry membrane in an air atmosphere and the contact angle was measured by using a goniometer (CA-X, Kyowa, Kaimenkagaku Co., Tokyo, Japan) as soon as possible. The reported values were the mean of at least 10 experiments and the standard deviation was within ca. $\pm 8\%$.



Fourier Transform Infrared Spectroscopy (FT-IR)

In order to investigate the changes of chemical structure between the unmodified and the modified PVC membranes and confirm the grafting of NVP onto the membrane, a Fourier transform infrared spectroscopy (FT-IR, Nicolet Magna-IR spectroscopy 550, WI) was used.

Field Emission Scanning Electron Microscopy (FE-SEM)

The morphology of a membrane affects the filtration performance. Therefore, the morphological changes of membranes after grafting were investigated. The surfaces of the unmodified and the modified PVC membranes were observed by field emission scanning electron microscopy (FE-SEM, JEOL-6330F, Kyoto, Japan). The morphology of the membranes before and after crossflow filtration was also confirmed by FE-SEM.

Crossflow Filtration Experiments

The crossflow filtration apparatus consisted of a crossflow plane module cell (length \times width \times height: $110 \times 25 \times 3$ mm size, effective membrane area 27.5 cm^2), a circulation pump (Masterflex[®] L/S Model 77310-01, Cole-Parmer Instrument, IL) for a stable feed supply, a peristaltic pump (Minipuls3, Gilson[®], WI) for a constant suction performance, a pressure transducer (Model 626A13TAE, MKS Instruments, MA) to detect the pressures of feed and permeate from the membrane module, a 2000 ml feed reservoir, a permeate collection reservoir, and an electronic balance connected with a personal computer as shown in Fig. 1. In the crossflow filtration of pure water, velocity of feed solution was 0.22 m/sec or 0.44 m/sec. The pump in the crossflow filtration unit was a centrifugal type and the permeate flow rate was controlled only by the revolutions per minute (rpm) of the suction pump. The rpm increases every 150 sec by stages. All the membranes in the filtration tests were initially immersed into the isopropylalcohol/H₂O (20/80 wt.%) mixture for 10 min before testing. The weight of permeate was measured every 30 sec with an electronic balance and then automatically recorded in an on-line computer. Also the transmembrane pressure (TMP) was obtained by the following equation,

$$TMP = \frac{P_1 + P_2}{2} - P_3$$

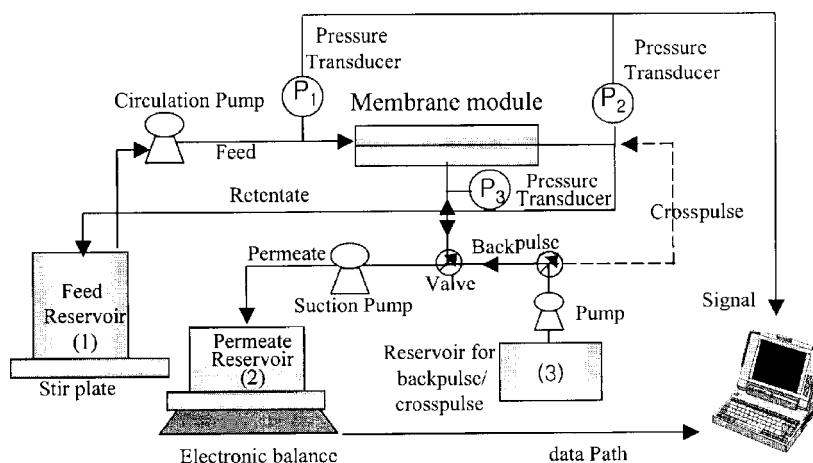


Figure 1. Schematic of crossflow filtration apparatus.

where P_1 and P_2 are feed pressures at the front and the back of crossflow module, respectively. P_3 is permeate pressures.

Crossflow Filtration Experiments with Backpulsing and Crosspulsing

To induce fouling, the feed solution, which contained the chemical oxygen demand (COD) of 1038 ppm and the mixed liquor-suspended solids (MLSS) of 2830 ppm, was used during the crossflow filtration. The sludge solution was sampled from the aeration tank in the membrane bioreactor (MBR). The ratio between COD and MLSS is low because the F/M (food/microorganisms) ratio in the MBR is low or all of the cells were not oxidized completely. For crossflow filtration without pulsing, the feed flows from reservoir to the membrane module at a flow rate of 0.066 m/sec for 1 hr. The retentate flows from the module back to the feed reservoir. The permeate flows to a computer-interfaced electronic balance which records the mass. The transmembrane pressure (TMP) is simultaneously recorded by a computer-interfaced pressure transducer and is calculated. For crosspulsing to remove the foulants on the surface of membrane, the pure water from a third reservoir flows periodically, reversing the flow direction of retentate at a flow rate of 0.132 m/sec. During backpulsing, the pure water from a third reservoir is sent through the permeate channel, up through the membrane in the direction opposite to that of feed flow. The pulsing is performed every 10 min and

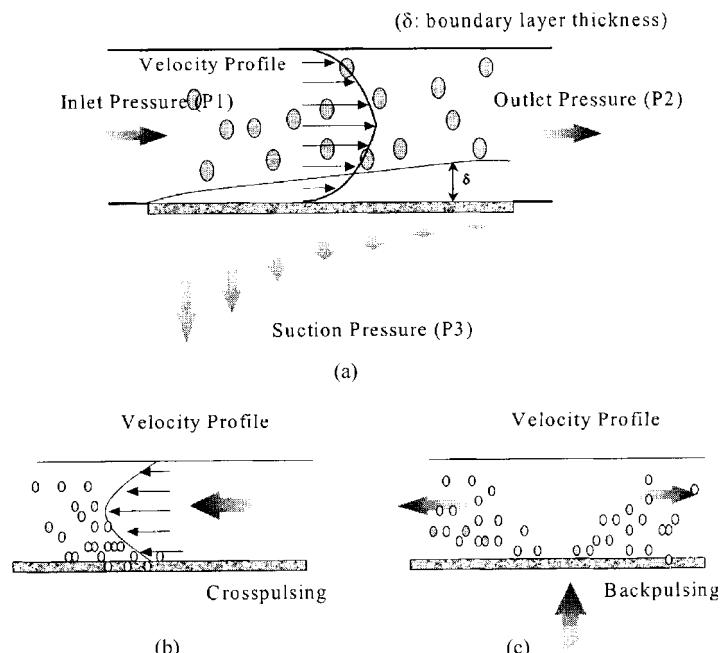


Figure 2. Schematics of the crossflow filtration and the mechanical pulsing: (a) filtration, (b) cross-pulsing, and (c) back-pulsing.

the pulsing time is 1 min. A schematic of velocity profile during filtration and pulsing is illustrated in Fig. 2.

RESULTS AND DISCUSSION

Surface Modification of the PVC Membranes

The characterization of PVC membranes and the modified PVC membranes (PVC-g-PNVP membrane) with NVP monomer onto the PVC membranes were summarized in Table 1. The use of a hydrophilic rather than a hydrophobic membrane helps reduce the membrane fouling. Generally, proteins adsorb more strongly at hydrophobic surfaces and are less readily removed than hydrophilic surfaces. Although we prepared a series of modified PVC membranes, we intend to report here for only one modified PVC membrane for pulsing effect.

**Table 1.** Characterization of the PVC membrane and PVC-g-PNVP membrane.

Sample	NVP conc. ^a (wt.%)	Grafting yield ^b ($\mu\text{g}/\text{cm}^2$)	Contact angle ^c (degree, °)	pore diameter ^d (μm)	Mean flow Flux ^e ($\text{L}/\text{m}^2 \text{h}$)	Resistance ^f (R_m , 10^9 m^{-1})
PVC	—	—	133.3	0.98	8800	4.09
PVC-g-PNVP	20	117.23	68.4	0.55	4970	7.24

^a NVP monomer was dissolved in pure water.

^b Grafting yield = $(w_g - w_o)/A$, where w_o and w_g are the weight of membrane before and after grafting reaction, respectively, A is the effective area of membrane surface.

^c Contact angle was measured by the sessile-drop method and the average estimated error was $\pm 8\%$.

^d Mean flow pore diameter was measured by PMI porometer.

^e Deionized water flux by dead-end filtration (Amicon cell, model 8050) at 1500 torr-(2 bar).

^f Resistance was calculated by the measured deionized water flux. $R_m = \Delta P / \eta J$, J is the hydraulic flux, R_m is the hydrodynamic resistance of the membrane itself, ΔP is the pressure difference between the feed and the permeate side of the membrane, and η is the viscosity of water.

Contact-angle measurements have been commonly used to characterize the polarity or the surface energy of the polymeric surface.^[17,18] However, such measurements are difficult to interpret for synthetic membranes due to capillary forces within pores, contraction in the dry state, heterogeneity, roughness, and restructuring of the surfaces. Nevertheless, the relative hydrophilicity or hydrophobicity of each sample can be easily obtained by this measurement. As shown in Table 1, the virgin PVC membrane showed the contact angle of 113.3°. However, the contact angle of PVC-g-PNVP membranes decreased to 68.4° due to hydrophilicity of NVP. These changes of contact angles meant that a hydrophobic PVC membrane effectively changed its surface characteristics into a hydrophilic membrane by the grafting of NVP onto the surface.

The variation of chemical structure through the grafting of NVP onto the PVC membrane surface was confirmed by FT-IR and shown in Fig. 3. The most significant change in the spectra of the modified PVC-g-PNVP membranes was the appearance of a red-shifted 1350 cm^{-1} absorption band due to C—N stretching vibration of NVP into an $\sim 1230 \text{ cm}^{-1}$ band without the variation of an 1730 cm^{-1} stretching band representing the C=O in PNVP. Also, the major characteristic peaks for PVC appeared at 800, 750, and 720 cm^{-1} , representing C—Cl stretching bands.

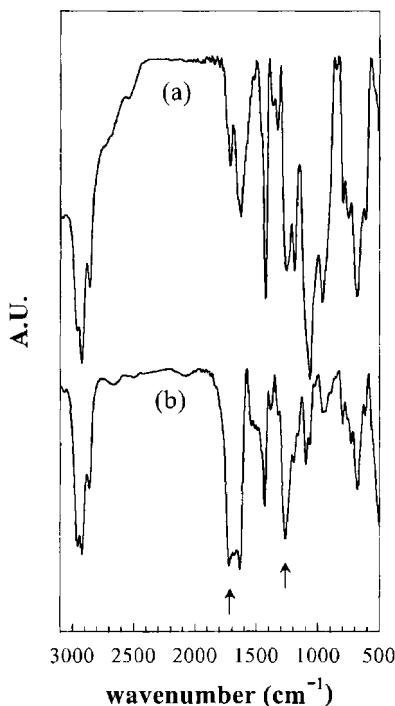


Figure 3. FT-IR spectra of (a) unmodified PVC membrane and (b) modified PVC membrane.

The morphological changes of a PVC membrane after grafting reaction were observed by FE-SEM as shown in Fig. 4. The pores on the membrane surface seemed to be narrowed after the grafting reaction. Surface pore size and pore size distribution of the membrane were further investigated using the capillary-flow porometer. The mean pore sizes of unmodified and modified membrane were 0.98 μm and 0.55 μm , respectively, as taken by the capillary-flow porometer (see Fig. 5). This confirms the results of the FE-SEM.

Filtration Tests

To investigate the effect of hydrophilicity induced by the grafting of NVP monomer on the membrane performance, deionized-water filtration experiments of the unmodified and the modified PVC membranes were carried out.

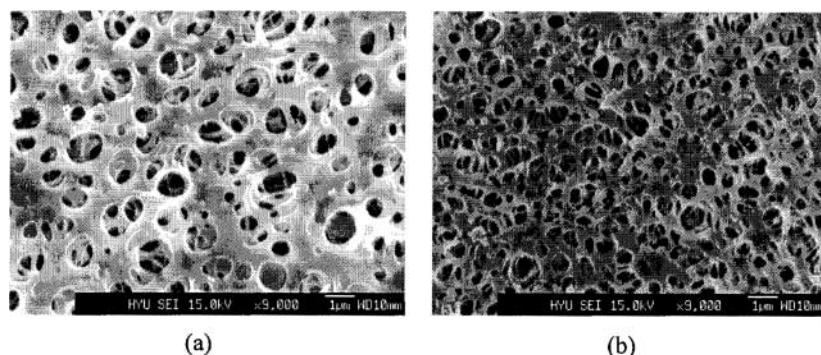
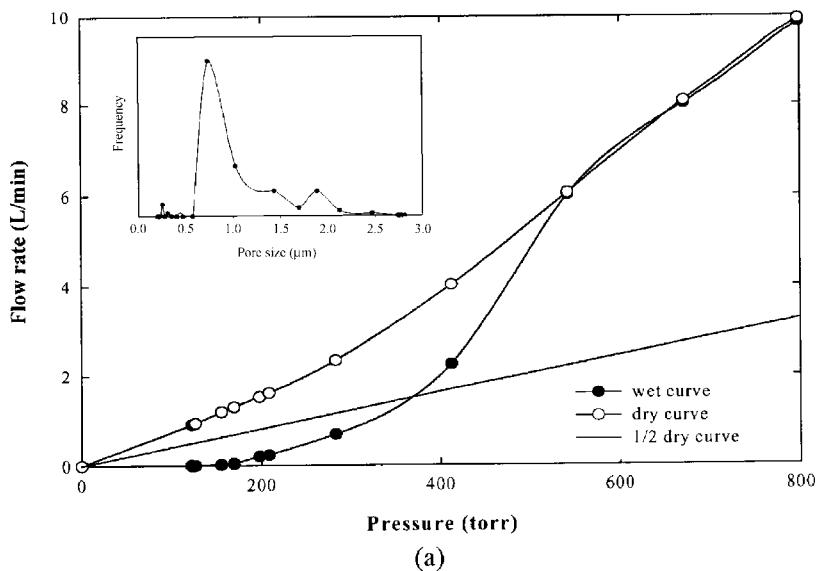


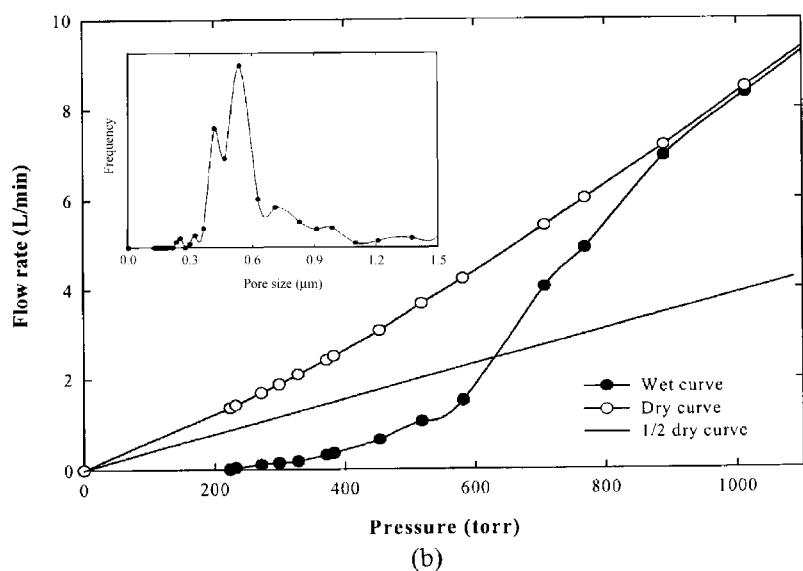
Figure 4. FE-SEM photographs (a) unmodified PVC membrane and (b) modified PVC membrane.

In the dead-end filtration test of membranes, the modified membranes showed a decrease in a deionized-water flux from 8800 LMH($\text{L}/\text{m}^2 \text{ h}$) for PVC to 4970 LMH for PVC-g-PNVP membrane due to the narrowed and plugged pores after modification.^[19] On the other hand, in the crossflow filtration test, the deionized-water flux of the modified membrane was higher than the unmodified membranes due to the reduced membrane resistance by increasing the hydrophilicity after surface modification. In the crossflow test, the suction speed increased every 150 sec by stages. Therefore, as the suction speed increased, the TMP increased and, thus, higher flux was obtained.^[20,21]

Figure 6 shows the effects of feed velocities of 0.22 and 0.44 m/sec for crossflow operation on the permeation water flux, respectively. As shown in Fig. 6, the starting TMP of modified membrane at 0 sec at the same condition is lower than that of unmodified PVC membrane for both 0.22 and 0.44 m/sec velocities. In view of the flux, the modified membrane has the higher permeation flux than the unmodified membrane. It means that membrane resistance in the crossflow filtration decreased, although the resistance of a membrane was higher in the dead-end filtration (see Table 1). These phenomena were due to the hydrophilicity of the membrane surface. At the same TMP, the difference of flux between modified and unmodified membranes would increase. Although the TMP between unmodified and modified membrane increases gradually, the rate of TMP increase of modified membrane is lower than that of unmodified membrane. At the velocity of 0.22 and 0.44 m/sec, the difference in flux is not detected. However, note that TMP increased largely at high velocity.



(a)



(b)

Figure 5. Pore distribution and air-flow rate of (a) unmodified PVC membrane, and (b) modified PVC membrane using capillary-flow methods (wet and dry flow method).

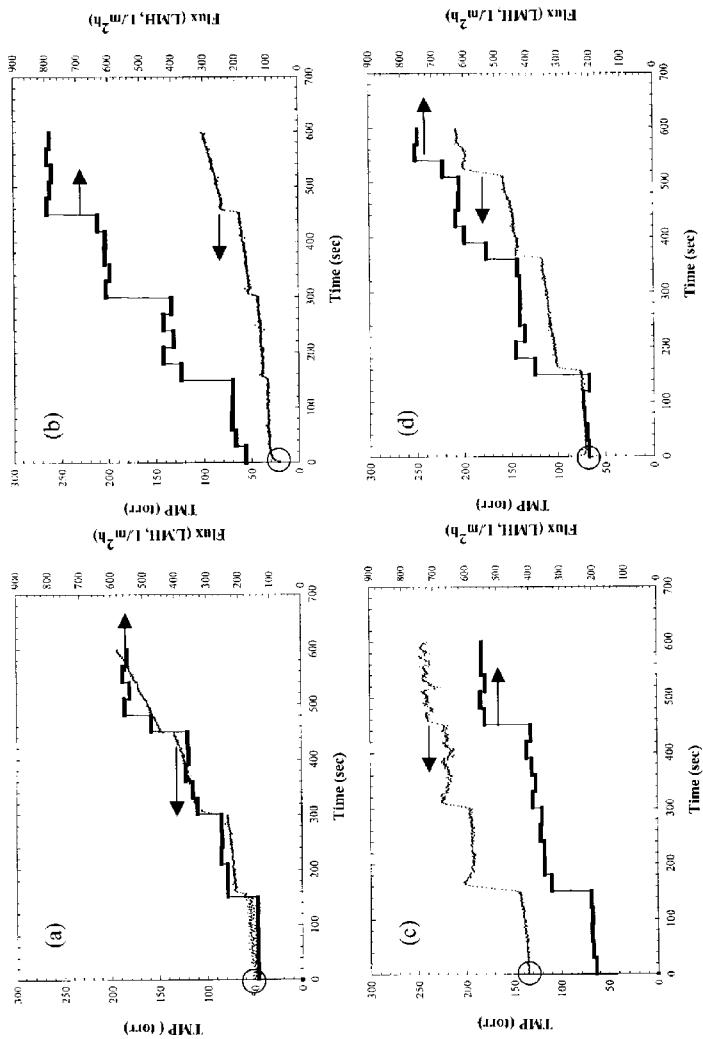


Figure 6. Permeate flux and TMP profiles for crossflow filtration of (a) unmodified PVC membrane at feed velocity of 0.22 m/sec, (c) unmodified PVC membrane at feed velocity of 0.44 m/sec, and (d) modified PVC membrane at feed velocity of 0.44 m/sec.

Backpulsing and Crosspulsing

The crosspulsing and backpulsing were used as cleaning methods to recover the flux and to reduce fouling for filtering activated sludges. Typical cleaning agents remove exterior foulants and attack the membrane, resulting in a decrease in its lifetime. Backpulsing is one approach to the problem in which the permeate is periodically forced back through the membrane in the reverse direction to normal permeate flow in order to flush out the accumulated fouling material from the membrane pores and the membrane surface. If the permeate pressure increases until it is higher than the pressure on the feed side of the membrane, then reverse filtration will occur and clean purified water will be forced to flow from the permeate side of the membrane to the feed side. If backpulsing removes foulants from the membrane, the flux recovers to its value before fouling begins.

In this study, the combination of surface modification and pulsing was carried out to determine the effectiveness in reducing membrane fouling. Figure 7 showed that the recovered flux of modified and unmodified membrane after removal of the foulants from the membrane surface were about 61% and 34% of the initial flux, respectively. Also, TMP of modified membrane was lower than that of unmodified membrane. These results suggest that the adhesive interactions of the MLSS with the hydrophilic membrane surfaces are weaker than those with a hydrophobic surface. When the combination of backpulsing and surface modification was adopted, as

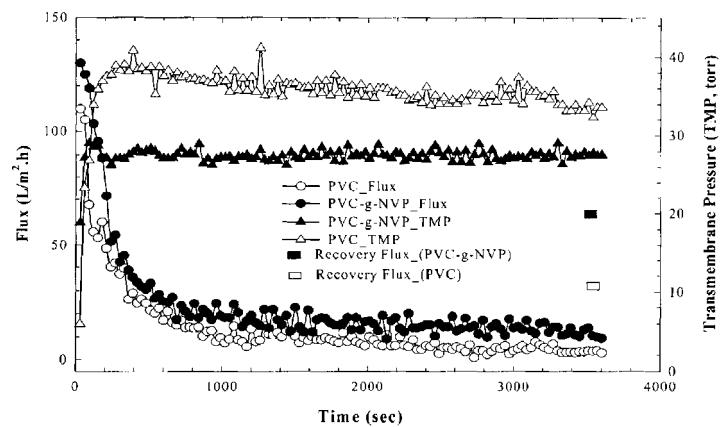


Figure 7. Permeate flux and TMP as a function of time without pulsing and recovery of flux.

Table 2. Average permeation flux and TMP as a function of time with backpulsing or crosspulsing.

Cleaning process	PVC membrane		PVC-g-PNVP membrane	
	TMP (torr)	Flux (L/m ² h)	TMP (torr)	Flux (L/m ² h)
No pulsing	39.6	13.07	26.5	23.35
Backpulsing	55.2	46.9	44.3	73
Crosspulsing	43.3	25.1	35.3	36.45
Removal rate of COD ^a	95.06%		92.78%	
Removal rate of MLSS ^b	98%		97%	

^a COD was measured by the micro-COD method proposed by HACH.

^b MLSS was measured according to standard methods [APHA, 1995].

shown in Fig. 8, for the unmodified PVC membrane the cumulative permeate volume after 60 min of filtration with backpulsing is 4.16 times that obtained without backpulsing. In contrast, the cumulative mass of the permeate after 60 min of filtration with backpulsing using the modified PVC membrane is 6.33 times that obtained using the unmodified PVC membrane. Ultimately,

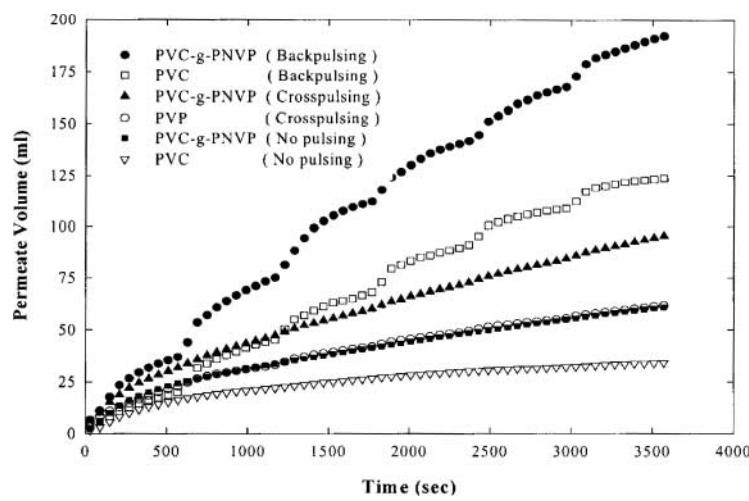


Figure 8. Accumulated permeate volume as a function of time.

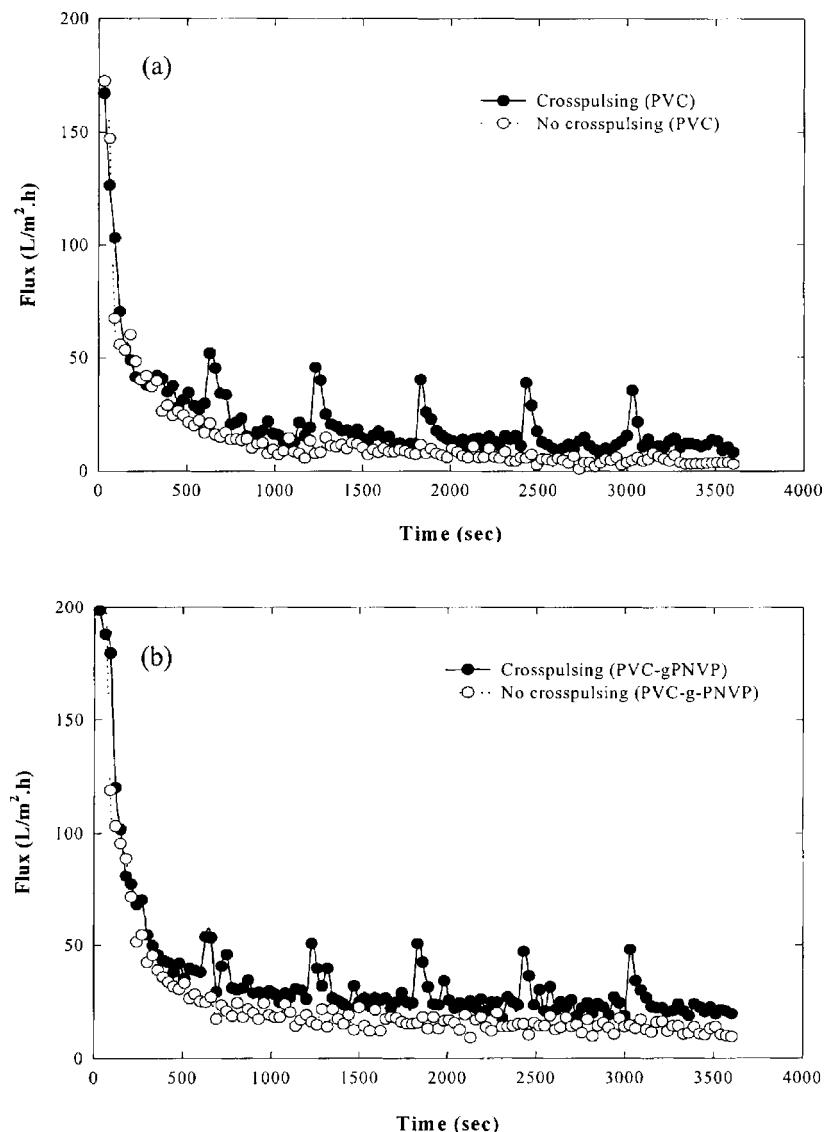


Figure 9. Permeate flux as a function of time with and without crosspulsing: (a) unmodified PVC membrane and (b) modified PVC membrane.

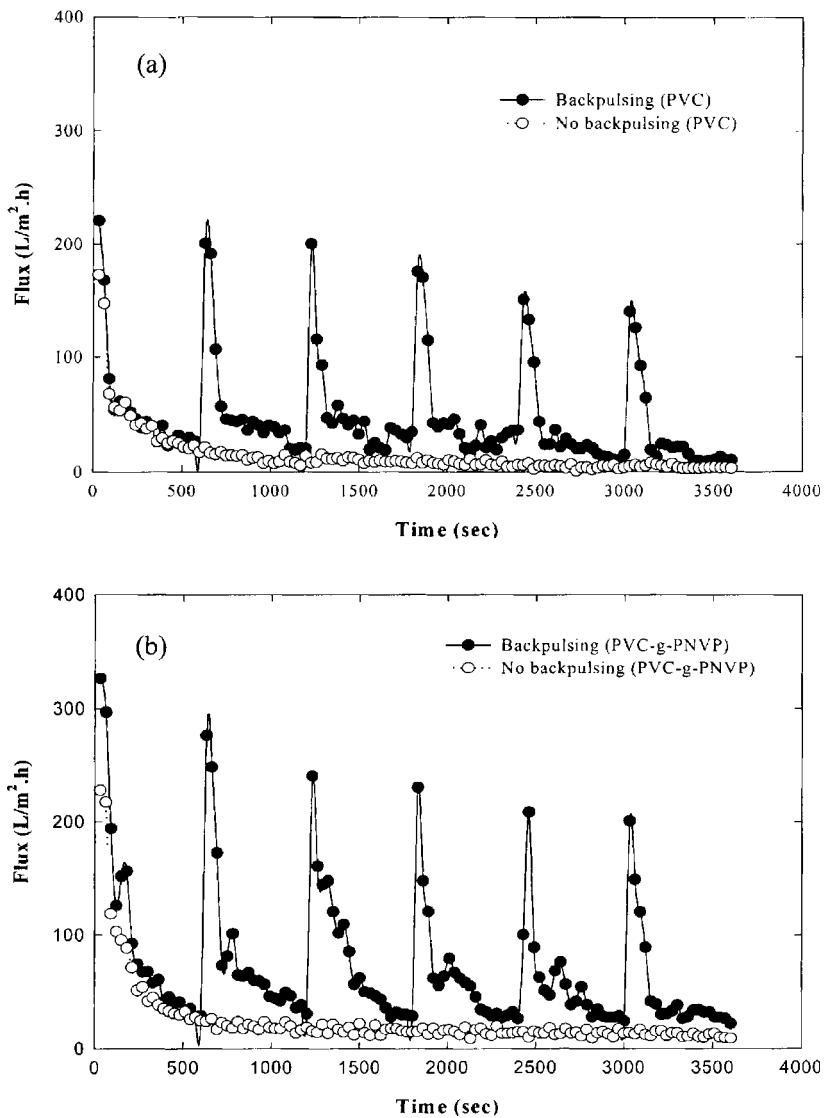


Figure 10. Permeate flux as a function of time with and without backpulsing: (a) unmodified PVC membrane and (b) modified PVC membrane.

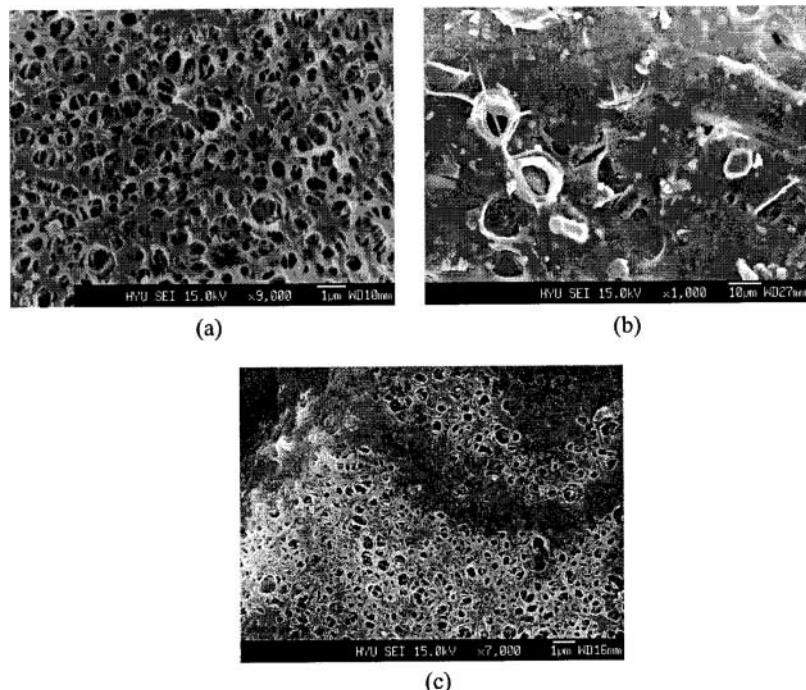


Figure 11. The photographs of the surface of PVC membrane (a) before the permeation test, (b) after the permeation, and (c) after pulsing.

the cumulative permeate volume enhancement was obtained. Ma et al.^[22,23] reported the similar results demonstrating the synergistic effects of backpulsing and surface modification.

Figures 9 and 10 showed the permeate flux as a function of time with and without backpulsing or crosspulsing. After filtration for 60 min, 3.6-fold and 5.6-fold enhancements in the average permeate flux were noted for PVC-g-PNVP membrane filtering 2830 ppm MLSS using only backpulsing and a combination of backpulsing and surface modification, respectively (see Table 2). The recovered flux for the modified PVC membrane is slightly better than for the unmodified PVC membrane. It is well-known that the hydrophilic membrane maintains higher flux than the hydrophobic one.^[24] As shown in Table 2, the removal rate of COD was 95% for unmodified and 93% for modified membranes, respectively. The removal rate of MLSS was 98% for unmodified and 97% for modified membranes. The permeate COD and MLSS concentration of



the unmodified membrane were lower than those of the modified membrane. The difference in the solute-rejection rate between modified and unmodified membranes was mainly due to the degree of sieving and/or adsorption onto the cakes deposited over the membrane, and partly due to adsorption into membrane pores and surface.^[25] For modified membranes, the recovered flux with backpulsing (5.6-fold) is higher than with crosspulsing (2.8-fold), indicating that the deposition of MLSS in the interior of the membrane pore is the dominant fouling mechanism and the membrane surface fouling is then of less importance because the crosspulsing removes the foulants only on the membrane surface.

The surfaces of membrane before and after backpulsing were observed using the FE-SEM photographs as shown in Fig. 11. After backpulsing, the foulants was removed from the surface of membrane [see Fig. 11(c)]. The higher flux enhancements and lower TMP obtained for the modified PVC membrane indicate that the membrane fouling could be effectively reduced by a combination of backpulsing and surface modification.

CONCLUSIONS

The microporous PVC membrane with the open of pore of 0.98 μm was modified to obtain PVC membrane (0.55 μm) by grafting the 20 wt.% aqueous NVP solution on the membrane surface with a 5-min UV-assisted polymerization technique to increase the surface hydrophilicity of PVC membrane.

In the crossflow filtration test of deionized water, the flux of the modified membrane was higher than the unmodified membranes due to the reduced membrane resistance by increasing the surface hydrophilicity after surface modification. Grafting NVP onto PVC membrane reduced pore size and increased membrane hydrophilicity. Increasing membrane hydrophilicity increased the flux even with smaller pore size.

To confirm the effect of the pulsing on the recovery of flux in the presence of active sludge suspensions, both unmodified and modified PVC membranes were tested in a crossflow microfiltration system. 3.6-fold and 5.6-fold enhancements in the average permeate flux were noticed for membrane filtering 2830 ppm MLSS using backpulsing alone and a combination of backpulsing and surface modification, respectively. These results suggest that the adhesive interactions of the bacteria with the hydrophilic membrane surfaces are weaker than those with a hydrophobic surface and the more or less diluted protein concentration in the sludge solution at NVP layer. The recovered flux with backpulsing is higher than that with crosspulsing,



indicating that the deposition of MLSS in the interior of the membrane pore is the dominant fouling mechanism. The permeate flux of modified membrane is slightly better than that of unmodified membrane. Backpulsing is efficient and foulants seem to attach less on modified membrane. The TMP of modified membranes is lower than that of unmodified membrane. It means that at the same TMP, the difference of flux between modified and unmodified membranes would be increased. The higher flux enhancements and lower TMP obtained for the modified PVC membrane indicate that the membrane fouling is reduced further by an effective combination of backpulsing and surface modification.

ACKNOWLEDGMENTS

Dae Sik Kim and Jong Seok Kang are grateful to the Brain Korea 21 Program sponsored by the Korea Ministry of Education for a scholarship. This work is supported by the Korea Ministry of Science and Technology under the National Research Laboratory Program in the year 2001.

REFERENCES

1. Al-Malack, M.H.; Anderson, G.K. Coagulation-crossflow microfiltration of domestic wastewater. *J. Membr. Sci.* **1996**, *121*, 59–70.
2. Cabassud, C.; Laborie, S.; Laine, J.M. How slug flow can improve ultrafiltration flux in organic hollow fibres. *J. Membr. Sci.* **1997**, *128*, 93–101.
3. Nakanishi, K.; Kessler, H.G. Stability and rinsing behavior of deposited layers. *J. Food Sci.* **1985**, *50*, 1726.
4. Heran, M.; Elmaleh, S. Prediction of cross-flow microfiltration through an inorganic tubular membrane with high-frequency retrofiltration. *Chem. Eng. Sci.* **2001**, *56*, 3075–3082.
5. Ma, H.; Christopher, N.; Robert, H.; Davis, H. Membrane fouling reduction by backpulsing and surface modification. *J. Membr. Sci.* **2000**, *173*, 191–200.
6. Kuberkar, V.T.; Davis, R.H. Microfiltration of protein-cell mixtures with crossflushing or backflushing. *J. Membr. Sci.* **2001**, *183*, 1–14.
7. Kim, K.J.; Fane, A.G.; Fell, C.J.D. The performance of ultrafiltration membranes pretreated by polymers. *Desalination* **1988**, *70*, 229–249.



8. Stengaard, F.F. Characteristics and performance of new types of ultrafiltration membranes with chemically modified surfaces. *Desalination* **1988**, *70*, 207–224.
9. Kang, J.S.; Shim, J.K.; Huh, H.; Lee, Y.M. Colloidal adsorption of bovine serum albumin on porous polypropylene-g-poly(2-hydroxyethyl methacrylate) membrane. *Langmuir* **2001**, *17*, 4352–4359.
10. Shim, J.K.; Na, H.S.; Lee, Y.M. Surface modification of polypropylene membranes by γ -ray induced graft copolymerization and their solute permeation characteristics. *J. Membr. Sci.* **2001**, *190*, 215–226.
11. Yamagishi, H.; Crivello, J.V.; Belfort, G. Evaluation of photochemically modified poly(arylsulfone) ultrafiltration membranes. *J. Membr. Sci.* **1995**, *105*, 249–259.
12. James, E.; Pieracci, J.; Belfort, G. Photochemical modification of poly(ether sulfone) and sulfonated poly(sulfone) nanofiltration membranes for control of fouling by natural organic matter. *Desalination* **2000**, *132*, 133–142.
13. Pieracci, J.; Crivello, J.V.; Belfort, G. Photochemical modification of 10 kDa polyethersulfone ultrafiltration membranes for reduction of biofouling. *J. Membr. Sci.* **1999**, *156*, 223–240.
14. Taher, N.H.; Dessouki, A.M.; El-Arnaouty, M.B. Radiation initiated graft copolymerization of N-vinylpyrrolidone and acrylamide onto low density polyethylene films by individual and binary system. *Radiat. Phys. Chem.* **1998**, *45*, 437–444.
15. Kawai, T.; Lee, Y.M. Preparation of asymmetric porous membranes of poly(vinyl chloride). *Polymer* **1997**, *38*, 1631–1637.
16. Cheryan, M. *Ultrafiltration and Microfiltration Handbook*; Technomic Publishing Company, Inc.: Pennsylvania, U.S.A., 1998; 72.
17. Nabe, A.; Staude, E.; Belfort, G. Surface modification of polysulfone ultrafiltration membranes and fouling by BSA solutions. *J. Membr. Sci.* **1997**, *133*, 57–72.
18. Andrade, J.D. *Surface and Interfacial Aspects of Biomedical Polymers*; Plenum Press: New York, 1985; Vol. 1, 249.
19. Shim, J.K.; Lee, Y.B.; Lee, Y.M. pH-dependent permeation through polysulfone ultrafiltration membranes prepared by ultraviolet polymerization technique. *J. Appl. Polym. Sci.* **1999**, *74*, 75–82.
20. Yi, H.; Kim, J.H.; Hyung, H.; Lee, S.H.; Lee, C.H. Cleaner production option in a food (*Kimchi*) industry. *J. Cleaner Prod.* **2001**, *9*, 35–41.
21. Arnot, T.C.; Field, R.W.; Koltuniewicz, A.B. Cross-flow and dead-end microfiltration of oily-water emulsions; Part II. Mechanisms and modelling of flux decline. *J. Membr. Sci.* **2000**, *169*, 1–15.



22. Ma, H.; Luis, F.; Davis, H. Factors affecting membrane fouling reduction by surface modification and backpulsing. *J. Membr. Sci.* **2001**, *189*, 255–270.
23. Ma, H.; Nielsen, R.; Davis, H. Membrane surface modification and backpulsing for wastewater treatment. *Sep. Sci. Technol.* **2001**, *36*, 1553–1569.
24. Futamura, O.; Katho, M.; Takeuchi, K. Organic waste water treatment by activated sludge process using integrated type membrane separation. *Desalination* **1994**, *98*, 17–25.
25. Chang, I.S.; Bag, S.O.; Lee, C.H. Effects of membrane fouling on solute rejection during membrane filtration of activated sludge. *Process Biochem.* **2001**, *36*, 855–860.

Received February 2002

Revised July 2002