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## **The Influence of Membrane Surface Properties on Fouling in a Membrane Bioreactor for Wastewater Treatment**

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### **ABSTRACT**

Flat sheet submerged membranes coupled with a membrane bioreactor (MBR) have been run for 200 days to evaluate membrane performance during wastewater treatment. The chlorinated poly(vinylchloride) (CPVC) membranes prepared in this study have different characteristics such as the degree of hydrophobicity or hydrophilicity and different pore sizes. Poly(vinylpyrrolidinone) (PVP) was used as the pore-forming agent and to increase the wettability of the surface. A relatively hydrophilic membrane (CCP-2) showed the characteristics of high flux, low trans-membrane pressure (TMP), and low membrane filtration index (MFI) in

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comparison with a hydrophobic membrane (CP-2). The hydrophilic membrane (CCP-2) showed a better recovery efficiency in a pure-water flux than that of the others owing to the hydrophilized surface characteristics as well as large pore sizes. These results suggest that useful reduction in membrane fouling can be achieved by the control of pore size using PVP as well as induction of hydrophilicity on the membrane surface by chemical cross-linking. Consequently, it was considered from the results of water flux and removal efficiency that the introduction of hydrophilic polymer to membrane effectively improved final membrane performance. CCP-2 membrane (1.15  $\mu\text{m}$ , crosslinked by PVP) showed the best performance possible for use in actual MBR application.

*Key Words:* Membrane bioreactor (MBR); Chlorinated poly(vinyl-chloride) (CPVC); Membrane fouling; Activated sludge; Hydrophobic/hydrophilic membrane.

## INTRODUCTION

In recent years, new membrane separation techniques developed for use in wastewater treatment have promoted the development of the membrane bioreactor (MBR). Membrane filtration replaces the conventional sedimentation unit for separation of the treated water from the sludge and also serves as an advanced treatment unit for coliform bacteria and suspended solids (SS), which cannot be removed completely by conventional processes. The use of submerged membranes has significantly reduced the power consumption of MBRs and increased the potential for the application of membranes in wastewater treatment.<sup>[1,2]</sup> However, the development of MBRs has been limited by problems of membrane fouling during filtration of the activated sludge. Recent research on domestic wastewater treatment using MBR have focused on methods of controlling membrane fouling.<sup>[3,4]</sup> These include hydrodynamic cleaning, using a high cross-flow velocity, optimization of chemical or operational conditions, and modification of the membrane surface.<sup>[5,6]</sup> Membrane fouling is caused by blocking of membrane pores by cells, cell debris, organics, colloids, and particles on the membrane surface (external fouling) or as deposition and adsorption of small particles or macromolecules (internal fouling) within pores of the membrane.<sup>[7]</sup>

The flux decline observed during the microfiltration of wastewater results from an increase of resistance in the filtration system. This is related to the permeability of the gel layer or surface cake formed by colloidal or particulate material on the membrane surface and to the effective size of membrane pores



affected by the adsorption of dissolved material within the membrane pore structure.<sup>[8]</sup>

The important features of these membranes are the control of pore size and permeation performance. Membrane surface properties are also important because the interactions between the polymers and their environments occur chiefly at their surfaces. In general, filtration membranes having hydrophilic surfaces can reduce fouling.<sup>[9,10]</sup> The hydrophobic membranes are very susceptible to protein fouling by adsorption, giving rise to a fast flux decrease and an increasing demand for frequent cleaning cycles. Various methods of changing the membrane surface chemistry<sup>[11,12]</sup> that have the potential to reduce or eliminate adhesive fouling have been reported. In our previous studies,<sup>[13,14]</sup> microporous chlorinated poly(vinylchloride) (CPVC) membranes were prepared by water vapor induced phase inversion technique. We confirmed that the amount of poly(vinylpyrrolidinone) (PVP) and relative humidity (RH) plays a significant role in the control of surface pore size in membrane preparation.<sup>[13]</sup> However, as PVP could leach during the filtration process, the PVP was immobilized on the microporous CPVC membrane by a chemical cross-linking.<sup>[14]</sup> This reduced the depletion of PVP from the membrane and maintained the hydrophilicity.

The objective of the present study is to compare the performance of previously prepared CPVC membrane with or without PVP in actual MBR operation for up to 200 days.

## EXPERIMENTAL

### Membranes

A CPVC (Nippon Carbide Ind. Co. Inc., Tokyo, Japan) with a chlorine content of about 63–68% was used as the membrane-forming polymer. The preparation and characteristics of CPVC membranes and the use of PVP as an additive as well as the cross-linking material has been reported.<sup>[13,14]</sup> Cross-linking of the membrane (CCP-1, CCP-2) was carried out using potassium persulfate ( $K_2S_2O_8$ , Aldrich Chemical Co., Milwaukee, WI).<sup>[15]</sup> The CPVC/PVP (CP-1, CP-2) membrane prepared was saturated in potassium persulfate aqueous solution of 4000 ppm and then followed by a heat treatment at  $85^\circ\text{C} \pm 3^\circ\text{C}$  for 16 hr. In the oven, the membrane was dried while PVP was cross-linked. The characteristics of prepared membranes are shown in Table 1. As shown, the CCP-1 and CCP-2 membranes after the cross-linking treatment maintained a lower contact angle in comparison to the CP-0(CP-0\*), CP-1, and CP-2 membranes. Therefore, the CP-0(CP-0\*), CP-1, and CP-2 membranes



**Table 1.** Characteristics of membranes.

Sample code	R1			R2		
	CP-0	CP-1	CP-2	CP-0*	CCP-1	CCP-2
Contact angle <sup>a</sup>	110	89	70	110	80	63
Pore size (μm) <sup>b</sup>	0.6	0.8	1.2	0.6	0.77	1.15
Membrane module	Plate and frame type					
Effective filtration area	0.0609 m <sup>2</sup> (long × wide: 29 × 21 cm <sup>2</sup> )					

<sup>a</sup>Contact angle was measured by the sessile drop method and the average estimated error was  $\pm 8$  wt%.

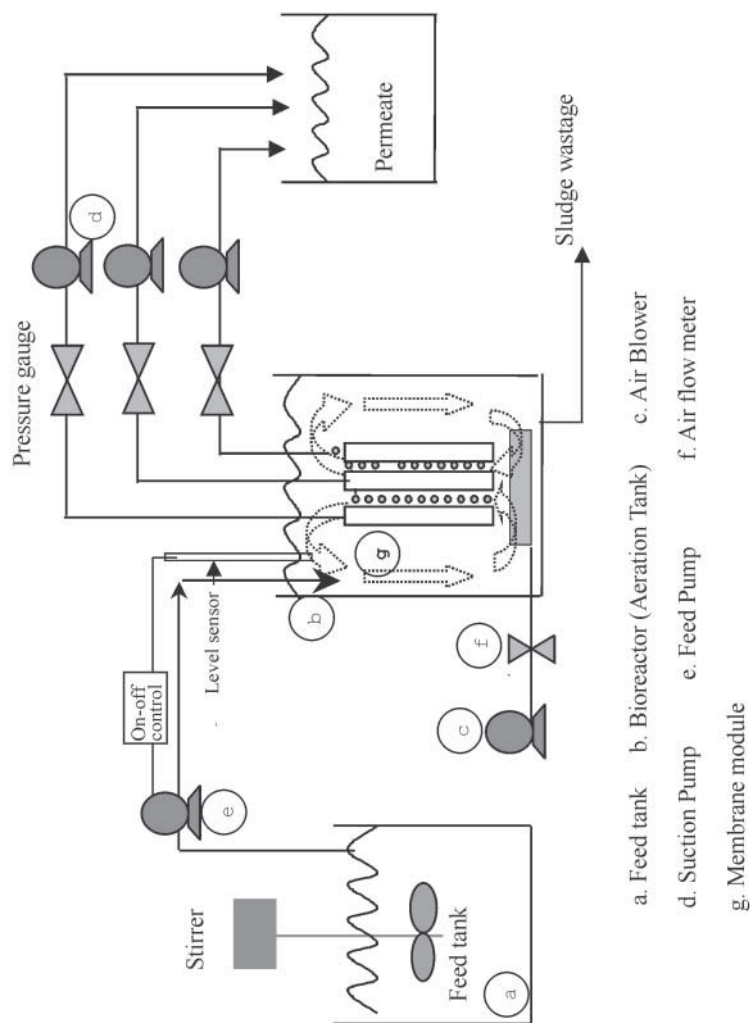
<sup>b</sup>Pore size were calculated by PMI Porometer (CFP-1200-AEC, USA). The CCP-1 and CCP-2 denoted membrane after cross-linking treatment.

were hydrophobic and the CCP-1 and CCP-2 membranes were relatively hydrophilic.

### Laboratory-Scale Membrane Bioreactor

Figure 1 shows the schematic diagram of the lab-scale MBR unit. The equipment consisted of a vessel (volume 70 L) in which three microfiltration membranes (named as CP-0, CP-1, CP-2 during R1, and CP-0\*, CCP-1, CCP-2 during R2) were immersed. Initially, the reactor was filled with activated sludge collected from the wastewater treatment plant in Seoul, Korea. Activated sludge was acclimated to the synthetic feed over 20 days prior to the experiments. Table 2 shows the composition of the synthetic wastewater. Table 3 shows the operating conditions of the bioreactor. To supply oxygen for the bioreactor and to minimize membrane fouling, the membrane module was aerated along the membrane surface. The airflow rate was maintained at 5–10 L/min, and dissolved oxygen (DO) levels between 0.5 and 3 mg O<sub>2</sub>/L were maintained in the bioreactor. The organic loading rate was 1.02–1.21 kg chemical oxygen demand (COD)/m<sup>3</sup> day. The hydraulic residence time (HRT) was 11.6 hr and the sludge retention time (SRT) was set at 35 days by sludge extraction after the solids concentration had developed sufficiently. Usually, filtrations are bringing to different modes such as under constant trans-membrane pressure (TMP) in dead-end filtration or constant feed flow rate in cross-flow filtration. However, the object of this study is not the investigation of optimal operation condition, but the mutual comparison of performance of membranes stated above. Therefore, the variation of flux and





**Figure 1.** Lab-scale flat and frame type submerged membrane bioreactor system.

**Table 2.** Composition of synthetic wastewater.

Glucose	672.5 mg/L	Glutamic acid	287.5 mg/L
CH <sub>3</sub> COONH <sub>4</sub>	220.2 g/L	NaHCO <sub>3</sub>	557.5 mg/L
NH <sub>4</sub> Cl	32.5 mg/L	KH <sub>2</sub> PO <sub>4</sub>	50.0 mg/L
K <sub>2</sub> HPO <sub>4</sub>	67.5 mg/L	MgSO <sub>4</sub> ·7H <sub>2</sub> O	27.5 mg/L
MnSO <sub>4</sub> ·H <sub>2</sub> O	7.5 mg/L	FeCl <sub>3</sub> ·6H <sub>2</sub> O	2.5 mg/L
CaCl <sub>2</sub> ·2H <sub>2</sub> O	12.5 mg/L	NaCl	20.0 mg/L

TMP was measured with time. Before start-up with synthetic wastewater, the TMP and flux of all the membranes were measured to obtain  $R_m$  using the tap water for 1 hr. After measuring  $R_m$ , the tap water flux of all membranes was set to 30 L/m<sup>2</sup> hr. The permeate of synthetic wastewater was extracted by a suction pump under intermittent operation in a 10-min cycle, 5 min on and 5 min off. The pressure gage was installed in order to monitor the variation of TMP between the membrane and suction pump. To maintain a constant level in the reactor, a peristaltic pump providing influent wastewater and a level sensor were used. Separated suction pumps were connected to each of the modules to observe the flux. The treated water was drawn through the membrane by a partial vacuum that was created inside the membrane module by a pump. To clean fouled membranes, the membrane was taken from the reactor. First, the membrane surface was flushed with water and cleaned with a sponge to remove the cake layer. After water cleaning, the pure-water flux was measured to find the flux recovery rate and to obtain the resistance  $R_m + R_f$ . The chemical cleaning was carried out using 1 wt% sodium hypochlorite solution and 1 wt% oxalic acid solution. The chemical cleaning method has been reported earlier.<sup>[2]</sup>

The MBR was run for 200 days, and the results were classified into two periods (R1 and R2) according to the different membrane conditions such as hydrophobic/hydrophilic and pore size. Cleaning cycle, R1, is divided into

**Table 3.** Average operating condition of the membrane bioreactor.

Substrate concentration (mg/L COD)	1200
MLSS (mg/L)	Avg. 3,000–4,500
Sludge viscosity (g/cm sec) <sup>[3]</sup>	1.4–1.7
F/M ratio (kg COD/kg MLSS d)	Avg. 0.2–0.4
SRT (sludge retention time: day)	35
DO (dissolved oxygen: mg/L)	0.5–3
Reactor volume (L)	70
Temperature (°C)	20–25
Suction–idle time (min)	5–5



period (A), (B), and (C). R2 is divided into period (D) and (E). The hydrophobic membranes having different pore size, named as CP-0, CP-1, and CP-2, were used during period R1. Hydrophobic (CP-0\*) and hydrophilic (CCP-1 and CCP-2) membranes were operated during R2. The membranes operated during period R1 were taken out from the reactor at day 108 and the new membranes (CP-0\*, CCP-1, and CCP-2) were immersed into the reactor.

### Analytical Methods

The MBR system was monitored daily, and measurements of pH, DO, temperature, SS, and sludge volume index (SVI) were recorded. The flux and TMP were also measured daily, after disconnecting the air flow. The analyses were performed according to American Water Works Association (AWWA) Standard Methods.<sup>[16]</sup> The COD was measured on a weekly basis in accordance with a US Environmental Protection Agency (EPA)-approved method utilizing a Hach Laboratory Method 8000 (DR/2010, Hach). A DO meter (Oximeter, Oxi 538, WTW, Fort Myers, FL, USA) measured the DO in the reactor.

### Resistance Analysis

The resistance-in-series model is applied to evaluate the filtration characteristics. According to this model, the permeate flux ( $J$ ) can be expressed as follows:

$$J = \frac{\Delta P}{\mu R_t}, \quad (R_t = R_m + R_c + R_f) \quad (1)$$

where  $\Delta P$  is the TMP,  $\mu$  is the viscosity of the permeate solution, and  $R_t$  is the total resistance ( $\text{m}^{-1}$ ).  $R_m$ ,  $R_c$ , and  $R_f$  represent the resistance of the membrane itself, the cake resistance, and the fouling resistance due to adsorption and pore plugging, respectively. The experimental procedure to obtain each resistance value was as follows:

- $R_m$  was obtained from the water flux measurement with pure water.
- $R_t$  was calculated from the flux of sludge filtration.
- $R_m + R_f$  was obtained from the pure-water flux after removing the cake layer.

The  $R_f$  was obtained from procedures (a) and (c), and  $R_c$  from procedures (b) and (c). The membrane filtration index (MFI) was obtained by line-fitting





of  $t/V$  vs.  $V$  with the result of colloidal filtration using the equation of dead-end filtration:<sup>[11,17,18]</sup>

$$\frac{t}{V} = \frac{\mu C_f \alpha}{2A_m^2 \Delta P} V + \frac{\mu R_m}{A_m \Delta P} \quad (2)$$

$$\frac{\mu C_f \alpha}{2A_m^2 \Delta P} = \text{MFI} \quad (3)$$

where  $\alpha$  and  $C_f$  are the specific resistance of the adsorbed protein layer and the concentration of bulk solution of feed, respectively.  $A_m$  is membrane area.

## RESULTS AND DISCUSSION

### Variation of Mixed Liquor Suspended Solids, Food-to-Mass Ratio, and Sludge Volume Index with Time

Figure 2 shows the variation of mixed liquor suspended solids (MLSS) and food-to-mass (F/M) ratio in a bioreactor as a function of time. The resulting concentration of MLSS in the reactor was 1100–5100 mg/L, and the corresponding F/M ratio was 0.2–0.9 kg COD/kg MLSS-day. Sludge was intermittently withdrawn from the reactor to maintain its concentration.

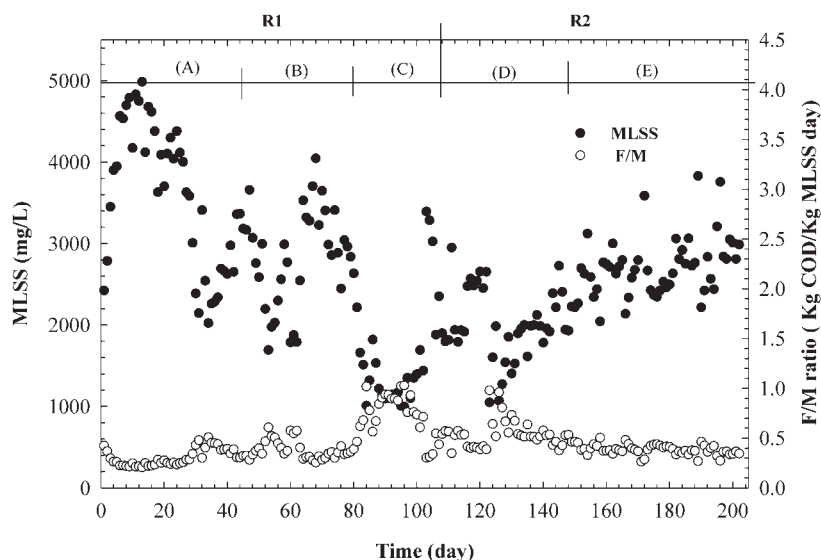


Figure 2. Variation of MLSS and F/M ratio with time.



The average values of the MLSS and the F/M ratio were 3000 mg/L and 0.32 kg COD/kg MLSS-day, respectively. The higher the concentration of microorganisms, the lower the F/M ratio becomes, with the effect that the microorganisms utilize a growing portion of the carbon content of the feed for maintenance purposes and consequently less for growth. As shown in Fig. 2, the MLSS increased rapidly at the beginning. As time went on, the sludge concentration decreased. Finally, the MLSS stabilized at about 3000 mg/L, after which a sludge-bulking episode occurred. In the activated sludge process, this is one of the most common problems caused by the growth of filamentous organisms. Filamentous bulking is one of the main factors leading to biomass loss in the effluent.<sup>[19]</sup> As a consequence of the sludge bulking, the sludge concentration fell to 1100 mg/L and the F/M ratio increased to 0.9 kg COD/kg MLSS-day. Figure 3 shows the SVI, which is a parameter of the sludge condition (its settleability). During the operation, the SVI was monitored to check the sludge characteristics. As shown in Fig. 3, at about the eightieth day from the start of operation, the SVI increased to 380 mL/g. At that time, the presence of filamentous organisms could be confirmed by microscopic observations. Figure 4 shows the filamentous bacteria observed in the bioreactor during sludge bulking. Characteristic long, thin, and flexible filaments, which were embedded in slime matrices, produced large amounts of

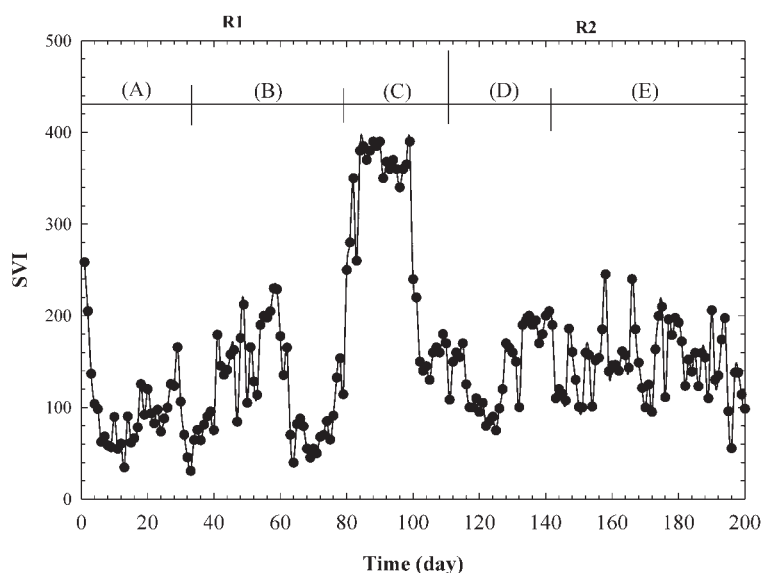
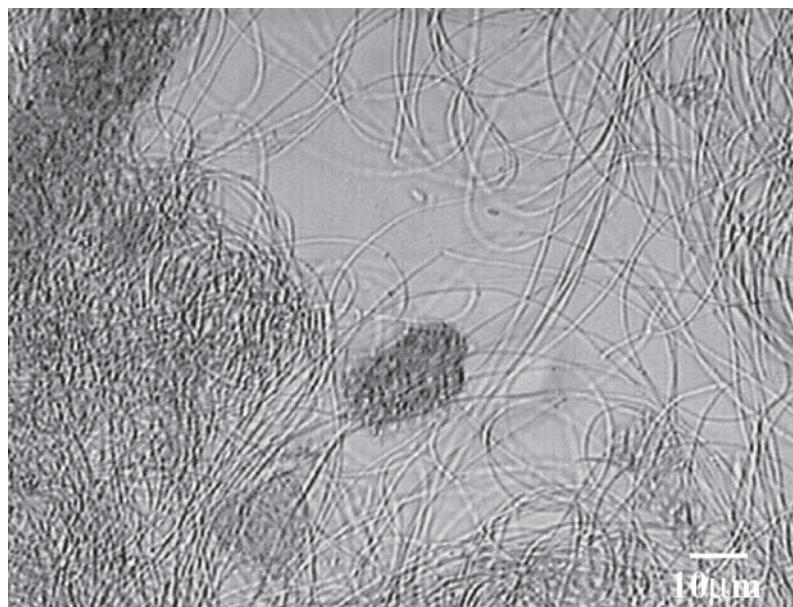


Figure 3. Variation of SVI with time.



**Figure 4.** The filamentous bacteria that were observed in period (C) (sludge bulking).

extracellular polymeric substances (EPS) and formed a typical aggregate.<sup>[20]</sup> Generally, it is considered that sludge bulking is no longer a problem in the MBR system because higher volumetric loading rates and smaller reactor volumes can be realized. It is possible that the absence of secondary clarification and pre-treatment are also helpful.<sup>[11]</sup> Although MBRs have been said to be a stable system regardless of sludge settleability, the abrupt change of sludge characteristics, characteristic of a bulking state, should be prevented in MBRs to maintain long-term stability of membrane filtration.<sup>[2]</sup> The ratio of sludge bulking and the type and the size of microorganism in an operating MBR accelerate membrane fouling and flux decline. It is concluded that the characteristics of membrane filtration depend on the internal environment of the MBR reactor and the growth factor of the sludge.

### Flux and Transmembrane Pressure Variation with Time and Flux Recovery

The variations of the flux and TMP during the operation are shown in Figs. 5 and 6. During period (A), immediately after start-up with wastewater,

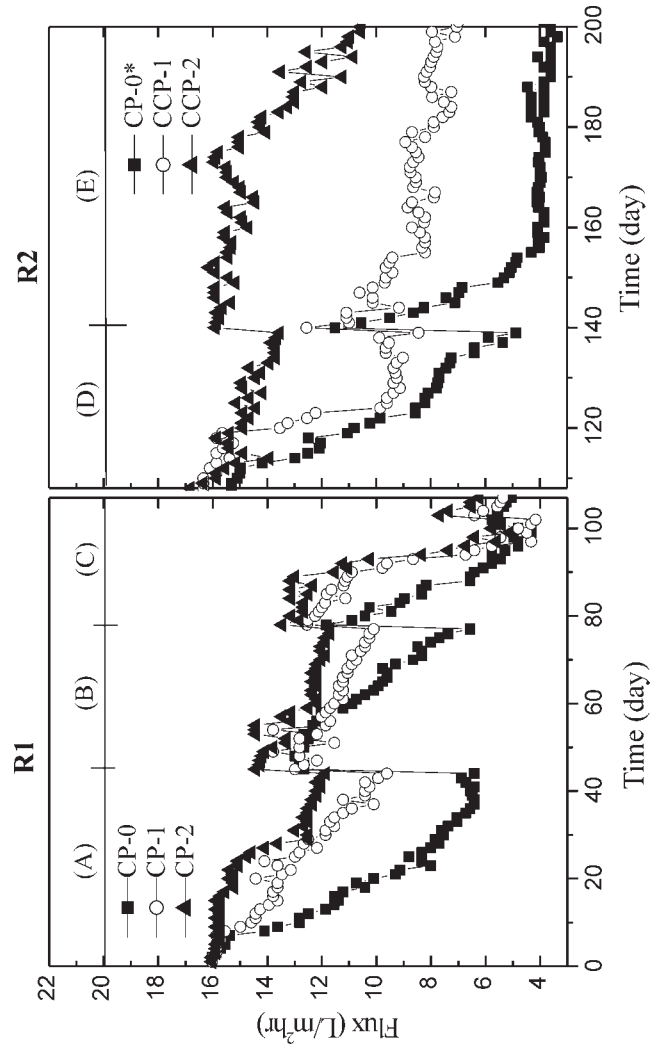


Figure 5. Variation of flux with time.

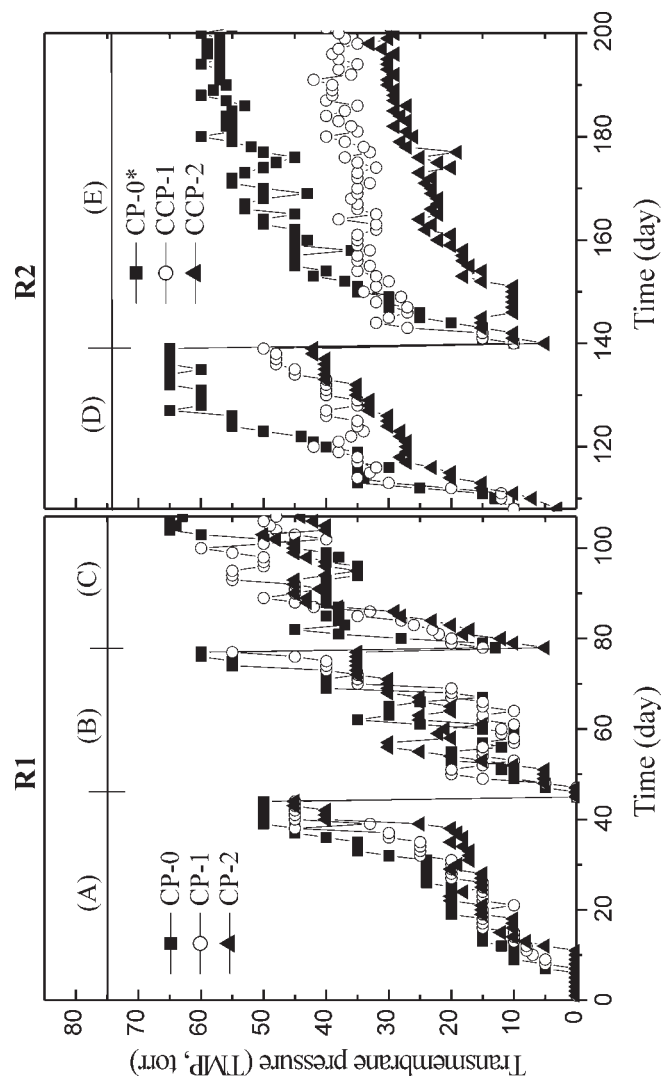


Figure 6. Variation of TMP with time.

the TMP increased and the flux decreased. As shown in Figs. 5 and 6, the highest flux and lowest TMP were obtained with CP-2 and CCP-2 during period R1 and period R2, respectively. The flux decline is due to the deposition of MLSS, such as slimy substances and lipids. These substances adhere very quickly to membrane surfaces. Therefore, the membrane resistance and TMP increased and the flux decreased. Concentration polarization and the fouling of membranes are inherent problems in a membrane process. The fouling substances were removed more easily when the membrane was washed. Therefore, an efficient cleaning technique is required. The formation of a thick gel layer was observed on the membrane surface on days 44 and 80. Therefore, sponging and washing with tap water was carried out and the pure-water fluxes were measured. The following equation describes the recovery of a pure-water flux:

$$\text{recovery of pure-water flux (\%)} = \frac{J_t}{J_i} \times 100 \quad (4)$$

where  $J_i$  and  $J_t$  refer to initial tap-water flux and water flux after cleaning, respectively. The flux recovery rate is shown in Table 4. During the R1, the range of flux recovery was 46.25–52.9% of its initial water flux in period (B) (on day 44) and 44.33–49% in period (C) (on day 80). The difference in flux recovery rate between CP-0 and CP-1 was 2.35% (=48.6% – 46.25%) and was 6.65% between the CP-0 and CP-2 membranes (=52.9% – 46.25%). The flux recovery rate of CP-0 and CP-2 on day 44 and day 80 was reduced from 46.25% to 44.33% and from 52.9% to 49%, respectively. This result implied that the solutes or fine colloids that were not easily cleaned by physical washing in bulk solution were deposited into membrane pores.

**Table 4.** Flux recovery rate after washing.

Sample code	Flux recovery rate (%)		
	R1		R2
	44 day	80 day	140 day
CP-0	46.25	44.33	
CP-1	48.6	46.8	
CP-2	52.9	49	
CP-0*			40
CCP-1			47.37
CCP-2			57.3



In addition, during the R2, when membranes were fouled in period (E) (on day 140), the membranes were cleaned. The difference of flux recovery rate between CCP-1 and CP-0\* membrane was 7.37% ( $=47.37\% - 40\%$ ) and between CP-0\* and CCP-2 was 17.3% ( $=57.3\% - 40\%$ ). The CCP-2 membrane showed better recovery efficiency in a pure-water flux than the others, owing to the membrane morphology such as hydrophilic surface characteristics as well as the large pore size and so on. Compared with the difference of flux recovery rate (6.65% between CP-0 and CP-2) on day 44, the higher difference of flux recovery rate (17.3% between CP-0\* and CCP-2) was obtained on day 140. Consequently, to obtain higher flux recovery rates, the induced hydrophilicity of the membrane surface is more effective than the large pore size. These results suggest that the solutes on the hydrophilic membrane were more easily washed because the adhesive interactions of the MLSS with the hydrophilic membrane surfaces were weaker than those with a hydrophobic surface.

The physiological changes in the activated sludge had a significant effect on the additional resistance to membrane filtration. The magnitude of flux decline increased in the order: normal activated sludge floc < pin-point activated sludge floc < bulking activated sludge floc.<sup>[20]</sup> A similar observation was made in this experiment, i.e., changes of TMP coincided well with changes in the condition of the activated sludge. The increase in the rate of TMP is an important factor in evaluating the system performance because it is directly related to the rate of membrane fouling.

When the operation was moved into period (C), a dramatic TMP rise and a flux decline were observed owing to sludge bulking. It was believed that the cause of the sludge bulking was a sudden high organic loading rate. The settleability of the sludge became considerably worse and resulted in a decrease in MLSS concentration. In fact, the sludge within the MBR can be in many physiological states during normal operation of the MBR process because the sludge is composed of living microorganisms. In this period (C), the performance was less stable than in period (A) or period (B). The characteristics of filamentous bacteria led to a tighter resistant layer forming on the surface of the membrane, resulting in a further flux decline.

It is known that the use of filtration membranes having hydrophilic surfaces can reduce fouling. The hydrophilic functional groups form hydrogen bonds with water, and the wetted surface prevents hydrophobic interactions between membrane and solutes. As shown in Figs. 5 and 6, although the environmental conditions for each period were different, it was considered from the results of water flux and removal efficiency that the introduction of hydrophilic polymer to membrane evidently improved final membrane performance.



### Membrane Fouling

Formation of surface cake is the major cause of fouling and flux reduction.<sup>[21]</sup> The variation of the total membrane resistance ( $R_t$ ) with time is shown in Fig. 7. The  $R_t$  of CP-2, having larger pore size than other membranes (CP-0, CP-1), is the lowest in period R1, and the  $R_t$  of hydrophilic membrane CCP-2 is the lowest in period R2. A gentle increase of  $R_t$  occurred with the hydrophilic membrane (CCP-1, CCP-2), but  $R_t$  of CP-0\* increased rapidly in period R2. In particular, the total resistance of all membranes increased suddenly during a period of sludge bulking [period C]. A measure of fouling tendency can be obtained by performing fouling tests. A flux decline can be measured as a function of time. The slope of the straight line obtained by plotting the cumulative volume ( $V$ ) vs. time/volume ( $t/V$ ) gives the MFI or specific resistance ( $\alpha$ ). The MFI is based on cake filtration occurring as a result of colloids adhering to the membrane. The higher the fouling potential of a given solution, the higher the MFI value will be.<sup>[19]</sup> Figure 8(a)–(c) shows a plot of  $V$  vs.  $t/V$  in periods (A), (C), and (E). The MFI was calculated from Eq. (2) in each period. Although the MFI was affected by various factors, it is possible to carry out a relative fouling potential comparison because  $v$ ,  $C_f$ , and  $A_m$  were constant in the same operating condition, while the only variables are  $\alpha$  and  $\Delta P$ . The TMP of CP-0 is higher than CP-2 in period (A). Therefore, the MFI of CP-0 will be lower than that of CP-2, according to Eq. (3). However, the MFI of CP-0 is higher than that of CP-2 [see Fig. 8(a)], which implies that the  $\alpha$  of CP-0 is higher than that of CP-2. This result was confirmed by the values of  $R_c$  of CP-0 and CP-2 in period (A), because  $\alpha$  can be used as an alternative to express the cake-layer resistance.<sup>[16]</sup> The MFI declined in the order CP-0 > CP-1 > CP-2 in periods (A) and (C), and in the order CP-0\* > CCP-1 > CCP-2 in period (E). This result implied that the fouling potential of the membranes had been reduced in the same proportion.

A set of resistances measured during filtration of activated sludge in each period is shown in Table 5. The cake resistance ( $R_c$ ) appeared to be the controlling resistance, whereas the fouling resistance ( $R_f$ ) was relatively small. The cake layers deposited over the CP-0(CP-0\*) membrane would be tighter than those of the CP-2 or CCP-2 membrane. The difference of  $R_c$  between CP-0\* and CCP-2 ( $300.76 = 438.76 - 138$ ) was higher than that between CP-0 and CP-2 ( $104.28 = 258.88 - 154.7$ ), owing to the hydrophilicity of the membrane surface.

Although the pore sizes of the membranes are in the range 0.6–1.2  $\mu\text{m}$ , the floc size of activated sludge particles ranged from 2 to 300  $\mu\text{m}$ .<sup>[20]</sup> Therefore, the cause of fouling resistance ( $R_f$ ) is not attributed to the floc itself but to the solute and fine colloids in bulk solution.<sup>[17]</sup> The value of  $R_f$  of the CP-0(CP-0\*) membrane also exhibited higher values than that of the CP-2 and





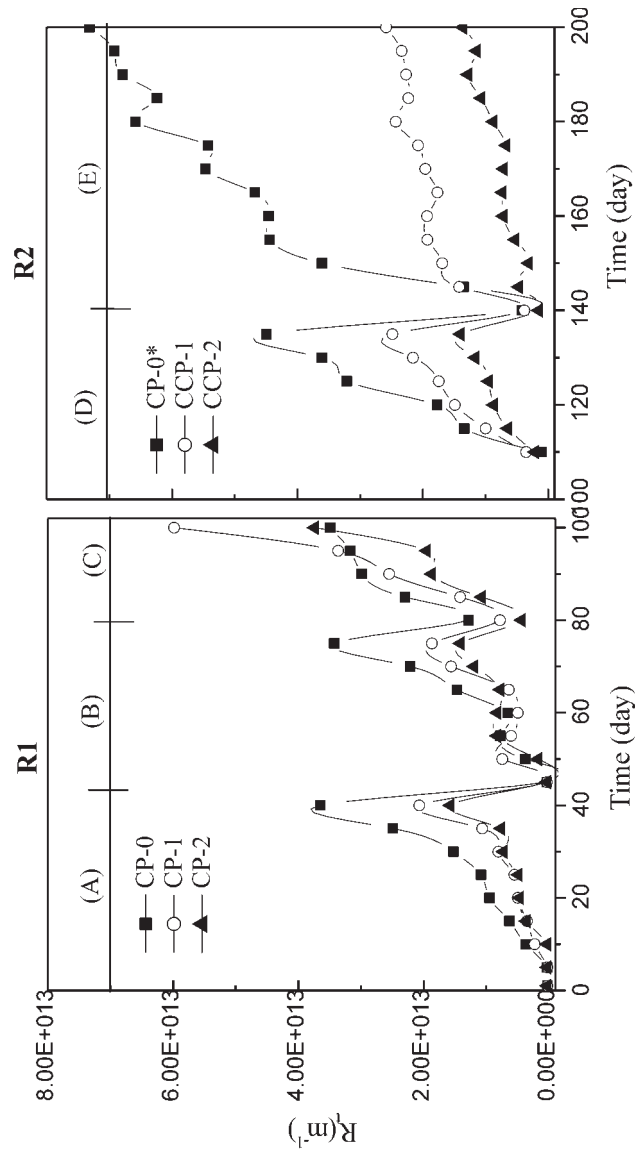


Figure 7. Variation of the total membrane resistance ( $R_t$ ) with time.

CCP-2 membranes. This indicates that the solutes were more easily adsorbed onto the surface and deposited into the pores of the CP-0(CP-0\*) membranes than those of CP-2 and CCP-2 membranes. Although the pore size of CP-0 is smaller than that of the others, deposition and adsorption of small particles or

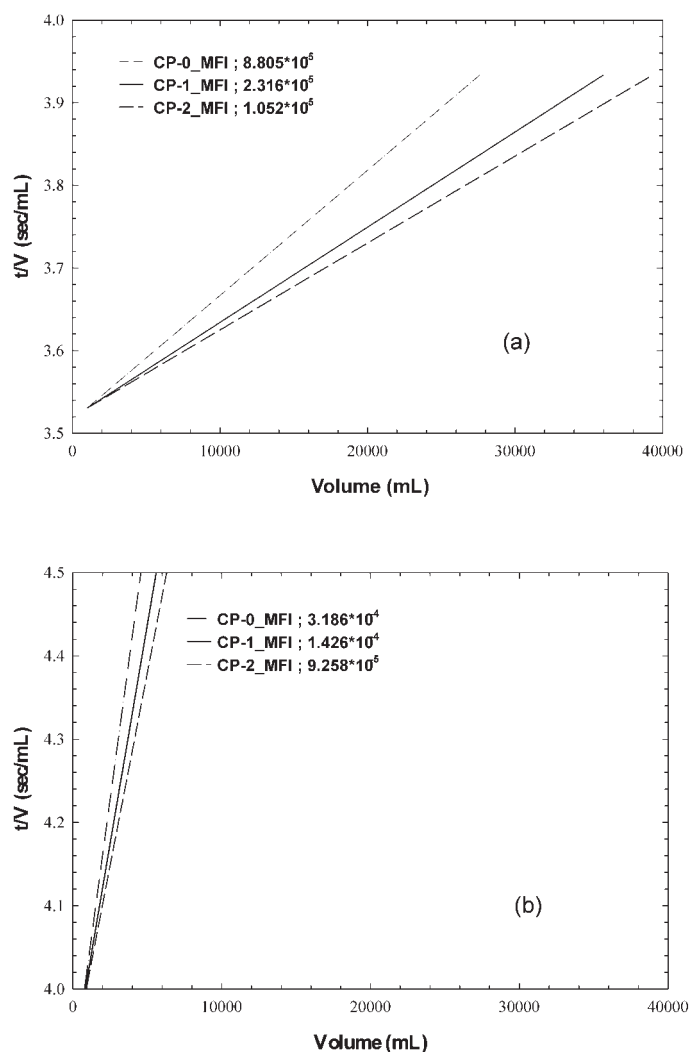


Figure 8. A plots of  $t/V$  vs.  $V$ : (a) period (A), (b) period (C), and (c) period (E).

(continued)



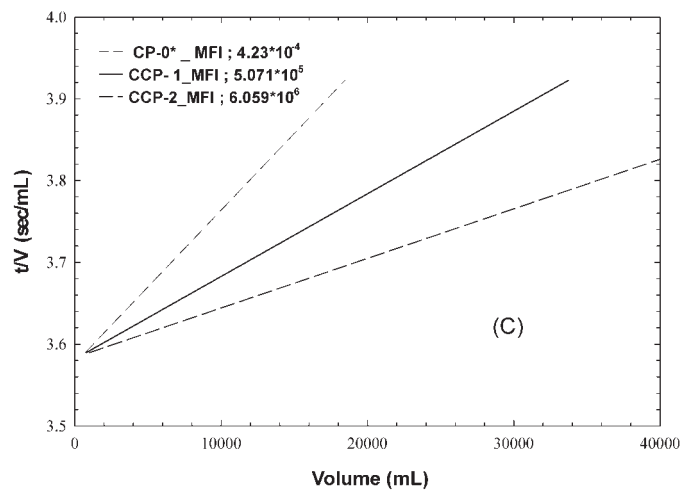


Figure 8. Continued.

solute within the pores of the CP-0 membrane are much greater (shown by the high TMP). The difference of  $R_f$  between CP-0\* and CCP-2 was higher than that between CP-0 and CP-2. This result implied that membrane fouling could be reduced further using the hydrophilic membrane.

### Water Quality of Effluent

Analysis on the feed and the effluent was carried out when the reactor operation was stabilized, so that the SRT and HRT were operated in a normal

Table 5. A series of resistance of the membranes.

Sample code	$R_t$	$R_m$	$R_c$	$R_f$
44 day ( $R \times 10^{11} \text{ m}^{-1}$ )				
CP-0	264.93	3.45	258.98	2.50
CP-1	207.14	2.68	202.80	1.66
CP-2	157.49	1.92	154.70	0.88
140 day ( $R \times 10^{11} \text{ m}^{-1}$ )				
CP-0*	455.13	3.45	438.76	2.92
CCP-1	248.49	2.30	244.64	1.55
CCP-2	140.03	1.53	138.00	0.50



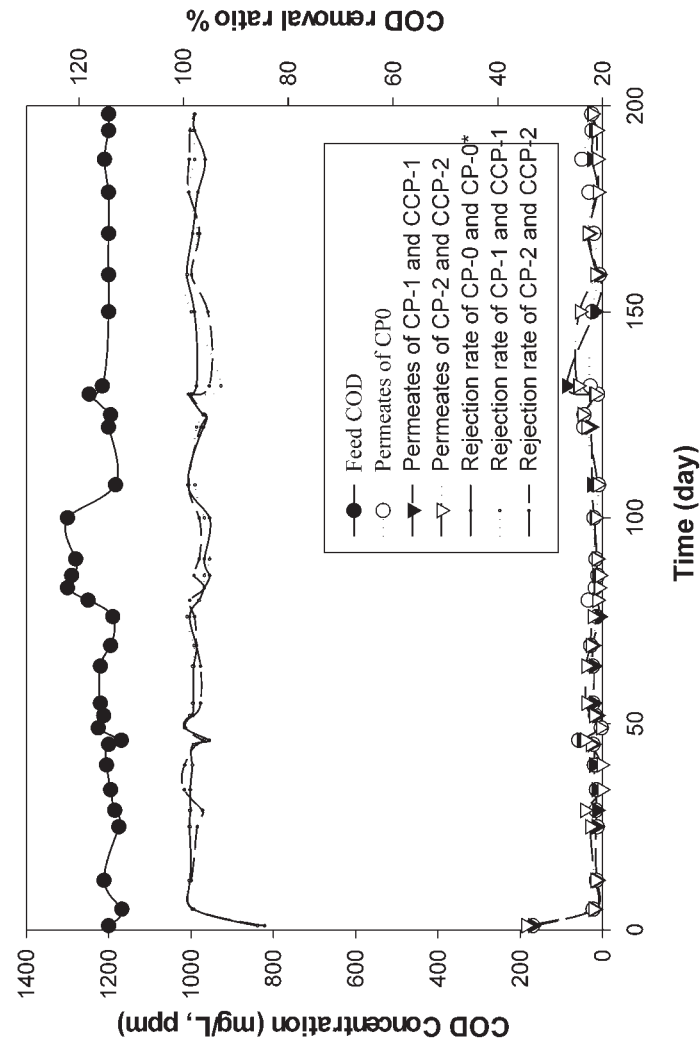


Figure 9. Variation of COD concentration of influent and effluent with time.

condition. The COD removal is shown in Fig. 9. The COD and MLSS removal rates of all the membrane systems over the operating period were about 97% and 99%, respectively. This result shows that the submerged MBR process is very effective in removing organic pollutants from wastewater.

## CONCLUSIONS

This study investigated the long-time MBR performance of hydrophobic or hydrophilic CPVC membranes prepared with or without PVP and simultaneously with or without chemical cross-linking. The TMP and  $R_t$  in period (C) (sludge bulking) were higher than those in periods (A) and (B), and the rate of decreasing flux was higher.

The highest flux and the lowest TMP were obtained with CP-2 and CCP-2 during period R1 and period R2, respectively. The pure-water flux of CCP-2 membrane showed better recovery efficiency than that of the others, owing to the hydrophilic surface characteristics and its large pore size. These results suggest that the adhesive interactions of the MLSS with the hydrophilic membrane surfaces are weaker than those with a hydrophobic surface. The cake resistance ( $R_c$ ) appeared to be a controlling resistance. The COD and MLSS removals of all the membranes over the operating period were more than 97% and 99%, respectively. Useful ways to reduce membrane fouling are the control of pore size using the co-polymer PVP, as well as induction of hydrophilicity on the membrane surface by chemical cross-linking. Consequently, it was considered from the results of water flux and removal efficiency that the introduction of hydrophilic polymer to membrane improved final membrane performance. CCP-2 membrane seems to be applicable in future long-time MBR operation.

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