

## Nanofiltration of Dye Solutions Through Polyamide Composite Membranes

Jonggeon Jegal<sup>†</sup>, Kyung-Sook Baek, and Kew-Ho Lee

Membrane and Separation Research Center, Korea Research Institute of Chemical Technology,  
Yusung, Daejeon 305-606, South Korea

(Received October 21, 2002, Accepted November 6, 2002)

**Abstract :** Nanofiltration of aqueous dye solutions was carried out using polyamide (PA) nanofiltration (NF) composite membranes. The PA composite membranes were prepared by the interfacial polymerization of piperazine (PIP) and trimesoyl chloride (TMC) on the surface of microporous polysulfone (PSf) ultrafiltration (UF) membranes. After characterization in terms of their permeation performance and surface ionic property, they were used for the separation of dye solutions such as Direct Red 75, 80, 81, and Direct Yellow 8 and 27. The separation conditions were varied to study the factors affecting on the permeation performance of the membranes: different concentrations of dye solutions, operating temperature and time, and flow rate of a feed solution. The surface property of the membrane, especially its ionic property, as a function of operating time was examined with a zeta-potentiometer and the relationship between the surface chemistry of the membrane and its permeation properties was also studied.

**Keywords :** nanofiltration, dye solution, polyamide, composite membrane, interfacial polymerization

### 1. Introduction

Nanofiltration (NF) process using a membrane has been attracting a considerable attention for the reuse of wastewater. One of the major applications of the NF process is the treatment of wastewater coming from textile dyeing industry for recycling hot water and salt [1-6]. With permeation characteristics of allowing monovalent ions to penetrate the membrane but rejecting multivalent ions, NF membranes seemed good to be used for this purpose, reuse of hot water and NaCl.

On this basis, polyamide (PA) composite NF membranes have been prepared in this study, using PIP and TMC as monomers, and microporous

polysulfone (PSf) ultrafiltration (UF) membranes as a support. Generally speaking, PA composite membranes have anionic surface due to the acyl chloride functional groups of the TMC remained unreacted and transformed into -COOH by their reaction with water [7-9]. They also have showed good permeation performances. Such characteristics of the PA NF membranes would be good for the separation of dye molecules from their water solutions, because the water-soluble dye molecules have anionic charges. The dyes used in this study such as Direct Red 75, 80, 81 and Direct Yellow 8, 27 all contained  $\text{SO}_4^{2-}$  ions in their structure.

Using the PA NF membranes and the dyes, the relationship between the characteristics of the membrane and the dye solutions was studied: Effects of molecular weight of the dyes, concentration of the dye

---

<sup>†</sup> 주저자(e-mail : jggegal@kRICT.re.kr)

solutions, operating time and temperatures. The variation of the ionic character of the membrane surface during the separation process was also studied, using a zeta-potentiometer.

## Experimental

### Materials

UOP polysulfone (PSf) ultrafiltration (UF) membranes with MWCO of about 30,000 g/mol were purchased from Fluid System (Sandiego, CA) and used as a support for the formation of polyamide (PA) composite membranes. Piperazine (PIP) and trimesoyl chloride (TMC) purchased from Tokyo Kasei Co. (Tokyo Japan) were used as monomers for the interfacial polymerization of PA composite membranes. Triethylamine (TEA) bought from Tokyo Kasei (Tokyo Japan) was used as a catalyst of the interfacial polymerization. Polyethyleneglycol (PEG) with molecular weight of 600 g/mole (PEG 600) bought from the Junsei Co. (Tokyo Japan) and Direct Red 75 (Mw 990.80 g/mol), 80 (Mw 1373.09 g/mol) and 81 (675.61 g/mol) and Direct Yellow 8 (Mw 518.55 g/mol) and 27 (Mw 650.62 g/mol) from Aldrich Co (Milwaukee, WI) were used as the solutes of feed solutions. Other chemicals were also used as purchased.

### Preparation of PA composite membranes

PA composite membranes were prepared by the conventional interfacial polymerization of PA active layers on the surface of microporous PSf supports. Right after coating the support with a 1.0 wt% PIP solution in water containing 1.0 wt% of TEA, the excess amount of the PIP solution remained on its surface was removed. The support was then immersed into a 0.05 wt% TMC solution in hexane for 10 seconds for the interfacial polymerization. After which it was dried in air at room temperature for 2 hr. The PA composite membranes prepared so were kept in

distilled water until its use.

### Permeation Test

Separation of dyes out of solutions was carried out using PA composite membranes prepared in this study. A typical NF test set-up was used and operating pressure was controlled from 100 to 400 psi using backpressure regulators. Flux and rejection of the dye solutions were determined by the conventional method using a following equation:

$$\text{Rejection (\%)} = 100 \times (C_f - C_p) / C_f$$

Where  $C_f$  and  $C_p$  are the concentrations of the feed solution and permeate, respectively, measured by using a UV-VIS spectrophotometer.

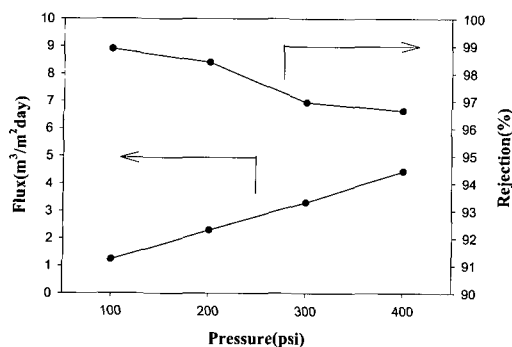
### Measurement of Zeta-potentials

The zeta-potentials of the surfaces of the membranes that were used for the separation of the dye solutions for a certain period of time were measured with an electrophoretic light scattering machine (Model: ELS-8000, Otsuka, Tokyo, Japan). In order to measure the zeta-potential of the membrane surfaces according to the conditions under which the membranes was used for the dye separation, membranes were retrieved from the separation cell, washed with distilled water lightly to remove any dust that can be detached from the surface and make problems during the measurement, and cut into three pieces. Each sample was then attached to the test cell and measured its surface zeta-potential.

## Results and Discussion

### Membrane Formation

It has widely been believed that a membrane with ionic charges on its surface is good for the separation of water-soluble organic materials, with less fouling problems. On this basis, for the separation of dye compounds from their solutions in water, polyamide



**Fig. 1.** Permeation properties of the polyamide composite membrane based on PIP and TMC as the 1000 ppm PEG 600 solution in water was used as a feed solution. Operating temperature was room temperature.

composite membranes based on PIP and TMC were prepared by the conventional interfacial polymerization, using UOP UF membranes with MWCO of about 30,000 g/mol as a support.

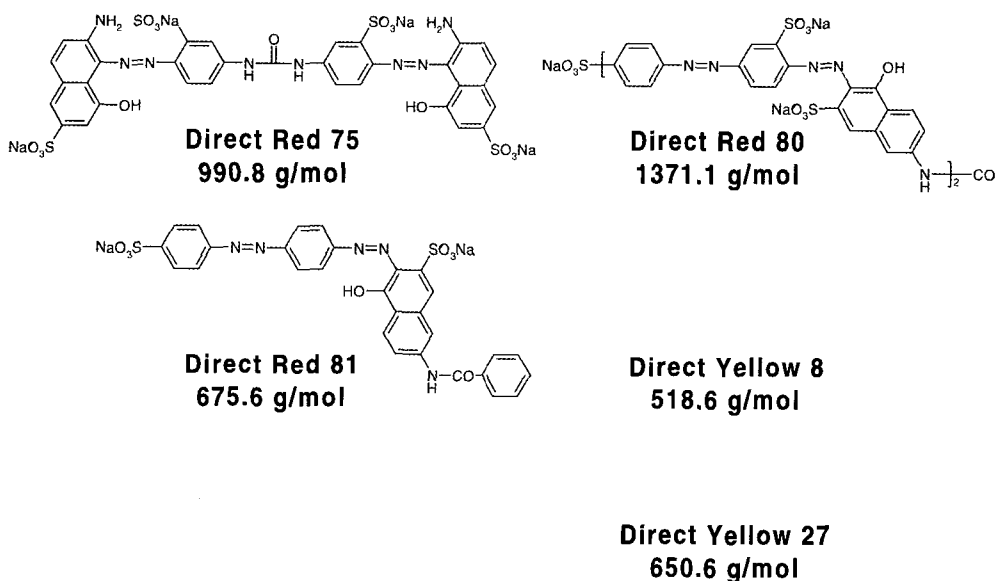
As expressed in the Experimental, the concentrations of PIP and TMC were 1.0 and 0.05 wt%,

respectively, and interfacial reaction time was 10 sec. The PA composite membranes prepared so showed a typical NF property, high rejection of di-valent ions such as  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  and low rejection of mono-valent ion such as  $\text{NaCl}$ , and high flux at a relatively low pressure as shown in Fig. 1. As a 1,000 ppm PEG 600 aqueous solution was used, the flux at 200 psi was about  $2.5 \text{ m}^3/\text{m}^2\text{day}$  with rejection of over 95%. The zeta-potential of the surface of the membrane, measured using a 0.1 mmol  $\text{NaCl}$  solution as an electrolyte, was about  $-35 \text{ mV}$ , reflecting its anionic character.

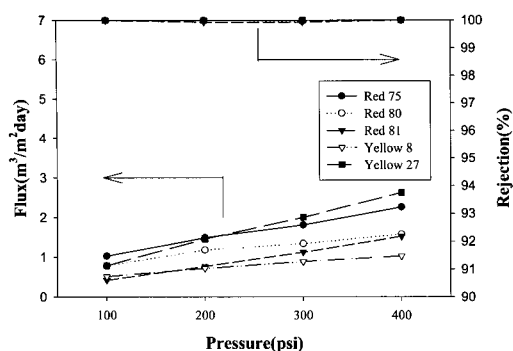
### Characteristics of the Dyes Used

To study the efficiency of the membrane separations of dyes, several direct dyes were used in this study. The chemical structures, molecular weights of the dyes (Direct Red 75, 80, 81 and Direct Yellow 8, 27) are as shown in Fig. 2. All of the dyes are composed of benzene and/or naphthalene rings connected by the

## Dye Compounds Used



**Fig. 2.** Chemical structures and molecular weights of the dye compounds used.



**Fig. 3.** The flux and rejection of the various dye solutions through the PA NF composite membrane. The concentration and temperature of the dye solutions were 1000 ppm and room temperature, respectively.

azo-linkages, and anionic groups are attached to the aromatic ring structures. Because of this anionic character, they were soluble in water. The molecular weights of those ranged from 516 to 1,373 g/mole.

#### Effect of Dye Species

Fig. 3 shows the flux and rejection of the 1,000-mg/L dye solutions through a PA composite

membrane. The rejection of all the dye solutions, regardless of the characteristics of the dyes, was about 100%, representing the high efficiency of the PA NF composite membranes for the separation of dye molecules from their solutions in water.

However, the fluxes appeared to be strongly dependent on the characteristics of the dyes: molecular weights, molecular shapes and zeta-potentials. The flux differences between different dyes were substantial. For example, at 400 psi, the flux of the Direct Yellow 8 solution was about only 30% of that of the Direct Yellow 27. The main reason for these large differences in flux is expected to be the membrane fouling by the dye molecules: the molecular weight, molecular shape (ratios between the length and width of the dye molecules), and zeta-potential representing the ionic characters of the dyes affected together on the membrane fouling. This speculation became obvious when considering the zeta-potentials of the membrane surfaces after certain period of time of membrane separation (Table 1).

The zeta-potential of the PA NF composite

**Table 1.** Zeta Potentials of the Surface of the PA Composite Membranes After Certain Periods of Time of Separation Processes with Different Dye Solutions. The Operating Pressure and Temperature Were 200 psi and Room Temperature, Respectively

Feed solution (1000 ppm)	Operating time (hrs)	Zeta-potentials (mV)
Membrane itself	0	-38.24
	2	-25.1
Direct Red 75	4	-18.6
	6	-12.4
	2	-24.8
Direct Red 80	4	-16.9
	6	-15.1
	2	-7.4
Direct Red 81	4	-7.0
	6	-4.5
	2	-20.68
Direct Yellow 8	4	-10.37
	6	-8.88
	2	-25.05
Direct Yellow 27	4	-18.89
	6	-17.73

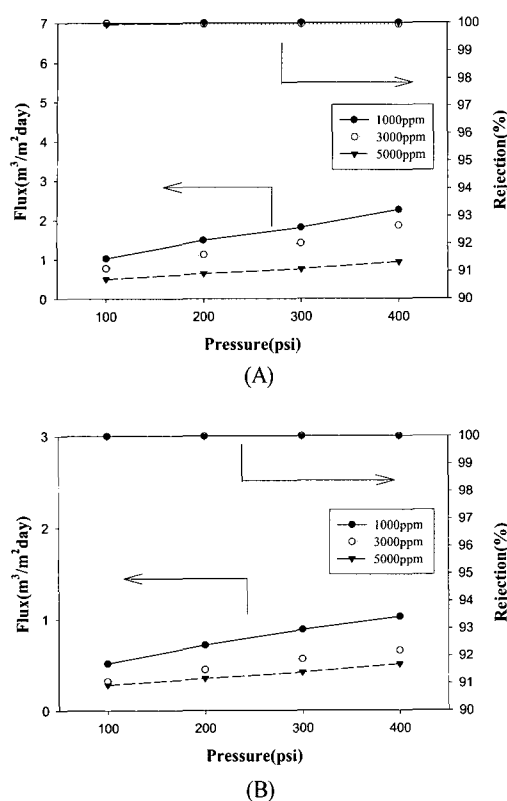


Fig. 4. Effect of the concentration of the dye solutions on the separation performances in the separation of (A) Direct Red 75 and (B) Direct Yellow 27. The concentration of the dye solutions was 1000 ppm.

decreased with increasing operation time, indicating the substantial membrane fouling. The dye layer accumulated on the membrane surface shielded the anionic groups presented on the surface of the membrane, and made it show smaller zeta-potentials. The order in the zeta-potentials obtained from different dye solutions was in the same way as the flux at 400 psi. The higher zeta-potential, the more flux was obtained. For example, as the Direct Yellow 27 was used, its flux was the highest and its zeta-potential was also highest, indicating less fouling.

Speaking about factors that could affect on the membrane fouling, it was not clear in this study, yet. The only possible explanation was the combined effect of the three major characters of the dyes: molecular

weight, molecular shape and ion content.

### Effect of Concentration

To study the effect of the concentration of dye solutions on the membrane separation performances using a PA NF composite membrane with MWCO of 500 g/mol, three different dye concentrations, 1000, 3000, and 5000 ppm, were used. Fig. 4 shows the permeation properties when Direct Red 75 and Direct Yellow 27 were used. For both dyes, for all the concentrations, the rejection was almost 100%, regardless of the different operating pressures. The flux, however, decreased with the increasing concentration. When the concentration reached 5,000 ppm, the flux became almost less than half of that of the 1,000 ppm dye solution. The solution diffusion model can explain such decrease in flux with the concentration of feed solution. According to the following equation, the flux of solvent decreases with increasing concentration by increasing the osmotic pressure and solution viscosity.

$$J_B = -C_{Bm} D_{Bm} \nu_B (\Delta p - \Delta \pi) / RT \delta$$

Where,  $J_B$  is solvent flux,  $C_{Bm}$  concentration of solvent in the membrane,  $D_{Bm}$  diffusion coefficient of solvent in the membrane,  $\nu_B$  viscosity of solvent,  $R$  gas constant,  $T$  Temperature,  $\delta$  membrane thickness,  $\Delta p$  pressure difference between both sides of the membrane,  $\Delta \pi$  osmotic pressure difference between both sides of the membrane.

Another possible reason for the decrease in flux was a membrane fouling. The slow slope of the flux curve as a function of operating pressure confirms the membrane fouling. With increasing concentration, the slope became slower, hinting more fouling by the dye molecules. The membrane fouling may be caused by the combined effect of the increased viscosity and the concentration polarization near the membrane surface. With increasing concentration, it is natural to increase the solution viscosity, and the increased viscosity hinders the diffusion of the dye molecules in the

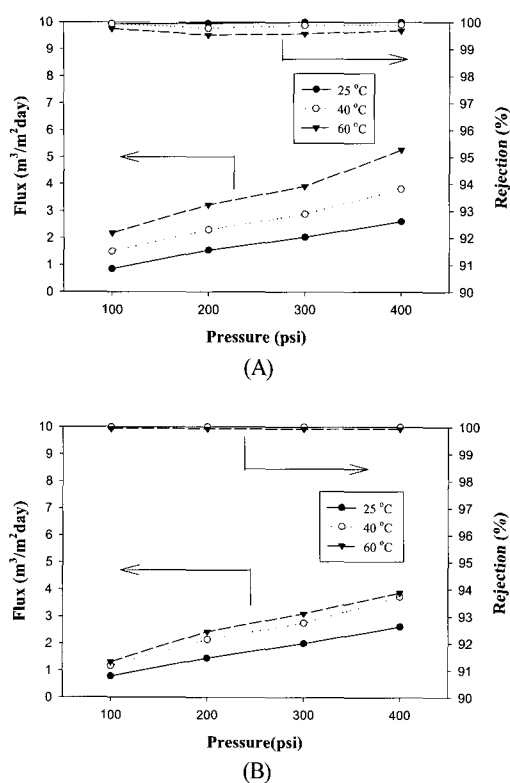


Fig. 5. Effect of the operating temperature on the separation performances in the separation of (A) Direct Red 75 and (B) Direct Yellow 27. The concentration of the dye solutions was 1000 ppm.

solution. So, the back-diffusion of the dye molecules rejected by the membrane near the membrane surface into the solution bulk became more sluggish as the concentration increased, causing substantial accumulation of the dye molecules near the membrane surface and resulting in the membrane fouling such as the cake formation. Such serious concentration polarization effect would be the major reason for the decrease of the flux of the dye solutions.

#### Effect of Operating Temperature

Operating temperature is one of the factors influencing on the membrane separation efficiency. According to the Solution-Diffusion Model, the flux increases with temperature, but the rejection of solute is independent. The flux of solvent is determined by

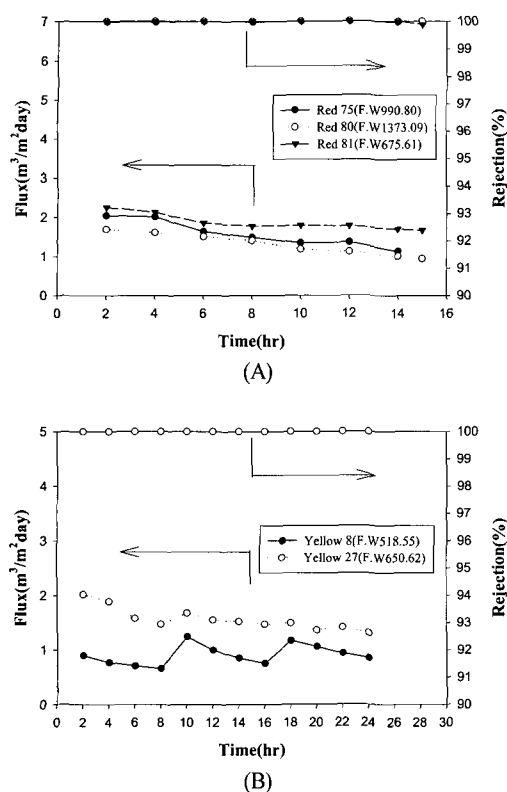
the diffusion coefficient of solvent, increasing with temperature, but the flux of the solute is mainly affected by the concentration difference between the both sides of a membrane (feed and permeate sides). So, according to the Solution-Diffusion theory, with increasing temperature, the flux and rejection both increase.

The separation performances of the dye solutions (for example, Direct Red 75 and Direct Yellow 27) through the PA NF composite membranes prepared are as shown in Fig. 5. For both solutions, the flux increased with increasing temperature, as expected, by the decrease in the solution viscosity and increase in the diffusivity of solution. But the rejection of the dyes did not show a clear dependence on the temperature. The rejection of Direct Yellow 27 was almost 100% for all the temperature used, while the rejection of the Direct Red 75 solution decreased slightly with temperature. This slight decrease in the rejection does not fit well into the Solution-Diffusion model, suggesting that there are some pores in the surface of the PA NF membranes used.

The slope of the flux line as a function of the operating pressure was found to increase with temperature. Without fouling, the flux line should be linear with a certain slope, passing zero flux point when the pressure is zero. But for all the separation process in this study, the slope of the curve was too slow to pass the zero flux point, having certain flux value, as the flux line was extrapolated into zero pressure, indicating that substantial amount of fouling is involved in the separation process. As the temperature increased, the slope increased, indicating less fouling, and this is because the back diffusion of the solutes in high concentration near the membrane into the bulk solution was improved by the increase in temperature.

#### Effect of Operating Time

With increasing operating time, it is general that the permeation performance of a membrane decreases



**Fig. 6.** Effect of operating time on the permeation characteristics of the dye solutions, (A) Red dyes and (B) Yellow dyes, through the PA composite membranes. The concentration of the dye solutions was 1000 ppm, and the operating pressure was 200 psi at room temperature.

gradually. Especially flux is more sensitive to the operating time. The reason for such decrease in permeation performance is known related to the fouling of the membrane. In the membrane separation process, because of the concentration polarization phenomenon induced by the selective permeation of solvent through the membrane, membrane fouling is inevitable. In this study, decrease in flux with operating time was also observed. Fig. 6 shows the behavior of the permeation characteristics of the membranes as a function of the operating time.

With increasing time, flux decreased depending on the characteristics of the dye solutions used, while the rejection of them remained constant at almost 100%.

For most of all the dye solutions, the flux decreased gradually, but the solution of yellow 8 showed different behavior. The yellow 8 solution showed a flux pattern reflecting the operating condition: For this study on the effect of the operating time, the separation process has been continued for 8 hours at 150 psi, and then stopped the operation and left the membrane at atmospheric pressure in the dye solution for another 8 hours, and then start the separation process again for 8 hours under the same condition until the total operation time reached 24 hours. When a yellow 8 solution was used, simple stopping the operation and leaving it in the solution recovered flux decreased.

This kind of permeation properties appeared to be related with the behaviors of the fouling layer accumulated on the membranes surface as shown in Fig. 7. For other solutions, the morphology of the fouling layer did not seem to depend on the operation time, but the yellow 8 solution showed an interesting result. In the beginning stage up to 4 hours of operation, the fouling layer was very thick, compared to other cases using other solutions, and the thick layer became very thin for the further operating time as shown after 6 hours of operation. The decrease in the thickness of the fouling layer might be due to the densification of the layer by the applied operating pressure, decreasing the flux further.

However, by leaving the membrane in the solution under atmospheric pressure, the thin fouling layer became thick by the swelling of the layer with water, which will be soft enough to be removed by the shear forces from the feed solution with the resume of the separation process. Such swelling and removing of the fouling layer by the feed solution always recovered the original flux as shown in Fig. 6.

## Conclusions

Polyamide composite NF membranes are good for the separation of dye solution and possible to be used

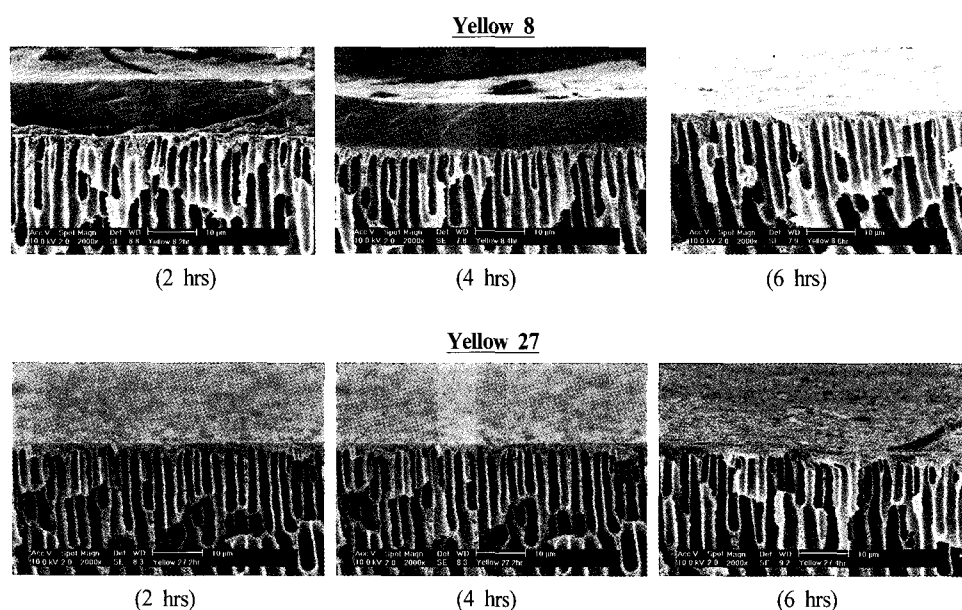


Fig. 7. Behaviors of the fouling layer accumulated on the surface of the PA composite membranes as a function of operating time.

for the reclamation of dye wastewater. The membrane with a MWCO of 500 g/mol is good enough to separate the common direct dyes. The operation conditions such as concentration and temperature of feed solutions, operating time before cleaning should be optimized for the successful application of the NF membranes to the wastewater in dyeing industries. Low concentration and high temperature of the feed of solution guarantee the better permeation performance of the NF membranes. However, the characteristics of the dye molecules such as the molecular weight, shape and ionic state also affect on the permeation.

## References

1. A. Rozzi, M. Antonelli, and M. Arcari, *Wat. Sci. Tech.*, **40**, No. 4-5, 409 (1999).
2. J. Sojika-Ledakowicz, T. Koprowski, W. Machnowski, and H. H. Knudsen, *Desalination*, **119**, 1 (1998).
3. G. Chen, X. Chai, P. Lock, and Y. Mi, *Journal of Membrane Science*, **127**, 93 (1997).
4. A. D. Dhale and V. V. Mahajani, *Waste Management*, **20**, 85 (2000).
5. H. Wenzel, H. H. Knudsen, G. H. Kristensen, and J. Hansen, *Desalination*, **106**, 195 (1996).
6. R. Jiraratananon, A. Sungpet, and P. Luangsowan, *Desalination*, **130**, 177 (2000).
7. J. Jegal, N.-W. Oh, and K.-H. Lee, *J. Appl. Polym. Sci.*, **77**, 347 (2000).
8. J. Jegal, N.-W. Oh, D.-S. Park, and K.-H. Lee, *J. Appl. Polym. Sci.*, **79**, 2471 (2001).
9. N.-W. Oh, J. Jegal, and K.-H. Lee, *J. Appl. Polym. Sci.*, **80**, 2729 (2001).