

Preparation and Characterization of Polyamide Nanofiltration Composite Membranes with TiO₂ Layers Chemically Connected to the Membrane Surface

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Received 15 March 2006; accepted 19 July 2006

DOI 10.1002/app.25767

Published online 19 April 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A polyamide (PA) nanofiltration (NF) composite membrane with TiO₂ layers was designed and prepared, in which the TiO₂ layers were chemically linked to the crosslinked polyamide layers of the membrane. In this study, TiO₂, one of the well known photo-catalysts effectively degrading organics with UV light, was introduced to the PA NF membrane by using 3-aminopropyltrimethoxysilane (APTMS), titanium (IV) isopropoxide (TIP) to improve its antifouling property. In particular, for this membrane, SiO₂ layers were formed between the TiO₂ layer and the crosslinked polyamide layer of the membrane to protect the organic parts of the membrane from the TiO₂ catalyzed UV degradation. The prepared membrane with TiO₂ layers was then characterized using sev-

eral analytical methods: scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and permeation tests. It was found that the prepared membrane was stable; especially the TiO₂ layer of the membrane was found to be stable after several times of use for permeation test. The membrane showed a typical NF property, despite of the presence of the TiO₂ layer. From long time tests with or without UV light, it was found that there was good antifouling effect on the membrane by the TiO₂ layer. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1267–1274, 2007

Key words: polyamide nanofiltration membrane; photocatalyst; titanium; antifouling; membrane fouling

INTRODUCTION

With growing concern about environment, membrane technology has been attracting a great deal of attention as one of the technologies most often used, especially for the wastewater treatment and pure water production. However, one of the problems that one cannot be avoided is membrane fouling by the contaminants in the feed water during the separation process.^{1–5} The materials contained in the feed water adhere to the surface of the membrane, the amount of the materials accumulating on it growing with help of the selective permeation of water through the membrane. Especially, organic materials that are sometimes sticky are the most notorious foulants, which would eventually block the pores of the membranes completely, bringing the membrane to its failure.

To solve such problems, many different ways have been tried so far and some of them were successful; in particular, cleaning with chemical cleaners was successful.^{6,7} However there is still a requirement to improve the antifouling properties of the membrane and to come up with a better way to treat the foulants accumulated on the membrane surface. There was a report about antifouling study with a membrane with TiO₂ layers on its surface.⁸ They claimed that the TiO₂ was good to protect the membrane from the biofouling by *E. coli*. They found good antifouling effect of TiO₂, but they neglected the fact the membrane they used was made of organic polymers so that it could be degraded by the TiO₂ by the same degradation mechanism. They just attached TiO₂ nanoparticles to the conventional polyamide nanofiltration (PA NF) membrane by the self-assembly process.

With the fact that TiO₂ is good to give membrane effective antifouling properties and that the membrane should have a layer to prevent photodegradation, a new PA NF membrane with TiO₂ layers was designed and prepared. The features of the membrane prepared in this study were as follows: The TiO₂ layers were connected to the crosslinked PA layer of the membrane through the formation of the

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Contract grant sponsor: Center for Nanostructured Materials Technology (under 21st Century Frontier R&D Programs of the Ministry of Science and Technology, Korea); contract grant number: 05K1501-01,210.

Journal of Applied Polymer Science, Vol. 105, 1267–1274 (2007)
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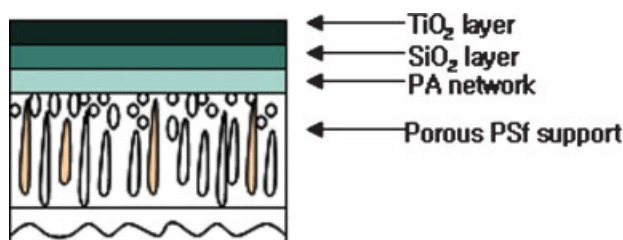


Figure 1 Schematic draw of the PA NF composite membrane with a TiO₂ layer on its surface. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

SiO₂-TiO₂ hybrid layers as shown in Figure 1, in which the SiO₂ layers were directly connected to the PA layer by the formation of amide linkage. The prepared membranes were then characterized using various analytical instruments such as field emission scanning electron microscope (FESEM), XRD, XPS, and others. The antifouling properties of the membranes were also studied. The details of this study are elaborated as follows.

EXPERIMENTAL

Materials

Polysulfone (PSf) ultrafiltration (UF) membranes with MWCO of about 30,000 g/mol, purchased from the Fluid System Co., were used as a microporous support. Monomers used for the formation of PA active layers were piperazine (PIP), and trimesoyl chloride (TMC) from Aldrich Company. ATMOS and TIP from Sigma-Aldrich and P25 TiO₂ from Degussa were used for the formation of TiO₂ layers and SiO₂ layers on the PA composite membrane surfaces. Other chemicals used in this experiment were used without further purification.

Preparation of PA composite membranes with TiO₂ layers

PA composite membranes with TiO₂ layers were prepared by the conventional interfacial polymerization of PA active layers on microporous PSf supports, followed by the sequential treatment with ATMOS, TIP and TiO₂ particles. The typical process used in this study was as below: A PSf support whose surface was cleansed with a dilute sulfuric acid solution in water (0.01M) was dipped for about 1 min into a 1.0 wt % PIP solution in water, in which 1.0 wt % of triethyl amine (TEA) was also dissolved as a catalyst, shaking sometimes. The surface of the support was then rolled with a rubber roller to remove the excess amount of the PIP solution remained on it and immersed into a 0.05 wt % TMC solution in hexane for 5 s for the interfacial polymerization of PA active layers on the PSf support. After which, it was kept in a hexane solution containing

0.1 wt % 3-aminopropyltrimethoxysilane (APTMS) for 30 min and then again in 1.0 wt % TIP solution in hexane for another 10 min. It was then immersed in the isopropanol solution that contained 10 wt % of distilled water and 1.0 wt % TiO₂ particles dispersed in the solution. The membrane prepared so was then dried in air at room temperature for 2 h and kept in distilled water before its use. The unreacted TiO₂ particles, just accumulated on the membrane surface, were removed by washing the membrane in distilled water for several times.

Characterization

The surface and cross section morphology of the PA composite membranes were studied with a field emission scanning microscope (FESEM) (Model: XL 30, Philips, USA). X-ray diffractometry (XRD) (Model: D/MAX IIIB Rigaku X-ray diffractometer) and X-ray photoelectron spectroscopy (XPS) (Model: ESCALAB MK-II, VG Scientific, England) were also used to characterize the TiO₂ layers of the membrane surfaces.

Permeation tests

The PA composite membranes were tested with various feed solutions such as 1000-ppm aqueous solutions of PEG 600, NaCl and Na₂SO₄ to determine their permeation performances, using a general RO test set-up. Using backpressure regulators controlled the operating pressure, ranging from 100 to 400 psi. Other test conditions were as same as in the previous report. Flux was measured by weighing the permeate penetrated through the membrane per unit time and a solute rejection was calculated from the concentrations of the feed solution and permeate using the following equation:

$$\text{Rejection} = 100 \frac{C_f - C_p}{C_f}$$

where C_f and C_p are the concentrations of the feed solution and permeate, respectively. C_f and C_p were measured using a high performance liquid chromatography (HPLC) (model Waters 501) that attached with a differential refractometer R401 as a detector.

Tests for antifouling property of TiO₂ layers

To test the antifouling performance of TiO₂ layers positioned on the membrane surface, UV light was used. For this experiment, a medium pressure mercury arc lamp was used to irradiate UV light on the membrane surface for the membrane cleaning. While operating the membrane, with 1000 ppm aqueous solution of PEG 600 as a feed solution, after 3 h of operation, it was stopped, and the membrane was

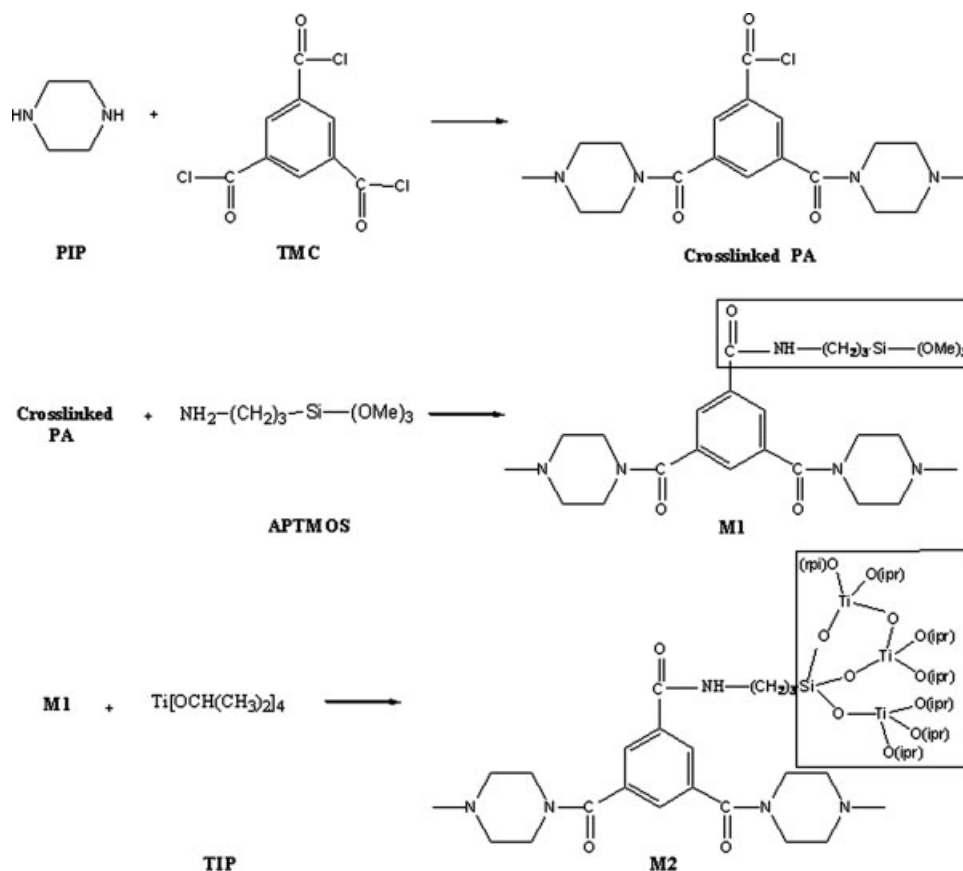


Figure 2 Reaction mechanism involved in the formation the PA NF composite membrane with TiO₂ and SiO₂ layers, where ipr is $-\text{OCH}(\text{CH}_3)_2$.

removed from the test cell and rinsed with just distilled water three times, without any physical treatment to clean the membrane surface, and with or without UV irradiation for 1 min. After cleaning, the membrane was relocated on the cell and operation was resumed again for another 3 h. This process was repeated five times, measuring the flux and rejection of the solute.

RESULTS AND DISCUSSION

Membrane preparation

The structural features of the PA NF composite membrane with a TiO₂ layer prepared in this study are such that the TiO₂ layer is connected to the membrane by the chemical bond formation, and that the SiO₂ layer, which is expected to work as a protecting layer of the membrane from the TiO₂ catalyzed UV degradation, presents between the TiO₂ layer and the crosslinked PA layer of the membrane as shown in Figure 1. TiO₂ is one of the hydrophilic photo-catalysts most often used for the photo-degradation of organics. TiO₂ has an excellent property of degrading organics with UV light irradiation. Because of its organics degrading property, people

in environmental field have often used it for their purpose of wastewater treatment and so on.^{9–11} The reason for us to use TiO₂ in this experiment was both its good organics degrading performance and its good hydrophilicity, to develop a functional PA NF composite membrane with a good antifouling performance.

For most of the membrane process for wastewater treatment, fouling occurs at the surface of the membrane by the concentration polarization effect caused by the selective permeation of water through the membrane. However, the easiness of the membrane fouling depends on several chemical, physical features of the membrane. For instance, a membrane with hydrophobic surface is easier to be contaminated by the materials in the wastewater by the hydrophobic–hydrophobic interaction than a membrane with hydrophilic surface. Also, when a membrane has rougher surface, it's easier for the foulants to be accumulated on the surface of the membrane. Considering these factors for the membrane fouling, it can be suggested that a membrane with a hydrophilic and smooth surface has better antifouling performance. In addition to that, when the membrane has functionality to easily remove the foulants from the membrane surface, it will be better.

So, TiO_2 was used in this study to form a PA NF membrane with good antifouling performance, and that is expected to be easy to remove the accumulated foulants by the TiO_2 catalyzed UV degradation. In the coating process of TiO_2 on the PA NF membrane surface, TiO_2 was chemically connected to the membrane by the reaction mechanism as shown in Figure 2 to improve the stability of the TiO_2 layer. Another structural feature of the prepared membrane, SiO_2 layer was also formed by the reaction mechanism of Figure 2 to protect the organic parts of the membrane from the UV degradation.

Expecting that the TiO_2 layer of the membrane will effectively photo-degrade the foulants accumulated on the top of the TiO_2 layer, it has also to be taken care of the organic parts of the membrane positioned below the TiO_2 layer, because without a protecting layer, it is certain that the organic part of the membrane will also be photo-degraded by the TiO_2 through the same UV degradation process of the foulants. So, SiO_2 layer was formed between the TiO_2 layer and the crosslinked PA layer of the membrane in this study.

Figure 2 shows the details of the reaction mechanism involved in the formation of the PA NF membrane with TiO_2 layer. For the preparation of the membrane, as explained in the Experimental section, interfacial polymerization technique, using PIP and TMC as monomers, was used, followed by the subsequent treatment with APTMOS and TIP. On the surface of the microporous PSf support, interfacial polymerization of PIP with TMC occurred, forming thin crosslinked PA layers. During the interfacial polymerization, however, not all of the $-\text{COCl}$ groups of the TMC reacted with PIP, so that some of the $-\text{COCl}$ groups remained unreacted. We used these unreacted $-\text{COCl}$ groups to form chemical bonds with TiO_2 layers. Amino group of the APTMOS that is the precursor of SiO_2 reacted with the $-\text{COCl}$ groups to form amide linkages, as one can see from the Figure 2. Then the APTMOS reacted further with TIP to form the structure M1 of the Figure 2. The APTMOS and TIP were then transformed into SiO_2 and TiO_2 , respectively, by the addition of water/isopropanol mixture solution in which 10 nm sized anatase TiO_2 particles were dispersed. By doing so, TiO_2 layers and SiO_2 layers were successfully formed on the surface of the PA NF membrane. The amide linkages acted as bridges connecting TiO_2 layer to the membrane.

Characterization

FTIR (ATR)

To see the formation of layers of TiO_2 and SiO_2 on the membrane surface, FTIR-ATR spectra were taken

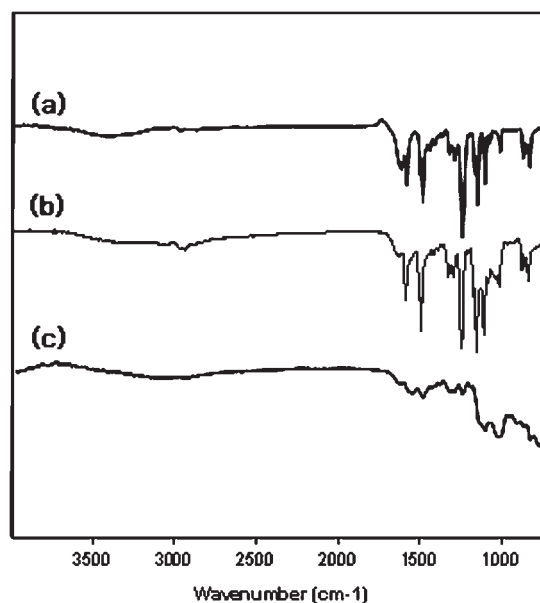


Figure 3 FTIR-ATR spectra taken at each step of the formation process of the PA NF composite membranes with TiO_2 layers; (a) just the PA-NF composite membrane, (b) after coating with APTMOS, (c) after coating with TIP.

as shown in Figure 3. During the formation process of the PA NF membrane with TiO_2 layers, FTIR spectra were taken from each step. Figure 3(a) shows the FTIR-ATR spectrum of the surface of the PA NF membrane before coating with APTMOS, showing a strong $-\text{C}=\text{O}$ stretching peak at 1700 cm^{-1} . Figure 3(b) shows the one after coating with APTMOS, which shows $\text{Si}-\text{O}$ stretching peaks around $1000\text{--}1100\text{ cm}^{-1}$. After coating with TIP on the top of the APTMOS layer, the spectrum became very much different as shown in Figure 3(c). The $-\text{C}=\text{O}$ stretching of the amide linkage of the crosslinked PA layer became very weak, indicating that the membrane surface was fully covered by the TIP layer. From these spectra, it was proved that the SiO_2 layer and TiO_2 layer were successfully formed on the surface of the PA NF membrane.

FESEM

Figure 4 shows the FESEM photographs of the surface and the fracture of the PA NF membranes with and without TiO_2 . It is found that the structure of the microporous PSf support is the combination of finger-like structure and sponge-like structure. The micro-pores were developed on the skin layer of the PSf support [Fig. 4 (a)]. Figure 4(b) shows the morphology of the membrane surface covered by nano-sized TiO_2 particles. From these photographs, it is possible to see the TiO_2 particles on the membrane surface but the distinction between the crosslinked PA layer and TiO_2 layer is hard to be observed.

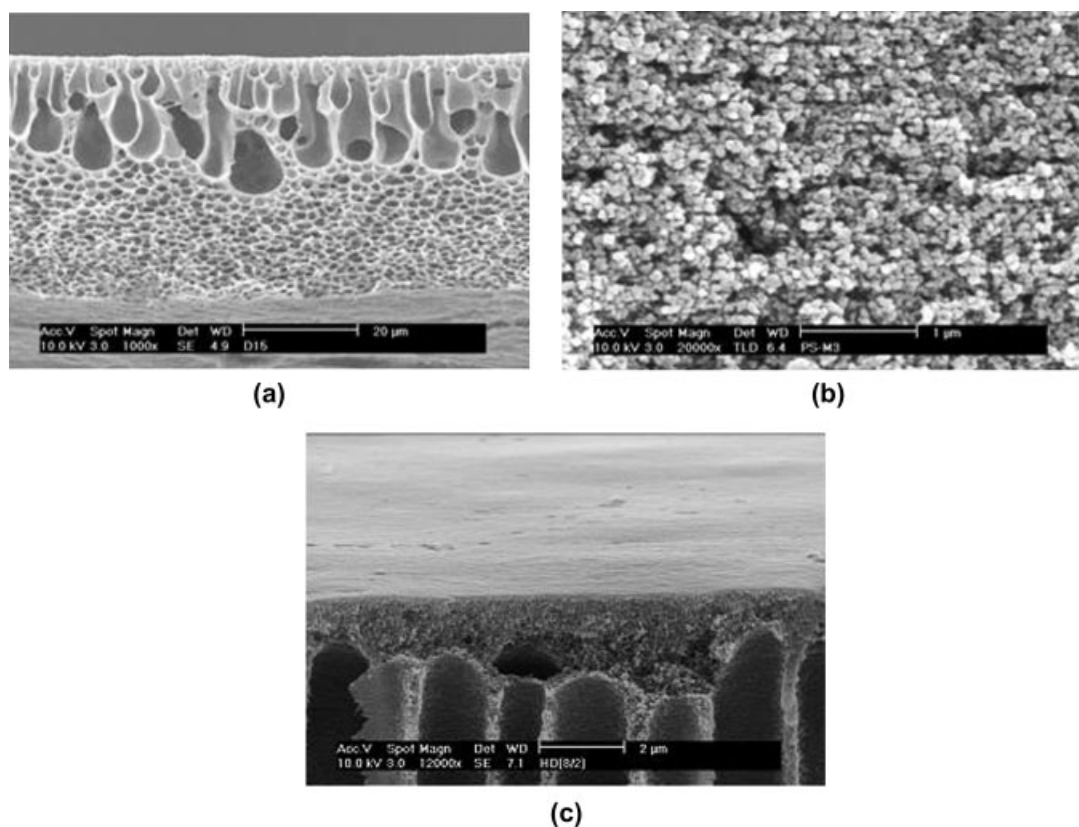


Figure 4 FESEM photographs of TiO₂ containing surface of the PA NF composite membrane; (a) Fracture, (b) Surface, (c) PA NF membrane without TiO₂.

XPS and XRD

To prove the formation of TiO₂ layers on the membrane surface, the XPS graph and the XRD pattern were also obtained as shown in Figures 5 and 6. The sharp peak of Ti 2p at 458 eV of the XPS graph strongly indicates the presence of the TiO₂ layers on

the membrane. The XRD pattern obtained from the membrane also confirms the presence of the TiO₂ layer. The sharp two peaks at around 25 degree of 2θ of the XRD pattern strongly indicate the presence of the anatase TiO₂ particles on the membrane sur-

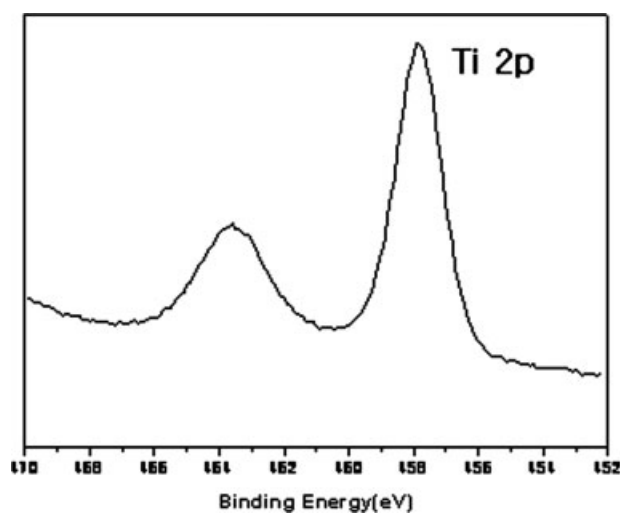


Figure 5 XPS graph of the TiO₂ containing surface of the PA-NF composite membrane.

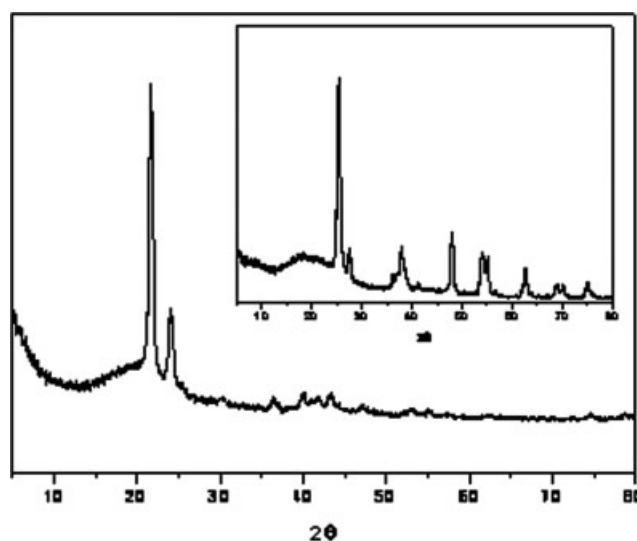


Figure 6 XRD patterns of the TiO₂ containing surface of the PA NF composite membrane (box: XRD patterns of the anatase TiO₂ powder).

face, as compared with the XRD pattern in a small box of the Figure 6 that was obtained separately from anatase TiO_2 powder sample. From these data, it is certain that the TiO_2 layer containing anatase TiO_2 particles was formed on the surface of the membrane.

Permeation performance

To figure out how the TiO_2 layer formed on the surface of the membrane affects on the permeation performance of the membrane, the flux and rejection of the PA NF membranes with TiO_2 were compared with those of a PA NF membrane without TiO_2 . The PA NF membrane without TiO_2 layers used in this study as a reference was prepared by the exactly same process as the membrane containing TiO_2 layers, using same monomers and same interfacial polymerization conditions, except for using TiO_2 .

Figure 7 shows the flux and rejection of the PA NF membrane without TiO_2 layers, when three different feed solutions (1000 ppm aqueous solutions of NaCl, Na_2SO_4 , and PEG 600) were used at 25°C. As expected, this membrane showed a typical NF performance: relatively high flux at moderate pressures and high rejections of divalent ions (SO_4^{2-}) and low molecular weight organics (PEG 600), but low rejection of NaCl, monovalent ion. The flux appeared to be dependent on the feed solutions used, exhibiting size effect of the solutes of the feed solutions. The flux for the NaCl solution was about $2.5 \text{ m}^3/\text{m}^2\text{day}$ at 200 psi, while the others were in the range of $1.5 \text{ m}^3/\text{m}^2\text{day}$. The behavior of the flux, depending on the feed solutions, is because this membrane was a NF membrane. In general, a NF membrane is known to have pores on its surface whose size is in the range of 1 nm. Because of the nanometer size pores, the permselective properties of a NF membrane are different from those of a RO membrane that is believed to have no pores on its surface. Relatively bigger size solutes such as Na_2SO_4 and PEG 600 have a tendency to plug the pores while the feed solutions penetrate the membrane, reducing the flux. However, small size solutes such as NaCl have less resistance from the membrane for its penetration, causing a high flux. This kind of flux behavior depending on the feed used is closely related to the solute rejection. The rejection of solutes is strongly dependent on the size of the solutes as well as the number of charges of the solutes. Usually large size solutes with higher charges show a high rejection. In this study, the rejection of the Na_2SO_4 and PEG 600 of this membrane was also fairly high, more than 80% at 200 psi, while that of the NaCl was as small as 30%.

Figure 8 shows the flux and rejection of the membrane having TiO_2 layers. Its performance turned

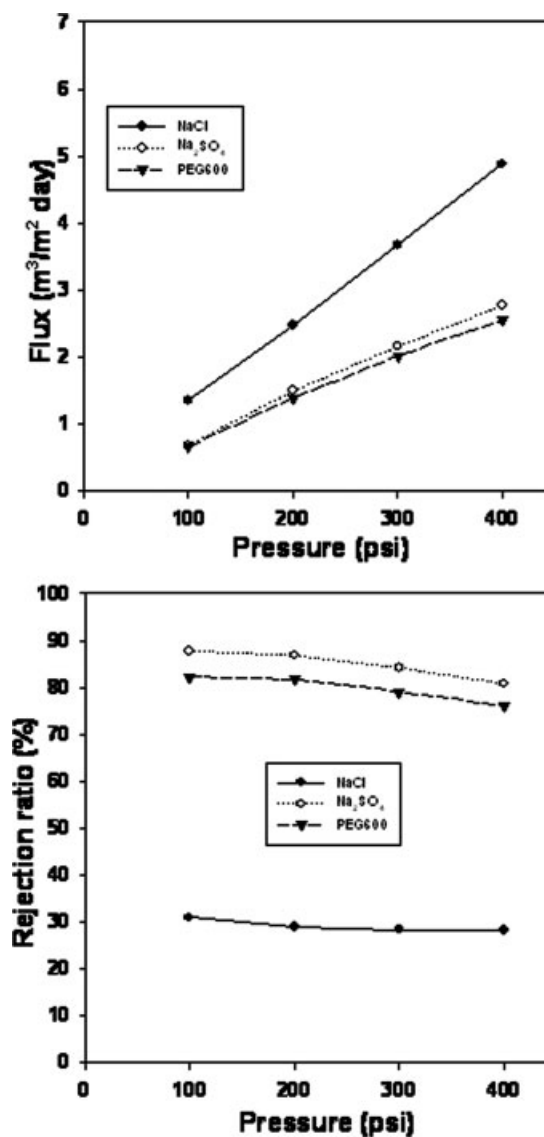


Figure 7 Flux and rejection of the PA NF composite membrane without TiO_2 layers, Feed solutions: 1000 ppm aqueous solutions of NaCl, Na_2SO_4 , and PEG 600.

out to be quite different from the membrane without TiO_2 layers. By coating the TiO_2 layers, over all flux of the membrane improved by about 28%, but the rejection pattern became completely different. As shown in Figure 8(b), at 200 psi the rejection of both Na_2SO_4 and PEG 600 are about 70 and 80%, respectively, decreasing with increasing operating pressure. The rejection of Na_2SO_4 decreased substantially from 90 to 70% by coating the membrane with TiO_2 layers, while the rejection of PEG 600 remained constant. The rejection of NaCl also slightly decreased. The variation of the membrane performances maybe due to the change in the chemical property of the membrane surface and different degree of crosslinking of the PA layers of the membrane induced by the coating of TiO_2 layers.

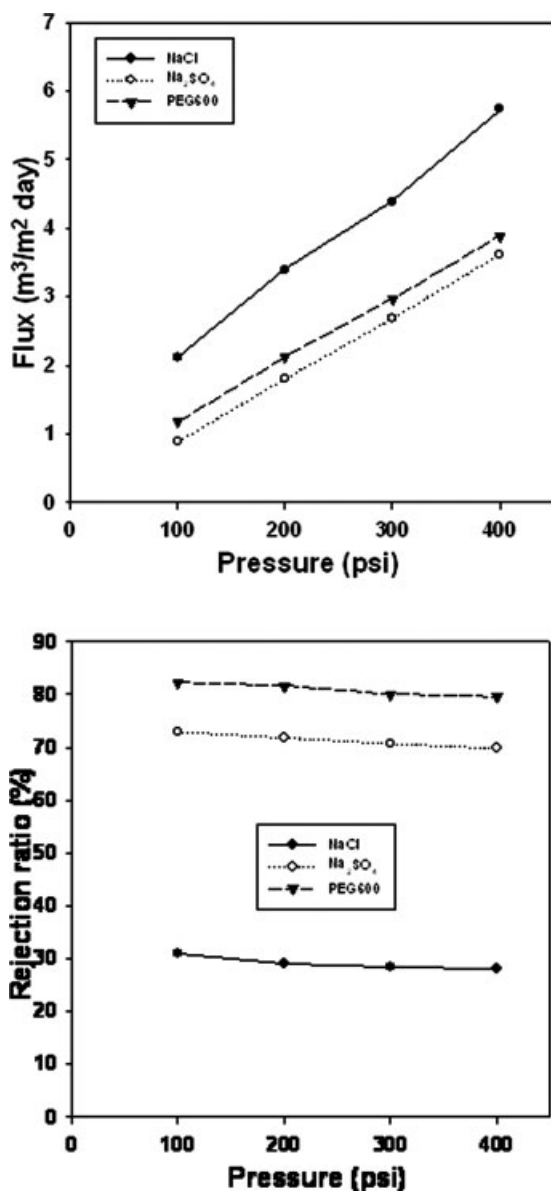


Figure 8 Flux and rejection of the PA NF composite membrane with TiO₂ layers, Feed solutions: 1000 ppm aqueous solutions of NaCl, Na₂SO₄, and PEG 600.

First of all, by coating the surface of the PA NF membrane with TiO₂, the chemical property of the membrane surface transformed from crosslinked PA layers with —COOH groups to TiO₂ layers, so that the anionic character of the membrane changed into nonionic state. Because of this change in the surface chemistry, the repulsion between the anionic groups of —COO[−] of the membrane surface and SO₄^{2−} from feed solution became very weak, causing low rejection of Na₂SO₄. As a result, the rejection of Na₂SO₄ decreased to 70% by coating the TiO₂ layers. However, PEG 600 without any charges was not affected, showing similar rejection ratio of about 80%. The rejection of NaCl also did not change substantially.

The flux increase by coating with TiO₂ layers can be explained by the slight decrease in the crosslinking degree of the crosslinked PA layers of the membrane with TiO₂ layer. Even though it is not easy to prove analytically, it is evident when considering the membrane preparation process. For the membrane preparation of the membrane with TiO₂ layers, the time for the interfacial polymerization of PIP with TMC was not long enough to have enough degree of crosslinking. Since APTMOS was consecutively reacted with the —COCl groups of the TMC right after the reaction with PIP, there was less chance for the amine groups of PIP to react with —COCl groups of TMC to give higher degree of crosslinking. The resulting lower degree of crosslinking of the PA layer produced relatively larger pores on the membrane, and the rejection decreased and flux increased substantially.

Antifouling properties

Figure 9 shows the normalized flux of the two types of membranes as a function of the operating time under different operating conditions. One of the membranes was the PA NF composite membrane without TiO₂ layers and the other was the PA NF composite membrane with TiO₂ layers. The feed solution used for this experiment was 1000 ppm aqueous solution of PEG 600.

When the membrane without TiO₂ layers was used, with periodic membrane cleaning with only water without UV irradiation on the membrane surface every 3 h of operation, the flux decline with time was as serious as seen in the Figure 9. This

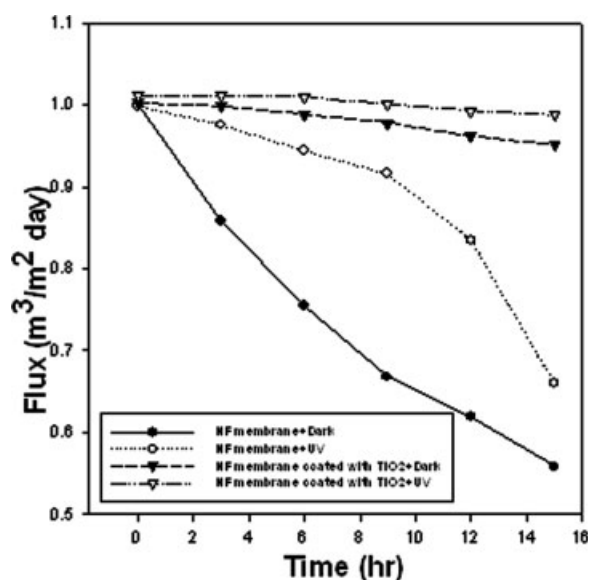


Figure 9 Behaviors of flux decline as a function of operating time using different types of membranes under different conditions.

kind of flux decline was improved by the exposure of the membrane to UV light for 1 min in the membrane cleaning stage, up to 9 h of operation, but after that the flux decline became also very fast.

However, when the membrane with TiO₂ layers was used, even without the UV irradiation, the flux decline became less significant. After 15 h of operation, only about 7% of flux was decreased. When UV light was irradiated on the membrane surface for cleaning, the cleaning effect became very good and the flux decline became almost negligible. Up to fifteen hours of operation, the flux decline was <2%.

From this result, it became evident that the TiO₂ layers coated on the NF PA membrane was effective for preventing the membrane from fouling. Also degradation of organics by the UV light with the aid of TiO₂ catalysis reaction improved the efficiency of the membrane cleaning with water, recovering the membrane flux.

CONCLUSIONS

A PA NF composite membrane with TiO₂ layers chemically connected to the polyamide layers of the membrane can be prepared by the consecutive treatment with APTMOS and TIP right after formation of PA NF composite membrane by the interfacial polymerization of PIP and TMC on the surface of microporous support. The TiO₂ layers coated on the outermost surface of the membrane was effective to

improve the antifouling property of the membrane by changing the membrane surface into nonionic hydrophilic state, and by helping cleaning of the membrane surface through the photo-degradation of the organic foulants. The TiO₂ coating onto the PA NF membrane was not harmful for the performance of the membrane. The flux and rejection of the membrane after coating with TiO₂ was in the range of nanofiltration.

References

1. Grozes, G.; Anselme, C.; Mallevalle, J. *J Membr Sci* 1993, 84, 61.
2. Lahoussine-Turcaud, V.; Wiesner, M. R.; Bottero, J. Y. *J Membr Sci* 1990, 52, 173.
3. Flemmer, R. L. C.; Buckley, C. C. A.; Groves, G. R. *Desalination* 1982, 41, 25.
4. Hwang, J.-E.; Jegal, J.; Lee, K.-H. *J Appl Polym Sci* 2002, 86, 2847.
5. Mo, J.; Hwang, J. E.; Jegal, J.; Lee, K. H.; Kim, J. *Membr J* 2004, 14, 230.
6. Sheikholeslami, R. *Desalination* 1999, 123, 45.
7. Mulder, M. *Basic Principles of Membrane Technology*; Kluwer Academic: Dordrecht, 1996.
8. Kim, S. H.; Kwak, S. Y.; Sohn, B. H.; Park, T. H. *J Membr Sci* 2003, 211, 157.
9. Matsunaga, T.; Tomoda, R.; Nakajima, T.; Nakamura, N.; Komine, T. *Appl Environ Microbiol* 1988, 54, 1330.
10. Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem Rev* 1995, 95, 69.
11. Mills, A.; Hunte, S. L. *J Photochem Photobiol A: Chem* 1997, 108, 1.