

Fouling Mitigation by TiO₂ Composite Membrane in Membrane Bioreactors

Yu-Chun Su¹; Chihpin Huang²; Jill Ruhsing Pan³; Wen-Pin Hsieh⁴; and Min-Chia Chu⁵

Abstract: Membrane bioreactors (MBRs) have attracted widespread attention in advanced water treatment because of their production of consistent and high-quality effluent. However, membrane fouling during operation has greatly hindered their application. Studies have suggested that a coating of TiO₂ nanoparticles on membranes may reduce membrane fouling by enhancing the hydrophilicity of the membrane. In this study, two membranes were coated with TiO₂ nanoparticles for membrane fouling mitigation. To evaluate the filtration performance of the TiO₂ composite membranes, a synthetic wastewater was prepared to model the municipal wastewater for the MBR operation. The mixed liquor from the MBR was used in the filtration test to evaluate the performance of the TiO₂ composite membrane. Filtration tests showed that membrane fouling was reduced substantially, which was attributable to the increased hydrophilicity of the membrane. Results also shows that optimal amount of coating is important in fouling mitigation. An ultrasonic washing test suggests that most of the TiO₂ particles were firmly coated on the surface of the composite membrane. DOI: 10.1061/(ASCE)EE.1943-7870.0000419. © 2012 American Society of Civil Engineers.

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Introduction

By combining an activated sludge reactor with a membrane unit, membrane bioreactors (MBRs) have emerged as promising solutions for wastewater treatment and reclamation. However, membrane fouling in MBRs has restricted their widespread application because it leads to decreased permeate flux or increased transmembrane pressure, thus requiring frequent membrane cleaning and replacement (Chang et al. 2002). Many strategies have been proposed to solve this problem, including physical or chemical cleaning (Liao et al. 2004), optimization of membrane characteristics (Yamato et al. 2006), optimization of operating conditions (Guglielmi et al. 2007), and optimization of biomass characteristics (Pan et al. 2010). Membranes with hydrophobic characteristics are prone to membrane fouling because of the hydrophobic-hydrophobic inter action between solutes, microbial cells, and membrane materials (Choi et al. 2002; Yu et al. 2005). Hydrophilic

modification of the membrane surface has therefore been proposed to reduce membrane fouling in MBRs.

Membrane modification with TiO₂ has become an alternative for reducing membrane fouling because of its photocatalytic effect and high hydrophilicity. The TiO₂ thin-film-composite membrane was first developed by Kwak et al (2001) and Kim et al (2003), but a degree of antibacterial fouling potential with ultraviolet (UV) light illumination was demonstrated. Recently, Madaeni and Ghaemi (2007) also reported that under UV irradiation, TiO₂ coating on reverse osmosis (RO) membranes could reduce membrane fouling resulting from photocatalysis and superhydrophilicity. Bae and coworkers investigated fouling mitigation in MBR systems by modifying membranes with TiO₂ nanoparticles (Bae and Tak 2005a, Bae et al. 2006). Polysulfone-TiO₂ and polyether sulfone-TiO₂ composite ultrafiltration membranes have been effective in reducing fouling when filtering bovine serum albumin and polyethylene glycol, respectively (Luo et al. 2005; Yang et al. 2007).

TiO₂ composite membranes have been prepared from two TiO₂ materials. Most TiO₂ composite membranes have been made by dip-coating involving the use of acidic TiO₂ colloidal sol (pH 1.5) (Luo et al. 2005; Bae and Tak 2005b; Bae et al. 2006; Kwak et al. 2001; Kim et al. 2003), which may damage the membrane. Madaeni and Ghaemi (2007) have tried to coat a membrane by using a commercial TiO₂ powder, P25, from Degussa. However, the TiO₂ particles were found easily detached from the membrane surface because of the weak adsorption between TiO₂ particles and the membrane.

In this research, a neutral sol was prepared containing 1% TiO₂ nanoparticles by chemical coprecipitation—peptization for a TiO₂ composite membrane. The particle size and crystal structure of the synthesized TiO₂ particles were characterized by use of a transmission electron microscope (TEM) and X-ray diffraction (XRD). Surface morphology and hydrophilicity of the composite membranes were studied by field-emission scanning electron microscopy (FE-SEM) and contact angle goniometer. The membrane dip-coated with the neutral sol to form the TiO₂ composite

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membrane was characterized by X-ray photoelectron spectroscopy (XPS). The fouling mitigation by the TiO₂ composite membranes made from acidic TiO₂ sol was examined and compared with that made from neutral TiO₂ sol.

Materials and Methods

Preparation and Characterization of Nanosized TiO₂ Particles

The neutral TiO₂ sol was prepared by a chemical coprecipitation-peptization method, as described in a previous study (Huang et al. 2007). Ammonium hydroxide (NH₄OH) was dropped into a 1-M titanium tetrachloride (TiCl₄) solution to form Ti(OH)₄. The yellow, transparent TiO₂ sol (1 wt% of TiO₂) formed after 2-h peptization with H₂O₂ (10%) and 24-h heating at 95°C. The prepared TiO₂ sol remained homogeneous for a long time without any noticeable sedimentation.

The acidic TiO₂ colloidal solution was prepared from the controlled hydrolysis of titanium tetraisopropoxide, Ti(OCH(CH₃)₂)₄ (Choi et al. 1994). A sample of 1.25 ml Ti(OCH(CH₃)₂)₄ (Aldrich, 97%) was mixed with 25 ml absolute ethanol. The solution was added drop by drop to 250 ml of distilled water (4°C), followed by pH adjustment to 1.5 with nitric acid. The mixture was stirred overnight until it was clear.

The crystal structure of TiO₂ particles was characterized by XRD with use of a Mac Science MXP-18 X-ray diffractometer and Cu K_α (voltage: 30 kV; current: 20 mA; λ = 0.154056 nm) radiation. The particle-size of TiO₂ was determined by use of a Philip TEM (Philip CM-200 TWIN) at 200 kV. Particle size distribution of TiO₂ particles was measured by use of a dynamic light-scattering particle-size distribution analyzer (Zetasizer Nano ZS, Malvern, United Kingdom).

Preparation of TiO₂ Composite Membranes

Two microfiltration membranes, cellulose acetate (CA) and mixed cellulose ester (MCE) membranes (Advantec MFS, Inc.) were chosen. Both have a nominal pore size of 0.2 μm. They were cut into a circle of 26.42 cm² to fit the experimental device. The virgin membrane was dipped in the TiO₂ sol for 10 min. Then the membrane was washed with distilled water and put into an oven at 50°C for 1 h. To investigate the effect of the TiO₂ amount on membrane fouling mitigation, the aforementioned coating procedure was performed one, two, and three times, respectively.

Characterization of Morphology and Chemical Composition of the Membrane Surface

The surface topography of the TiO₂ composite membrane was observed with use of a JEOL JSM-6700F FE-SEM.

The chemical composition of the membrane surface and the relative atomic concentrations of the individual elements were determined by XPS (Thermo VG-Scientific, United Kingdom) with a monochromatized K_α X-ray beam at 3.8 kW generated from an Al rotating anode. The reference to calibrate the binding energies was C 1s (284.8 V).

The contact angle goniometer (MagicDroplet Model 100, Future Digital Scientific) was used to characterize the hydrophilicity of the composite membranes by the sessile drop method. Contact angles were determined by taking the average of three measurements.

Fouling Test of the Composite Membranes

The membrane fouling tests for the composite membranes involved use of a stirred cell system (Fig. 1). The cell has a working volume of 200 mL and an effective membrane filtration area of 26.42 cm². The system can filter samples up to 4 L. The activated sludge used as the feed of the fouling test was taken from a 30-L submerged MBR system with a synthetic municipal wastewater influent. A synthetic feed was prepared to simulate the municipal wastewater, and the composition was as follows: sodium acetate, 210.58 mg/L; starch, 12.5 mg/L; beef extract, 20.83 mg/L; NH₄Cl, 55.83 mg/L; KH₂PO₄, 12.83 mg/L; MgSO₄ · 7H₂O, 29.58 mg/L; CaCl₂, 6.08 mg/L; FeSO₄ · 7H₂O, 7.25 mg/L; CuCl₂ · 2H₂O, 0.03 mg/L; MnCl₂ · 4H₂O, 0.05 mg/L; ZnSO₄ · 7H₂O, 0.06 mg/L; CoCl₂ · 6H₂O, 0.01 mg/L; Na₂MoO₄ · 2H₂O, 0.01 mg/L; H₃BO₃, 0.01 mg/L; and KI, 0.01 mg/L. The sample in the filtration cell was stirred at a constant rate for the duration of the experiment, and the data were automatically logged into a computer. The filtration experiments were carried out at 0.3-bar constant pressure maintained by a nitrogen cylinder.

A resistance-in-series model was used to assess the degree of membrane fouling

$$J = \frac{\Delta P_T}{\mu R_t} \quad (1)$$

where J = permeate flux (m³/m²s); ΔP_T = transmembrane pressure (Pa); μ = viscosity of the permeate (Pa s); and R_t = total filtration resistance (m⁻¹).

Ultrasonic Washing of TiO₂-Laden Membrane

To evaluate the stability of TiO₂ coating on the membrane, ultrasonic washing (40 KHz) was used. The relative atomic concentrations of elements on the membrane surface were

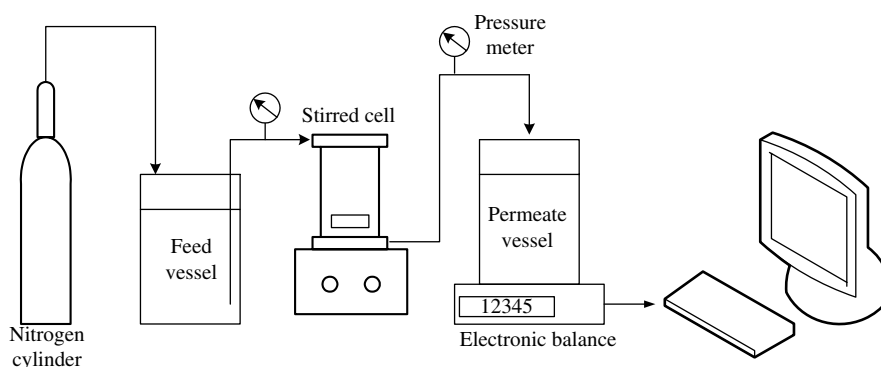


Fig. 1. Schematic diagram of the dead-end stirred cell system

quantified by XPS. The relative atomic concentrations of the individual elements can be calculated as follows:

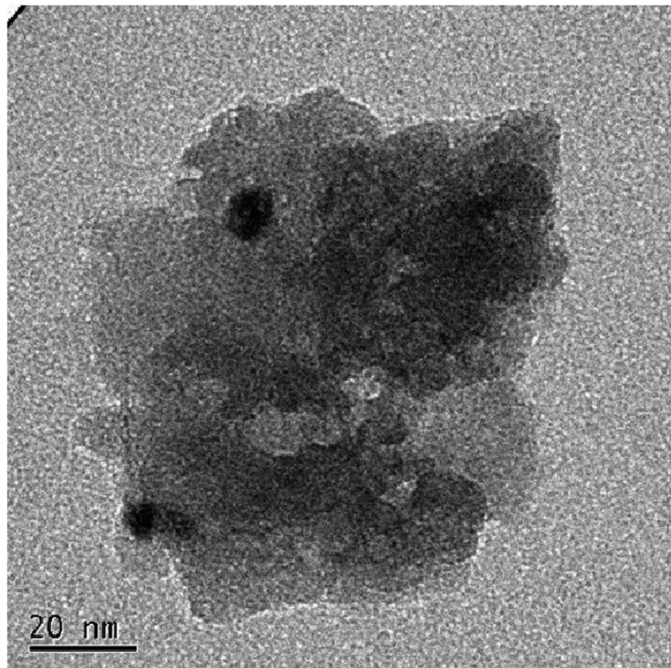
$$C_i = \frac{A_i/S_i}{\sum_j^m A_j/S_j} \quad (2)$$

in which A_i is the photoelectron peak area of the element i , S_i is the sensitivity factor for the element i , and m is the number of the elements in the sample.

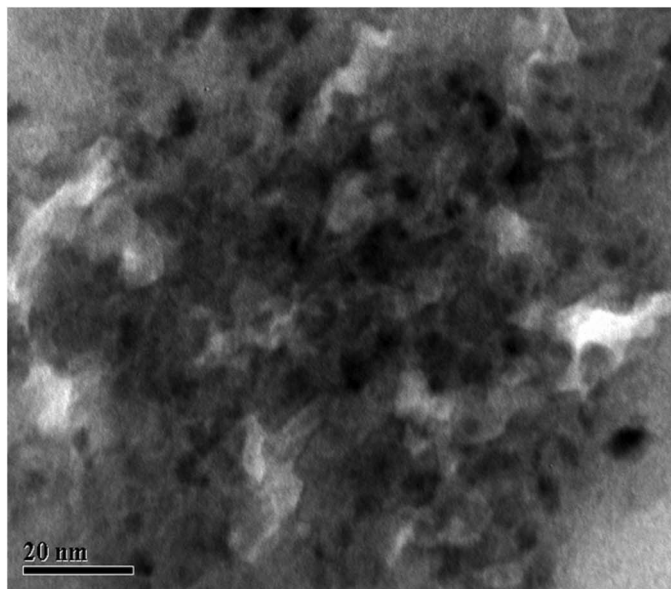
Results and Discussion

Particle Size and Crystal Structure of Synthesized TiO₂

The structures of the TiO₂ particles synthesized in neutral and acidic colloidal sol were directly observed by TEM. The black



(a)



(b)

Fig. 2. Transmission electron microscopy micrographs of the TiO₂ nanoparticles: (a) neutral sol; (b) acidic sol

spots displayed in Fig. 2 are the synthesized TiO₂ in neutral and acidic sol. All TiO₂ particles were < 10 nm regardless of the synthetic method used. Zetasizer further confirmed that most TiO₂ particles synthesized in neutral sol were < 10 nm (Fig. 3).

TiO₂ exists in three crystalline phases: anatase, rutile, and brookite. Rutile is thermodynamically stable, and the other two are metastable. The XRD diffraction pattern of the TiO₂ nanoparticles revealed the 2θ of the eminent peaks as 25.24° for anatase and 27.46° for rutile (Fig. 4). Therefore, the TiO₂ nanoparticles synthesized in acidic sol contained both anatase and rutile, which differs from results by Luo et al. (2005), Kwak et al. (2001), and Kim et al. (2003), who showed synthesized TiO₂ particles composed entirely of anatase. Thus, the acidic method may result in more than one mineral phase. However, the TiO₂ nanoparticles synthesized in neutral sol were composed entirely of anatase.

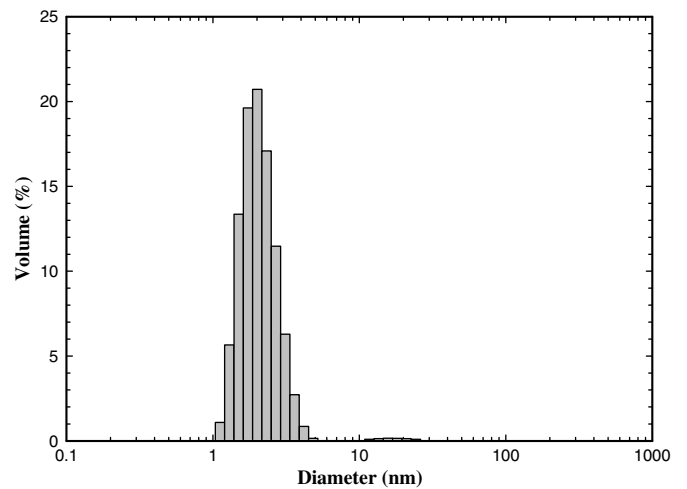


Fig. 3. Particle-size distribution of TiO₂ nanoparticles in neutral sol as determined by a dynamic light-scattering size distribution analyzer

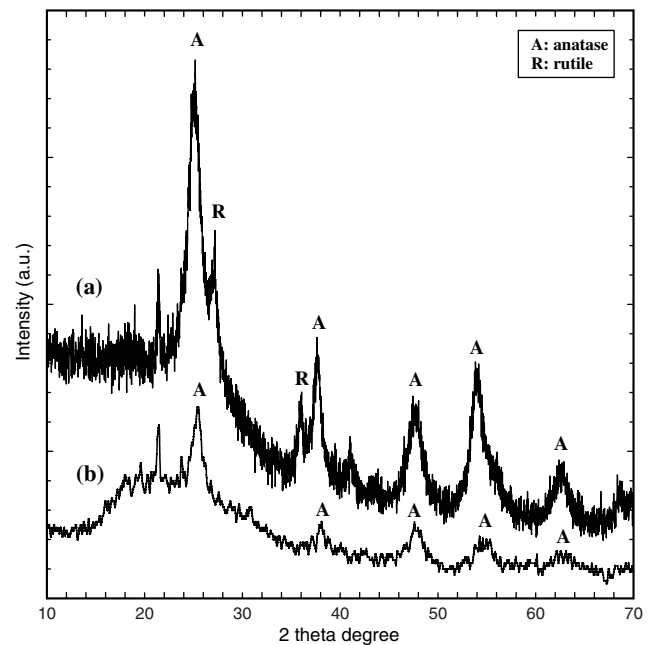


Fig. 4. X-ray diffraction patterns of the synthesized TiO₂ nanoparticles: (a) acidic sol; (b) neutral sol

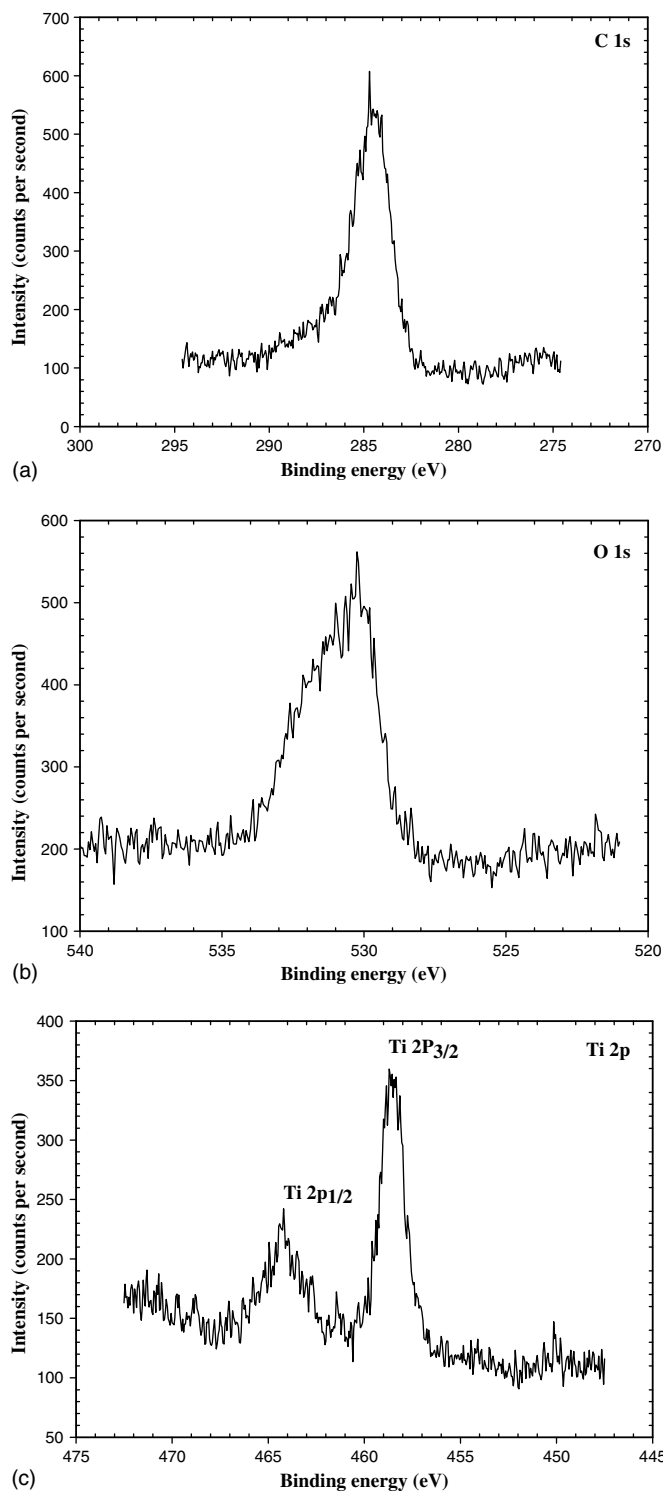


Fig. 5. X-ray photoelectron spectroscopy spectra for the cellulose acetate (CA)-TiO₂ composite membrane: (a) C; (b) O; (c) Ti

Table 1. Contact Angle of the Virgin Membrane and the Cellulose Acetate (CA)-TiO₂ Composite Membranes

	Contact angle (°)
Virgin membrane	89.13
Composite-1 ^a	80.72
Composite-2	21.18

^aComposite membrane with a single coating of neutral TiO₂ sol.

Surface Characterization of the Composite Membrane

The coating of TiO₂ nanoparticles on the surface of the composite membrane was confirmed by XPS. Fig. 5 shows XPS spectra of the CA – TiO₂ composite membrane. The electron binding energies of

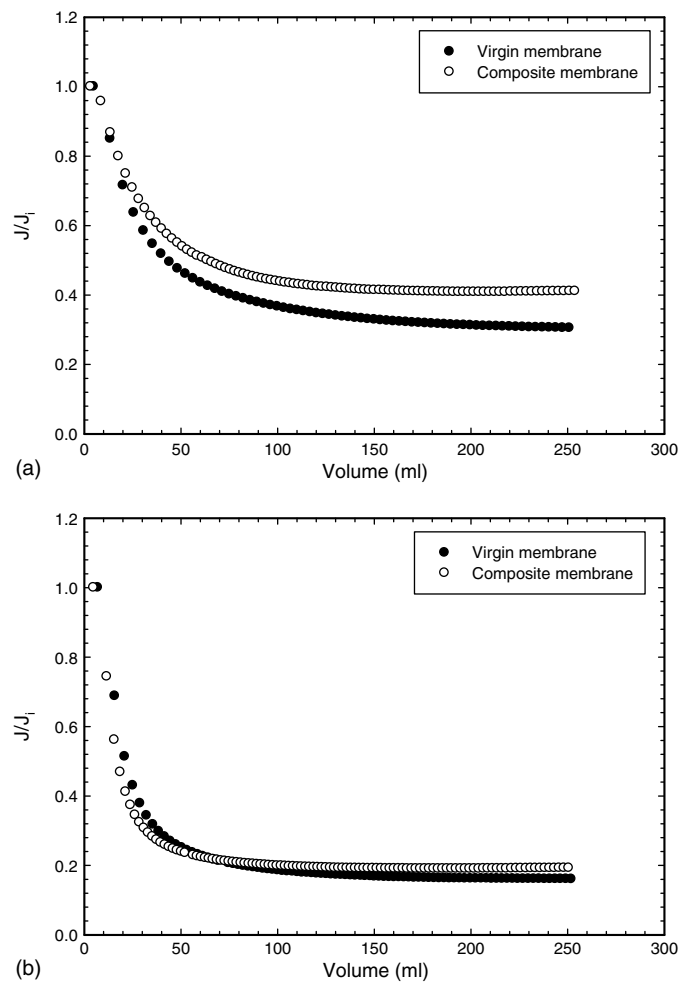


Fig. 6. Fouling mitigation patterns of the virgin and the TiO₂ composite membrane: (a) CA composite membrane; (b) mixed cellulose ester composite membrane

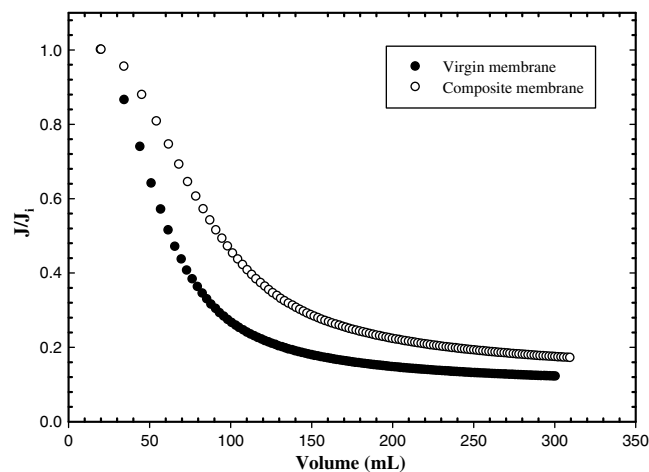


Fig. 7. Flux decline of the virgin and the CA-TiO₂ composite membrane (coated with acidic TiO₂ sol)

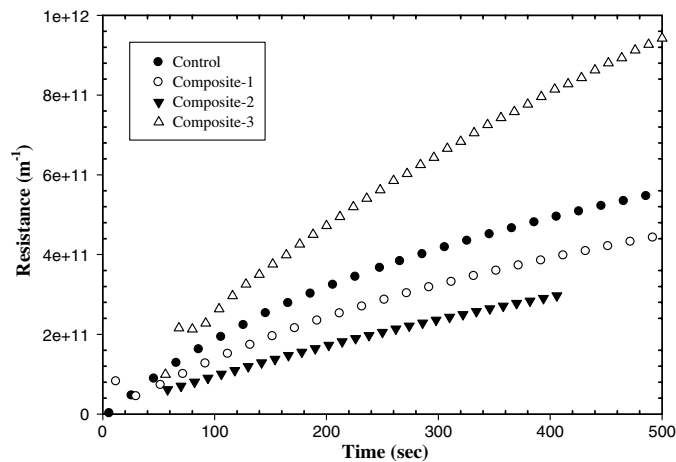


Fig. 8. Antifouling ability of CA-TiO₂ composite membranes with different dip-coating times in neutral TiO₂ sol (Composite-1, CA composite membrane with one coating; Composite-2, CA composite membrane with two coatings; Composite-3, CA composite membrane with three coatings)

the constituent elements were 284.6 eV for C 1s, 530.1 eV for O 1s, 464 eV for Ti 2p_{1/2}, and 458.5 eV for Ti 2p_{3/2}. The major constituents of the TiO₂ composite membranes are H, C, O, and Ti. Because XPS is insensitive to H, only C, O, and Ti can be detected. The XPS spectra of the CA-TiO₂ composite membrane confirmed

that TiO₂ was successfully coated on the membrane by the dip-coating method.

Table 1 shows contact angles of 89.13° for the virgin membrane and the TiO₂ composite membranes. After the membrane was coated once and three times with TiO₂ particles, the contact angles of the TiO₂ composite membranes decreased to 80.72° and 21.18°, respectively, which indicates the increase in hydrophilicity by the immobilization of TiO₂ nanoparticles on the membrane surface (Steen et al. 2002).

Fouling Mitigation of the Composite Membranes

The CA and MCE membranes were made into TiO₂ composite membranes by coating with neutral TiO₂ sol to evaluate the anti-fouling ability of the modified membranes. Fig. 6(a) shows the flux declines for the CA membrane and CA-TiO₂ composite membrane, and Fig. 6(b) shows them for the MCE membrane and MCE-TiO₂ composite membrane. The CA-TiO₂ composite membrane showed better antifouling ability than did the virgin membrane, whereas TiO₂ coating had no effect on fouling mitigation of the MCE membrane.

Fig. 7 shows the flux declines of the virgin CA membrane and the CA-TiO₂ composite membrane dip-coated in acidic TiO₂ sol; TiO₂ coating mitigated fouling. Results from Figs. 6 and 7 suggest that membrane modification can be a simple, effective way to reduce membrane fouling. To avoid the potential hazard of acidic TiO₂ sol on membrane, neutral sol was used for subsequent study.

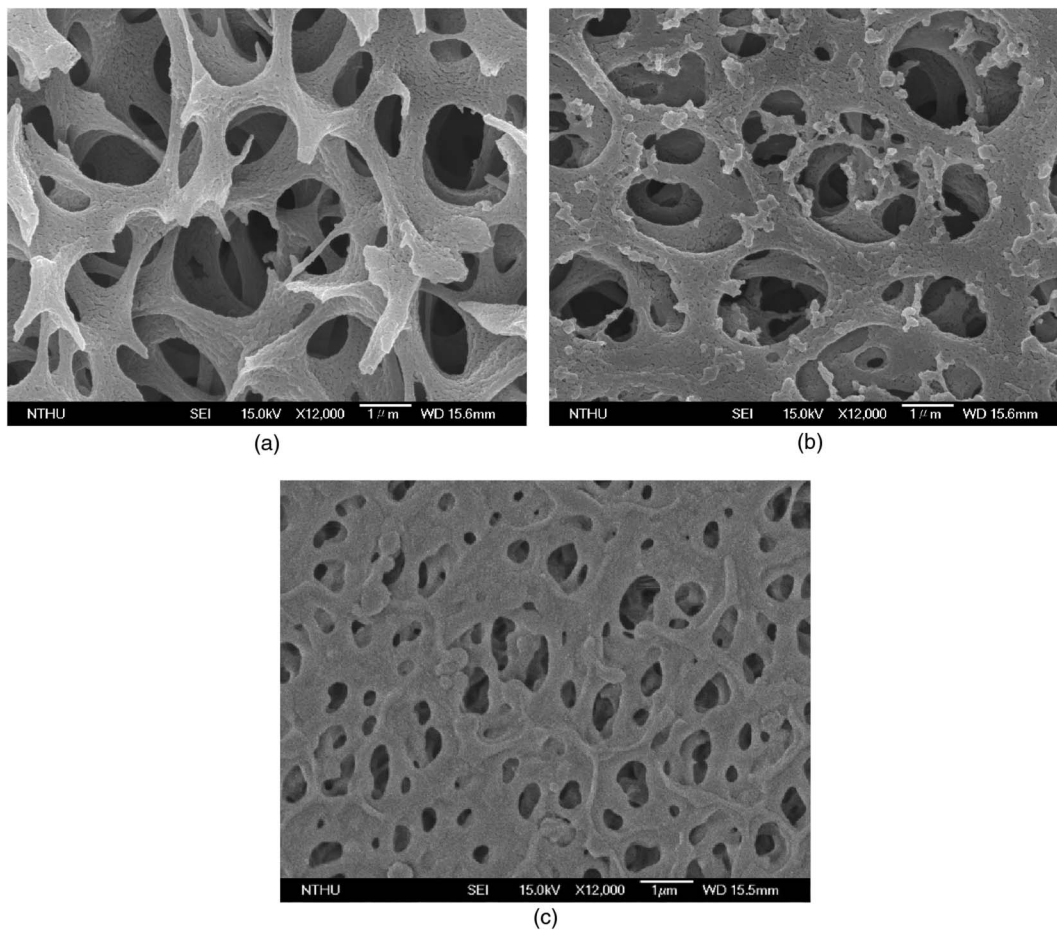


Fig. 9. Scanning electron microscopy micrographs: (a) virgin CA membrane; (b) CA composite membrane coated once with neutral TiO₂ sol; (c) CA composite membrane coated three times with neutral TiO₂ sol

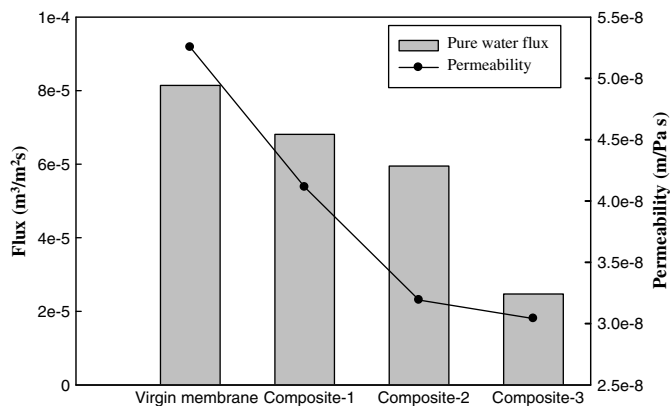


Fig. 10. Pure water flux and permeability of the virgin membrane and the TiO₂ composite membranes

The membrane was dip-coated in TiO₂ sol for various times to determine the optimal amount of TiO₂ particles on the membrane surface for the best fouling mitigation. Fig. 8 illustrates the filtration resistance for different coatings. Although a second coating further improved the filtration, three coats reversed the effect. Increasing the amount of TiO₂ particles on the membrane surface by increasing the number of coats ameliorated membrane fouling before a critical point was reached. SEM micrographs of the surface topography of the virgin membrane and the TiO₂ composite membranes strongly suggest that the higher filtration resistance of the three-coated membrane was due to blocking the membrane pores (Fig. 9). The virgin CA membrane shows a characteristic sponglike structure. The surface of the CA-TiO₂ composite membrane coated once by neutral TiO₂ sol was covered with TiO₂ in nodular shapes, but with a three coats, the surface pores had become severely blocked [Fig. 9(c)]. The loss of pores on the three-coated composite membranes contributed to the increased filtration resistance, as reflected in the pure water flux and the permeability of the virgin membrane and the TiO₂ composite membranes (Fig. 10). Therefore, the amount of TiO₂ on the membrane surface must be accurately controlled to obtain maximal anti-fouling effect.

Stability of TiO₂ Particles on Composite Membranes

Table 2 summarizes the relative atomic concentrations of elements remaining on the membrane surface after various ultrasonic washings. After ultrasonic washing for 3 min, the relative atomic concentration of titanium element decreased from 52.6 to 27.4%. No significant further reduction of Ti was observed with longer washing. Therefore, loosely attached TiO₂ particles were lost in the first

Table 2. Relative Atomic Concentrations of Elements on the TiO₂ Composite Membrane Surface under Various Ultrasonic Washing Conditions

Sample ^a	Relative atomic concentration (percentage)		
	C	O	Ti
Freshly prepared	8.3	39.1	52.6
After ultrasonic washing for 3 min	15.3	57.3	27.4
30 min	14.7	55.1	30.2
1 h	16.5	61.9	21.6

^aAnalysis was performed for the TiO₂ composite membrane.

couple of minutes of ultrasonic washing. Most TiO₂ particles were tightly bound onto the membrane even after vigorous membrane cleaning by ultrasonic washing.

Conclusions

This study concludes the following:

1. Membrane fouling is reduced by TiO₂ coating on the surface of CA membrane.
2. Both acidic TiO₂ sol and neutral TiO₂ sol particles are effective in modification of CA membranes for fouling reduction.
3. TiO₂ coating enhances the hydrophilicity of the membrane surface and the fouling mitigation.
4. The amount of TiO₂ coating must be optimized to mitigate membrane fouling.
5. Dip-coating the membrane in neutral TiO₂ sol provides stable fixation of TiO₂ particles on the membrane surface even after rigorous ultrasonic washing.

Acknowledgments

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References

- Bae, T. H., Kim, I. C., and Tak, T. M. (2006). "Preparation and characterization of fouling-resistant TiO₂ self-assembled nanocomposite membranes." *J. Membr. Sci.*, 275(1–2), 1–5.
- Bae, T. H., and Tak, T. M. (2005a). "Effect of TiO₂ nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration." *J. Membr. Sci.*, 249(1–2), 1–8.
- Bae, T. H., and Tak, T. M. (2005b). "Preparation of TiO₂ self-assembled polymeric nanocomposite membranes and examination of their fouling mitigation effects in a membrane bioreactor system." *J. Membr. Sci.*, 266(1–2), 1–5.
- Chang, I. S., Le Clech, P. L., Jefferson, B., and Judd, S. (2002). "Membrane fouling in membrane bioreactors for wastewater treatment." *J. Environ. Eng.*, 128(11), 1018–1029.
- Choi, J. G., Bae, T. H., Kim, J. H., and Randall, A. A. (2002). "The behavior of membrane fouling initiation on the crossflow membrane bioreactor system." *J. Membr. Sci.*, 203(1–2), 103–113.
- Choi, W., Termin, A., and Hoffmann, M. R. (1994). "The role of metal ion dopants in quantum-sized TiO₂: Correlation between photoreactivity and charge carrier recombination dynamics." *J. Phys. Chem.*, 98(51), 13669–13679.
- Guglielmi, G., Chiarani, D., Judd, S. J., and Andreottola, G. (2007). "Flux criticality and sustainability in a hollow fibre submerged membrane bioreactor for municipal wastewater treatment." *J. Membr. Sci.*, 289(1–2), 241–248.
- Huang, C. P., Hsieh, W. P., Pan, J. R., and Chang, S. M. (2007). "Characteristics of an innovative TiO₂/Fe⁰ composite for treatment of azo dye." *Sep. Purif. Technol.*, 58(1), 152–158.
- Kim, S. H., Kwak, S. Y., Sohn, B. H., and Park, T. H. (2003). "Design of TiO₂ nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane as an approach to solve biofouling problem." *J. Membr. Sci.*, 211(1), 157–165.
- Kwak, S. Y., Kim, S. H., and Kim, S. S. (2001). "Hybrid organic/inorganic reverse osmosis (RO) membrane for bacterial anti-fouling: 1. Preparation and characterization of TiO₂ nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane." *Environ. Sci. Technol.*, 35(11), 2388–2394.
- Liao, B. Q., Bagley, D. M., Kraemer, H. E., Leppard, G. G., and Liss, S. N. (2004). "A review of biofouling and its control in membrane separation bioreactors." *Water Environ. Res.*, 76(5), 425–436.

- Luo, M. L., Zhao, J. Q., Tang, W., and Pu, C. S. (2005). "Hydrophilic modification of poly(ether sulfone) ultrafiltration membrane surface by self-assembly of TiO₂ nanoparticles." *Appl. Surf. Sci.*, 249(1–4), 76–84.
- Madaeni, S. S., and Ghaemi, N. (2007). "Characterization of self-cleaning RO membranes coated with TiO₂ particles under UV irradiation." *J. Membr. Sci.*, 303(1–2), 221–233.
- Pan, J. R., Su, Y. C., Huang, C. P., and Lee, H. C. (2010). "Effect of sludge characteristics on membrane fouling in membrane bioreactors." *J. Membr. Sci.*, 349(1–2), 287–294.
- Steen, M. L., Jordan, A. C., and Fisher, E. R. (2002). "Hydrophilic modification of polymeric membranes by low temperature H₂O plasma treatment." *J. Membr. Sci.*, 204(1–2), 341–357.
- Yamato, N., Kimura, K., Miyoshi, T., and Watanabe, Y. (2006). "Difference in membrane fouling in membrane bioreactors (MBRs) caused by membrane polymer materials." *J. Membr. Sci.*, 280(1–2), 911–919.
- Yang, Y., Zhang, H., Wang, P., Zheng, Q., and Li, J. (2007). "The influence of nano-sized TiO₂ fillers on the morphologies and properties of PSF UF membrane." *J. Membr. Sci.*, 288(1–2), 231–238.
- Yu, H. Y., Hu, M. X., Xu, Z. K., Wang, J. L., and Wang, S. Y. (2005). "Surface modification of polypropylene microporous membranes to improve their antifouling property in MBR: NH₃ plasma treatment." *Sep. Purif. Technol.*, 45(1), 8–15.