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PVDF-TiO_2 coated microfiltration membranes: preparation and characterization

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Abstract. Organic fouling and biofouling pose a significant challenge to the membrane filtration process. Photocatalysis-membrane hybrid system is a novel idea for reducing these membranes fouling however, when TiO_2 photocatalyst nanoparticles are used in suspension, catalyst recovery is not only imposes an extra step on the process but also significantly contributes to increased membrane resistance and reduced permeate flux. In this study, TiO_2 photocatalyst has been immobilized by coating on the microfiltration (MF) membrane surface to minimize organic and microbial fouling. Nano-sized TiO_2 was first synthesized by a sol-gel method. The synthesized TiO_2 was coated on a Poly Vinyl Difluoride (PVDF) membrane (MF) surface using spray coating and dip coating techniques to obtain hybrid functional composite membrane. The characteristics of the synthesized photocatalyst and a functional composite membrane were studied using numerous instruments in terms of physical, chemical and electrical properties. In comparison to the clean PVDF membrane, the TiO_2 coated MF membrane was found more effective in removing methylene blue (20%) and *E-coli* (99%).

Keywords: TiO_2 photocatalyst; photocatalysis; microfiltration (MF); organic fouling; biofouling.

1. Introduction

Membrane filtration for water and wastewater treatment has become a very important technology because of its reliability in treatment. However membrane fouling decreases the membrane productivity and destroys the membrane irreversibly. Several approaches such as pre-treatment, membrane surface modifications, process optimization, periodic cleaning, etc. have been attempted to reduce the membrane fouling (Mulder 1997) however fouling still remains a major obstacle. The types of fouling reported include crystalline fouling, organic fouling, particulate and colloidal fouling, and microbial or biofouling (Flemming 1997, Kim *et al*. 2003).

Photocatalysis is a novel technology that utilizes light to completely decompose organic matter present in water with the help of semiconductor such as TiO_2. Photocatalysis is by far one of the most superior technologies in environmental purification because unlike many other technologies, photocatalysis does not serve as a mere phase transfer but completely degrades the organic pollutants

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by converting them to innocuous substances such as CO_2 and H_2O (Shon *et al.* 2008). When TiO_2 is irradiated by UV light, e-/h+ pair is formed and when it comes into contact with absorbed water, it gets oxidized by positive holes forming hydroxyl radicals $OH^\bullet$ and trapped electron forming $HO_2^\bullet$ with a strong oxidative and reductive decomposing power which reacts with organic matter. In the presence of oxygen, the intermediate radicals in the organic compounds and oxygen molecules undergo radical chain reactions and consume oxygen to finally form carbon dioxide (Kolen'ko *et al.* 2005, Shon *et al.* 2008). By taking advantage of this photocatalytic process, attempts have been made to develop a hybrid system with membrane and photocatalysis for advanced treatment. In such hybrid system, photocatalysis is usually performed using amorphous TiO_2 nanoparticles in suspension however the use of photocatalyst in suspension imposes a problem of having to be recovered from the treated water (Shon *et al.* 2008). The use of nano powder photocatalyst suspension poses additional filtration resistance and reduced permeate flux. Moreover, use of membranes with larger pore sizes such as MF would not be able to prevent all the nano powder catalyst from coming out with permeate.

Immobilization of the photocatalyst has been tried as an alternate to suspended photcatalyst. Polymer membrane can be coated with TiO_2 nanoparticles. The coating takes place in the form of hydrogen (H)-bonding interaction with the carboxylic (-COOH) functional group of aromatic polyamide in the thin-film layer of the membrane (Kim *et al.* 2003). When UV light is provided directly to the membrane surface, the photocatalysis could take place thereby preventing organic and biofouling. Further, the modification of the foulant occurring on the membrane surface by photocatalytic reaction would result in preventing the flux decline. For example, the foulant consisting of aromatic organics (coiled and compacted configuration) can be converted into aliphatic compounds (stretched and linear configuration) by photocatalytic reaction, which reduces membrane fouling. The application of UV light on the membrane surface could also improve the permeate flux due to increase in membrane pore size at higher temperature although it has been noted that some membranes are weakened by direct UV light (Ollis 2003). The coated photocatalyst has several advantages over the TiO_2 in suspension. Firstly there is no need for the filtration of suspended TiO_2 particles from the treated water. Suspended TiO_2 particles develop a cake layer on the membrane surface creating additional cake resistance and reducing permeate flux. The second advantage is the prevention of biofouling or microbial fouling on the membrane surface by photocatalytic action.

In this paper, the synthesis of nanoparticles TiO_2 by a sol-gel method using controlled hydrolysis of titanium tetraisopropoxide ($Ti(O–iC_3H_7)_4$) and coating the same on the membrane surface to obtain a TiO_2 coated functional MF membrane is reported. The concept of using the TiO_2 photocatalyst coated MF membrane is to develop a near zero fouling membrane filtration system for advanced water and wastewater treatment. The TiO_2 coated MF functional membrane would serve the dual purpose of filter and photocatalyst membrane to prevent organic fouling and biofouling. The characteristics of the synthesized nanoparticle TiO_2 photocatalyst and TiO_2 coated MF membrane were studied by applying numerous analytical instruments. The effectiveness of the TiO_2 coated MF membrane was examined using methyelene blue and *E-coli* as model pollutants in water.

2. Experimental

2.1 Preparation of nano-sized TiO_2 powders using sol-gel method

The nano-sized TiO_2 powder was manufactured using the sol-gel method based on the method

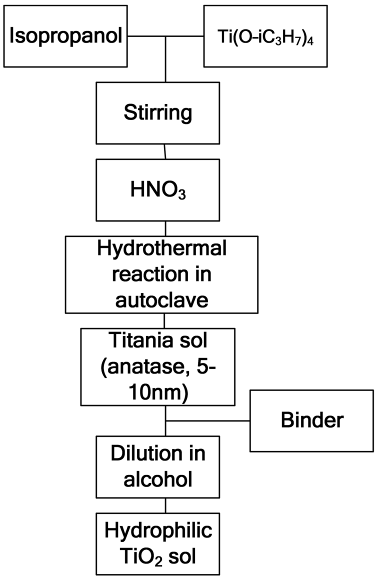


Fig. 1 Preparation of TiO_2 powder used in this study (Kolen'ko *et al.* 2005)

elaborated by Dagan and Tomkiewicz (1993) (Fig. 1). Firstly, alkoxides precursor (tetraisopropoxytitanium (IV) $Ti(O–iC_3H_7)_4$, 18.58 ml) was dissolved in absolute ethanol (51.0 ml). The hydrolysant consisted of distilled water (0.87 ml) and 2 M aqueous nitric acid solution (2.5 ml) diluted in absolute ethanol (15 ml). The hydrolysant was added drop-by-drop to the alkoxides solution at room temperature under continuous stirring (400 rpm). To obtain the powder from alcogel, drying was performed under supercritical conditions of a iC_3H_7OH. When the pore liquid is removed as a gas phase from the interconnected sol–gel network under supercritical conditions (critical-point drying method), the network does not collapse and a low density aerogel is produced. Alcogel was put into a stainless steel autoclave (volume = 150 ml; degree of filling by iC_3H_7OH, 80%). The solvents present in the alcogel (EtOH, H_2O and iC_3H_7OH) were replaced by iC_3H_7OH flow of 5 ml/min for 1 h at a pressure of 100 bar and a temperature of 300°C. At the end of supercritical drying, the autoclave was removed from the furnace and cooled to room temperature. Alcogel was put in the same autoclave as drying in isopropanol. The alcohol contained in the gel was replaced by liquid CO_2 and then, the system was brought above the critical point for 15 min, at a pressure of 70 bar and a temperature of 50°C. At the end of supercritical drying, the autoclave was removed from the furnace and cooled down to room temperature. Silane was used as a binder. The amorphous TiO_2 particles were also made with the sol-gel method however without the heating process of the binder. The nanoparticle TiO_2 photocatalyst obtained through this process is termed in this particular study as LT-1 photocatalyst.

2.2 Coating on the PVDF membrane surface with TiO_2

A hydrophobic polymer membrane Poly Vinyl Difluoride (PVDF, MF, Pure-Envitech, Korea) with pore size of 0.4 μm, pure water flux of 3300 $L/m^2 \cdot h$ at 30 kPa, and contact angle of 94° was used as substrate for coating TiO_2 photocatalyst. The characteristics of this membrane as provided by the

Table 1 Characteristics of PVDF membrane

Pore size	Contact angle(°)	Zeta potential at pH 7 (mV)	PWP** ($L/m^2 \cdot h$)
0.4 μm	94	-28	3300 at 30 kPa

* MWCO: molecular weight cut off
** PWP: pure water permeability

(a) (b)

Fig. 2 Two different techniques adopted for coating TiO_2 on the membrane surface. (a) dip coating and (b) sprayer used in nano particle spray coating

manufacturer are given in Table 1.

Two different techniques were used for coating TiO_2 on the membrane surface (Fig. 2). In the dipping method, the amorphous TiO_2 was mixed with the SiO_2 binder solution and the membrane was soaked in the solution for 1 hour. The membrane was then taken out and dried under the normal room conditions for one hour. The same procedure was repeated to get the second layer of coating on the membrane surface. In the spray method, TiO_2-SiO_2 mixture was sprayed on the membrane surface using a pressure spray (ABAC Deutschland GmbH D-78532 Tuttlingen, Germany). The membrane was coated with several layers of TiO_2.

2.3 Characterization of nano particle TiO_2

The crystal structure, particle size, and surface area of the photocatalyst obtained after drying the TiO_2 sol at 100°C was examined through X-ray diffraction (XRD) (Rigaku D/MAX-1200) pattern, TEM (JEOL, EIM-2000FXII) photo and nitrogen absorption.

The LT-1 photocatalyst prepared through the above sol-gel method was compared with commercially available photocatalytic powder, P-25 (Dequssa, Germany).

Surface areas and pore volumes of the LT-1 photocatalyst were obtained with nitrogen adsorption at – 196°C on a Micromeritics ASAP 2010C. The LT-1 photocatalyst were dehydrated under vacuum at 250°C for 5 h before the adsorption measurement.

2.4 Characterization of membranes

The membrane properties such as porosity, pore size and roughness was measured by atomic force microscopy (AFM, XE-100, PSIA Corp., Korea) and the data analyzed with computer software

(XEI, PSIA Corp., USA). The theory of the AFM is explained elsewhere (Lee *et al.* 2005).

Contact angle measurements using the sessile drop method with a contact angle meter (Tantec, Co., USA) were used to determine an index of membrane hydrophobicity; 20 μL of deionized water (Milli-Q water) was dropped onto the dried membrane surface and the contact angle was measured within approximately 10 seconds. Zeta potential on different membrane surfaces was measured by electrophoresis method (ELS 8000 Otzca, Japan) using polylatex in 10 mM NaCl solution as a standard particle. The pH of solution was adjusted with 0.1 N HCl and 0.1 N NaOH.

The clean and fouled membrane surfaces were analyzed for functional groups using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). The prepared membranes were examined by FTIR (460 plus, Jasco, Japan) equipped with an ATR accessory and the IR peak was analyzed with Bio-rad laboratories software. Scanning electron microscopy (SEM) is a useful tool for investigating the membrane structure during membrane fouling. SEM images of the TiO_2 coated membrane were carried out using the SEM (FE-SEM S-4700, Hitachi Corp., Japan). The voltage was 5 kV and the working distance was 12 mm. The magnification up to 5000 times was used here. The top and side views of the membranes from the SEM images were analyzed.

2.5 Evaluation of composite membrane performance

Cross flow membrane filtration unit (Nitto Denko Corp., Japan) was used to study the performance of the membrane (schematic diagram shown in Fig. 3). New membranes with an effective membrane area of 0.006 m^2 were used for each experiment to avoid the effect of residual fouling and to compare the results obtained under different conditions. The operating transmembrane pressure and cross-flow velocity were controlled at 50 kPa and 0.5 m/s for PVDF by means of by-pass and regulating valves, respectively. Photocatalysis experiment was performed by irradiating the membrane surface with UV light (352 nm) consisting of 3 lamps of 10 watt each places in parallel to each other. Methyelene blue was used as model pollutants and *E-coli* (ER2738) was used as a model microorganism for the removal by the membrane-photocatalysis hybrid treatment.

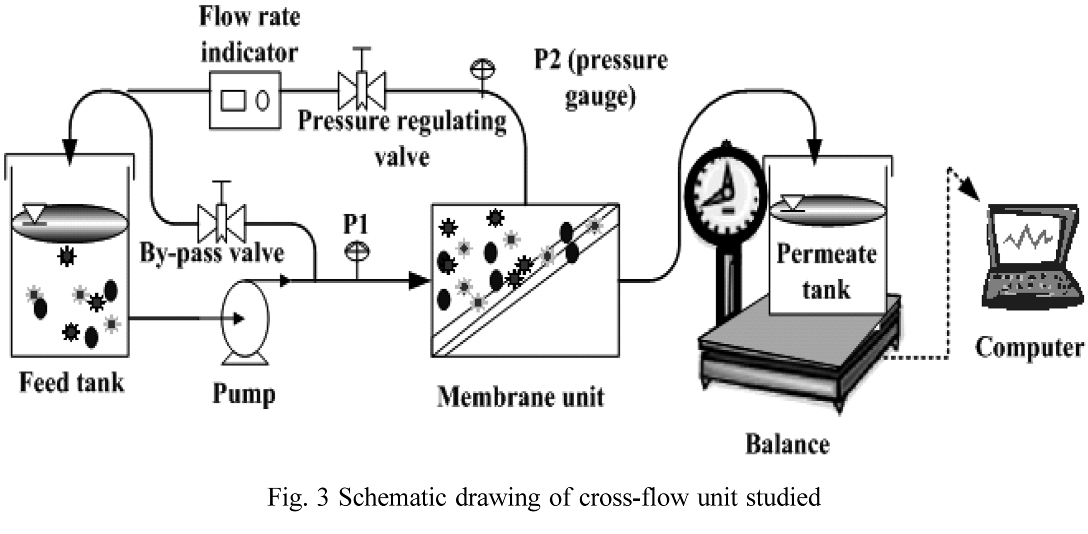


Fig. 3 Schematic drawing of cross-flow unit studied

3. Results and discussion

3.1 Crystal structure and particle size of the synthesized photocatalyst LT-1

A direct correlation between the photocatalytic activity and the surface properties have not been established however, the photocatalytic activity of TiO_2 is influenced by the phase composition, crystalline quality, morphology, particle size and size distribution, specific surface area, porosity, surface hydroxyl density and band gap (Kolen'ko *et al.* 2005, Shon *et al.* 2008). The characteristic of the synthesized TiO_2 (LT-1) particles was compared with the commercially available Degussa P25 as a reference photocatalyst.

The particle structures of LT-1 and P-25 were comparatively studied using XRD, TEM images and surface area. The XRD patterns of LT-1 and P-25 TiO_2 photocatalysts are shown in Fig. 4. LT-1 showed diffraction peaks at 25°, 38° and 48° which represent the anatase form of TiO_2. The commercial rutile form of TiO_2 shows diffraction peaks at 27°, 36° and 41° (Kim *et al.* 2003). The rutile content of P-25 by XRD patterns was observed to consist of only about 20%. Therefore LT-1 photocatalyst exhibited a majority of anatase diffraction peaks indicating that the photocatalytic potential of the LT-1 photocatalyst is higher than that of the P-25. TiO_2 in anatase form is considered to be more photoactive and practical for many environmental applications (Hoffmann *et al.* 1995).

TEM images show that the LT-1 exists in the form of a flaky and pyramidal shape of about 30 nm in length and 4-7 nm in width (Fig. 5). P25 exhibited a round and granular shape with a size of about 30 nm. The surface area of P-25 and LT-1 was determined to be about 50 m^2/g and 200 m^2/g respectively suggesting that the LT-1 with much larger surface area is more favorable to adsorb harmful organic matter and bacteria than the P-25.

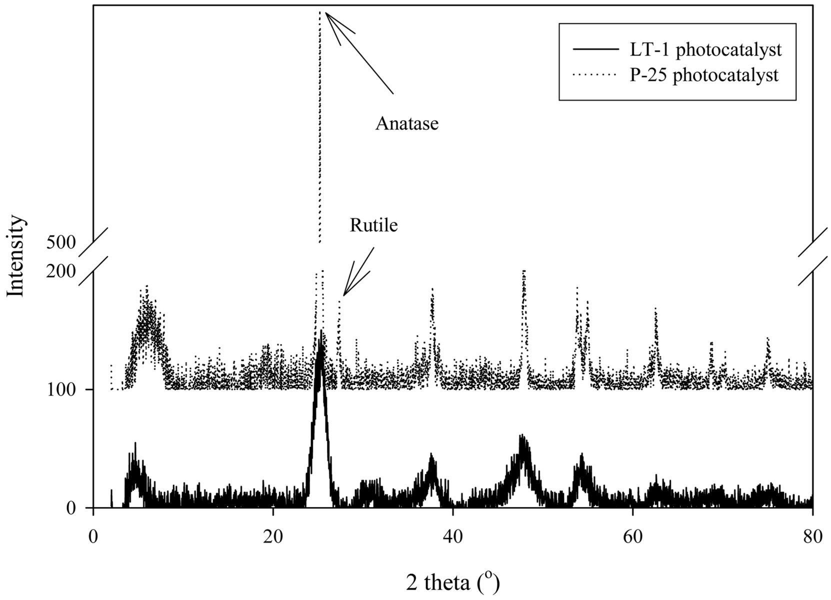


Fig. 4 XRD patterns of LT-1 and P-25

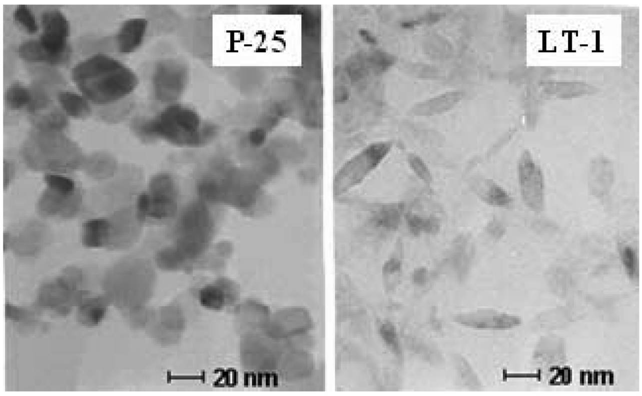


Fig. 5 TEM micrograph of the P-25 and LT-1 nanoparticles

3.2 Characteristics of PVDF membrane coated with LT-1 nano particles

The contact angles of the PVDF membrane coated with LT-1 photocatalyst using spray and dip coating techniques were comparatively studied. The results in Fig. 6 show that the contact angle of the clean membrane generally decreased after coating with TiO_2 or SiO_2 on its surface. The contact angle of the membrane with dip coating was 0° due to surface cracking resulted from excessive thickness of the coating layer. On the other hand, the membrane with spray coating did not show any change in the contact angle even after four layers of spray coating however, the contact angle decreased significantly after the eighth coating (Fig. 7). This shows that the PVDF membrane becomes hydrophilic in nature due to the membrane surface being completely covered by the TiO_2 coating layer during repeated spray coating. These results also indicate that the spray coating technique is more suitable than dip coating technique. In dip coating method, controlling the coating thickness

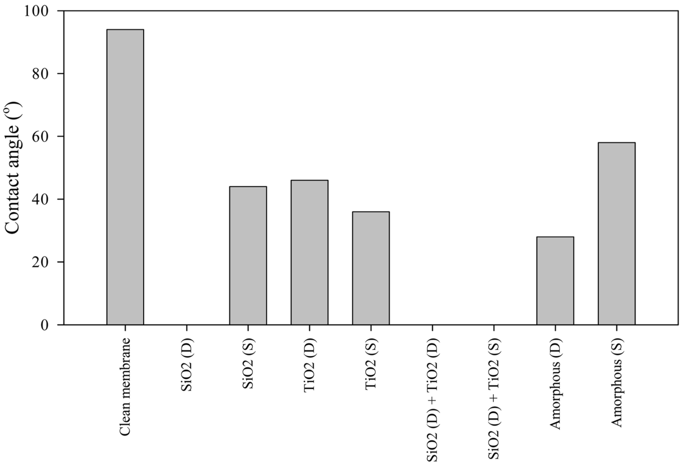


Fig. 6 Contact angle on PVDF membrane under different coating conditions. S: spray technique, D: dip technique

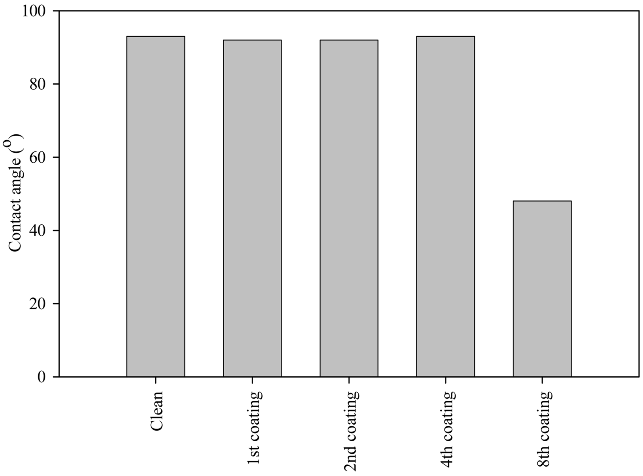


Fig. 7 Contact angles of different coating frequencies on PVDF membrane surface using spray technique

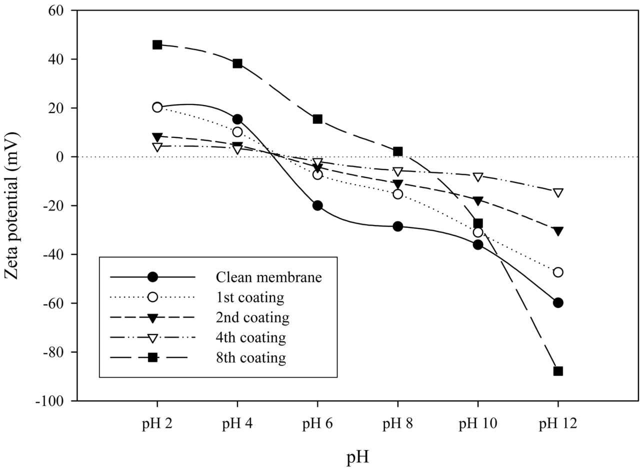
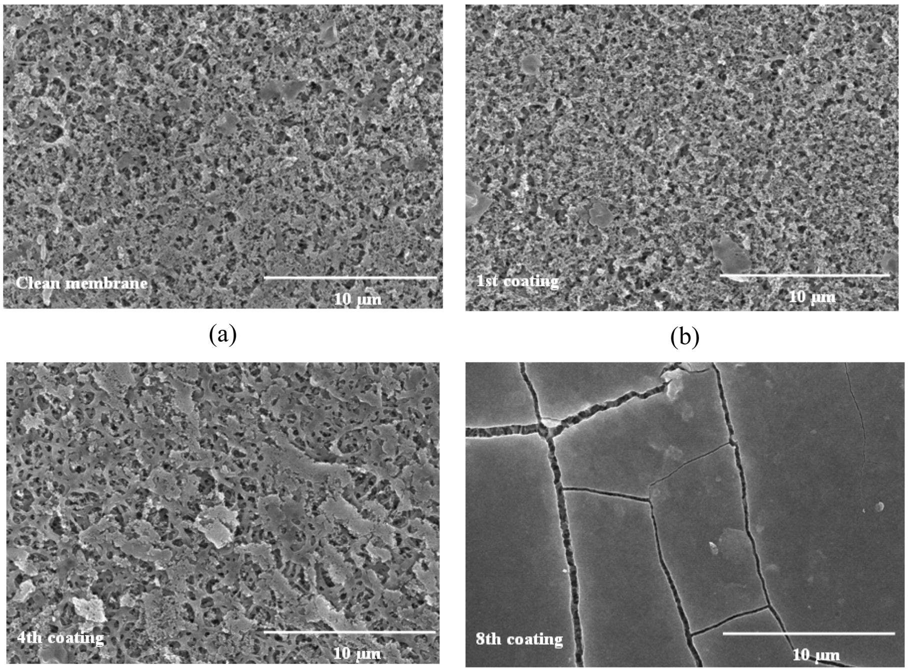


Fig. 8 Zeta potential of PVDF membrane surface as a function of solution pH, (background electrolyte concentration = 10 mM KCl)

was found difficult.

Fig. 8 shows the variation of zeta potential of a clean membrane and membranes coated with several layers of LT-1 photocatalyst as a function of pH. The iso-electric poi (IEP) of clean membrane and the membrane after 1st coating, 2nd coating and 4th coating was observed at pH 5, while after the 8th coating, the IEP was observed at pH 8.2. The IEP on the 8th coating membrane was therefore similar to that of LT-1 photocatalyst itself (IEP = pH 9). This result also suggests that when a dip coating method is adopted at more than pH 5, it leads to strong charge effect between LT-1 photocatalyst and PVDF membrane.

Figs. 9 shows the SEM images of PVDF membranes coated with different layers of LT-1 photocatalyst. The membrane was observed to be completely covered by TiO_2 particle after the



(a) (b)

(c) (d)

Fig. 9 Membrane surfaces of beam energies on SEM images of PVDF membrane after different coating frequencies (magnification of 5,000; 15 kV) using spray coating technique

eighth coating with a total TiO$_2$ thickness of 0.15 μm.

Fig. 10 presents 3D AFM images of LT-1 photocatalyst coated PVDF membrane. The images were analyzed by the XEI image processing tool (PSIA Corp., Korea) and the results shown in Table 2. When the PVDF membrane was coated with LT-1 photocatalyst, the porosity significantly decreased. A slight decrease in the average pore size of the membrane was also observed. However, the average roughness increased initially with the TiO$_2$ coating. As the number of coating layer is increased, the average roughness decreased indicating a complete TiO$_2$ coating layer on the membrane surface.

Fig. 11 shows the depth distribution of clean membrane and membranes coated with LT-1 photocatalyst. Here, the X-axis corresponds to depth while Y-axis corresponds to intensity of the selected depth. This displays the entire range of the height of the data points. The clean membrane indicated a homogeneous distribution of depth with the highest intensity at 0.63 m. However, after coating the membrane with LT-1 photocatalyst, the heterogeneous distribution of depth was shown to have the highest intensity of 0.65 μm (1st coating) and 0.18 μm (8th coating).

Fig. 12 shows the FTIR spectra of clean and coated membranes. Gu *et al.* (2005) reported that the intense absorption at 799 cm^{-1}, 1200 cm^{-1}, and 1400 cm^{-1} is a characteristic peak of PVDF, which represents CF$_2$ stretching and CH$_2$ twisting modes of PVDF. The PVDF membrane coated with LT-1 photocatalyst showed peaks at 1064 cm^{-1} and 2847 cm^{-1} were found, which represents alcohol and aldehyde functional groups. This may be due to H-bond as suggested by (Kim *et al.* 2003, Kolen'ko *et al.* 2005).

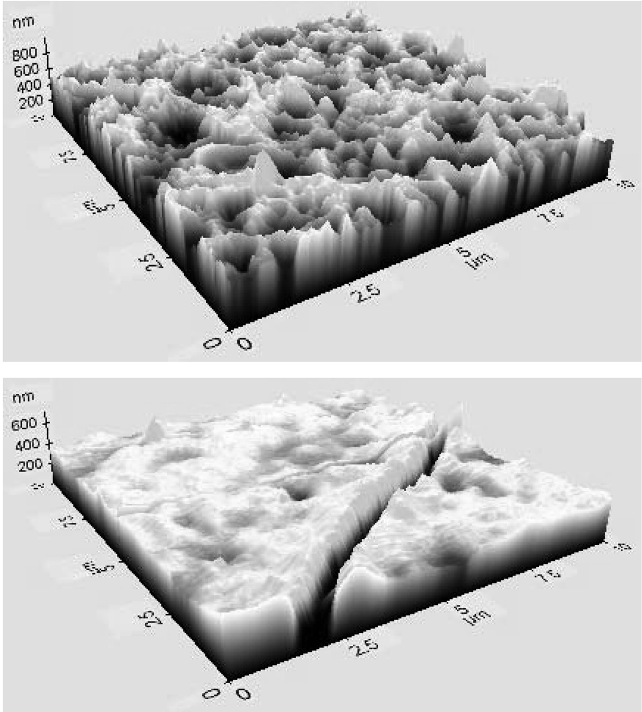


Fig. 10 Morphological changes of AFM images of coating PVDF membranes

Table 2 Characteristics of clean and coating PVDF membranes

	Porosity (%)	Pore size (µm)	Ra (µm)
Clean PVDF membrane	35	0.719	0.096
1st coating	7	0.599	0.195
8th coating	0.7	0.476	0.054

3.3 Filtration properties of TiO_2 coated MF membrane

The pure water flux of the PVDF membrane spray coated with several layers of LT-1 photocatalyst was evaluated. Pure water flux gradually decreased with more layers of coating (Fig. 13) and a linear correlation was observed between the number of coating layers and the permeate flux of the coated PVDF membrane (Fig. 14). The flux decrease was observed to be about 55% after the eighth coatings. This indicates that with more coating layers, the PVDF membrane surface is completely covered by the TiO_2 layer. The flux decline is therefore due to increased membrane resistance provided by the TiO_2 layer and also as a result of reduced pore size of the PVDF membrane (Refer Table 2).

3.4 Photocatalytic activity of TiO_2 coated MF membrane

The photocatalytic activity of the LT-1 coated PVDF membrane was tested by irradiating UV light

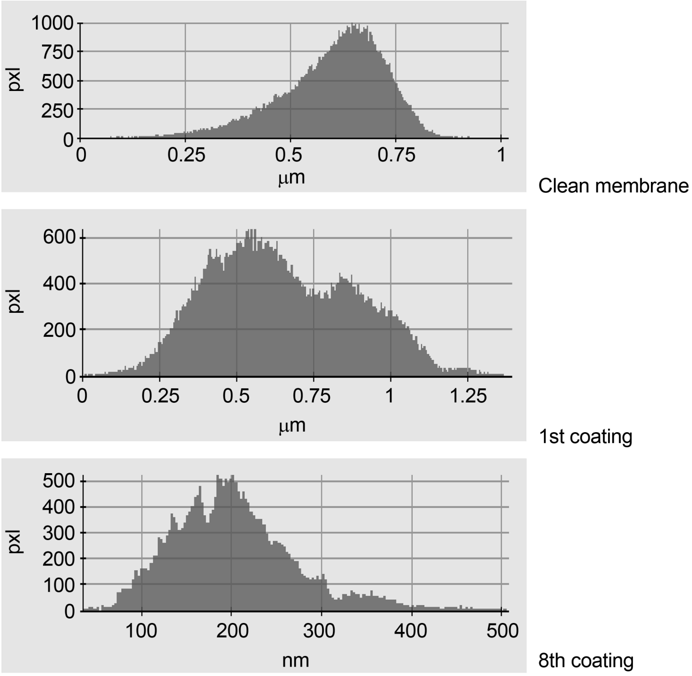


Fig. 11 Depth distribution of AFM image of clean and coating membranes (x axis: pixels)

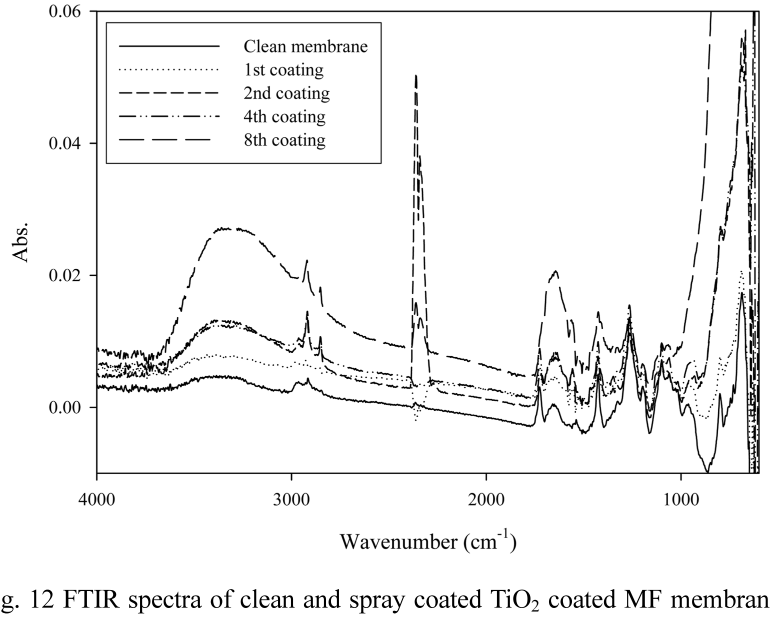


Fig. 12 FTIR spectra of clean and spray coated TiO$_2$ coated MF membranes

on the membrane surface during the crossflow filtration process. Methyelene blue (MB) and *E-Coli* were used in the feed water as models for organics and microorganisms respectively. As shown in

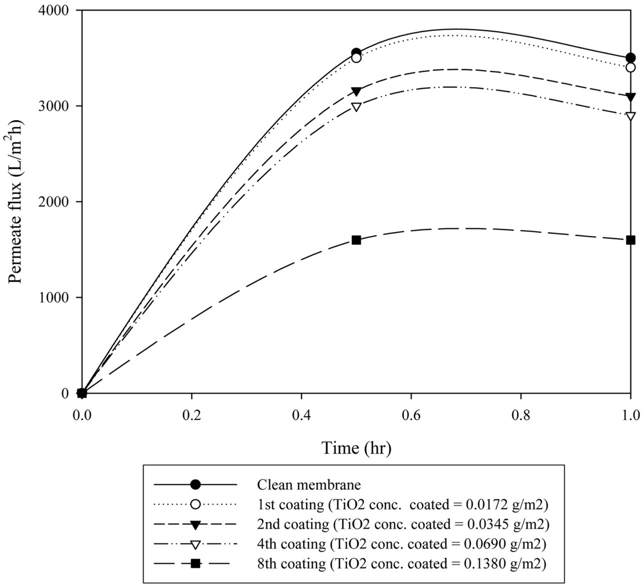


Fig. 13 Permeate flux of PVDF membrane after different TiO_2 coating frequencies with pure water (J_0 = 3550 L/m^2h at 30 kPa, cross-flow velocity = 0.5 m/s, Reynold's number: 735.5, shear stress: 5.33 Pa)

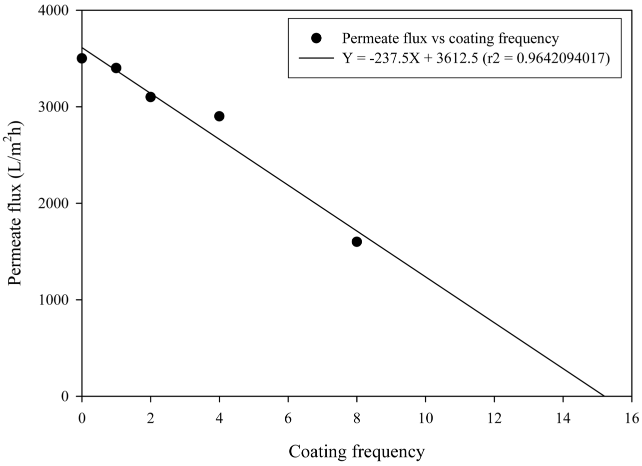


Fig. 14 Number of coating layers vs. permeate flux

Fig. 15, the removal efficiencies of MB increased with more layers of coating. The removal efficiency of MB was more than 20% after the eighth coating which is twice as high as the removal efficiency of an uncoated PVDF membrane. The number of coating layers did not have any significant influence on the removal of *E-coli* however, the E.Coli removal was consistently high (99%) within 10 minutes of photocatalytic activity (Fig. 16). These results indicate that if a photocatalyst is carefully coated on the MF membrane such as PDVF, it could be useful in reducing organic and biofouling.

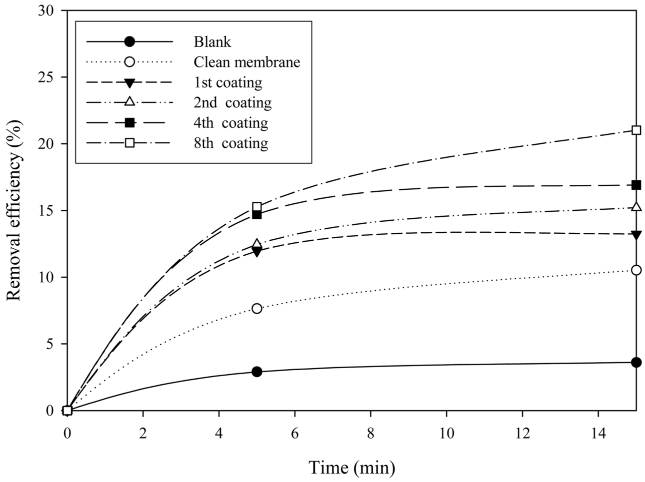


Fig. 15 Removal efficiency of methylene blue using photocatalytic reaction on coating membrane (initial concentration = 10.72 mg/L, coating membrane surface = 6 cm^2, UV lamp used = 3 Nos of 10 W each emitting at 352 nm wavelength, sample volume of methylene blue = 30 mL)

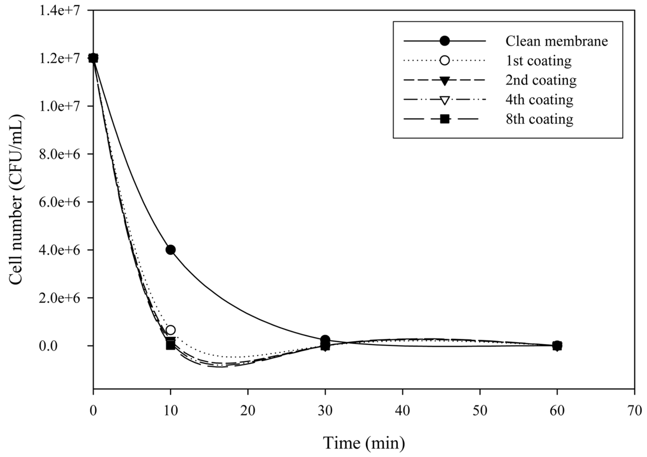


Fig. 16 Disinfection of E-coli with different coating frequencies

4. Conclusions

The following conclusions are drawn from this study:

- The nano sized TiO$_2$ photocatalyst was prepared by the sol-gel method using controlled hydrolysis of titanium tetraisopropoxide. The synthesized photocatalyst exhibited a flaky and pyramidal shape of about 30 nm in length and 4-7 nm in width. The synthesized TiO$_2$ existed mostly in anatase form and showed much larger surface area than the commercial Degussa P25.
- TiO$_2$ coated MF membrane was obtained by dip coating and spray coating techniques. Spray coating was found to be more suitable than the dip coating since dip coating resulted in excessive coating layer thickness which ultimately led to surface cracks. SEM images revealed

that the thickness of TiO_2 on the PVDF membrane surface after eight coats was about 0.15 μm. The TiO_2 coated PVDF membrane exhibited hydrophilic in nature.

- The pure water flux of the TiO_2 coated PVDF membrane decreased with more coating layers of TiO_2 on the membrane surface, the decline being linear.
- The TiO_2 coated MF membrane was successful in preventing organic fouling by MB and biofouling by *E-coli* in the presence of UV light on the membrane surface.
- Finally, the application of TiO_2 coated membrane could solve some of the critical problems of organic fouling and biofouling in membrane filtration.

Acknowledgements

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