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Research Article

Fouling Removal of UF Membrane with Coated TiO_2 Nanoparticles under UV Irradiation for Effluent Recovery during TFT-LCD Manufacturing

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An ultrafiltration (UF) membrane process was employed to treat the secondary effluent discharged from a manufacturing of thin film transistor-liquid crystal display (TFT-LCD) in this study. A bench-scale system was performed to evaluate the fouling removal of a UF membrane with coated titanium dioxide (TiO_2) nanoparticles under UV irradiation. The operating pressure and feed temperature were controlled at 300 KN/m^2 and 25°C, respectively. It was found that the optimum operating conditions were attained with TiO_2 concentrations of 10 wt% for both 5 KD and 10 KD MWCO. Continuous UV irradiation of 5 KD MWCO improved the permeate flux rate from 45.0% to 59.5% after 4 hours of operation. SEM-EDS analysis also showed that the photocatalytic effect had reduced the average thickness of cake fouling on the membrane from 6.40 μm to 2.70 μm for 5 KD MWCO and from 6.70 μm to 3.1 μm for 10 KD MWCO. In addition, the membrane contact angle was reduced from 54° to 44°. The photocatalytic properties of TiO_2 apparently increased the hydrophilicity of the membrane surface, thereby reducing membrane fouling.

1. Introduction

Plants in Taiwan are usually required to increase the recovery rate for their effluents, but the effluents usually contain many materials that need to be removed further, including suspended solids, colloid matter, and other trace elements; otherwise, the water quality cannot meet the requirements for reuse. In order to improve the quality, the upgrading method is needed. Membrane technology offers the greatest potential due to its relatively high removal rate, ease of setup, and relatively small requirements. However, membrane treatments have operating problems such as concentration polarization and membrane fouling [1]. In particular, fouling from the effluent causes serious problems. Concentration polarization and membrane fouling decrease the permeate flux and recovery rate while increasing the operating cost and shortening the membrane life [1–3]. Concentration polarization is induced by solute accumulation on the membrane. In a crossflow, this accumulation normally decreases, because solutes can be removed by shear force [4, 5].

Membrane fouling cannot be easily removed; however, there are many methods that prevent membrane fouling, such as the pretreatment of feed water and the cleaning of membranes. Pretreatment methods include sand filtering, coagulation followed by sand filtering, activated carbon adsorption, and dosing with oxidants or antifouling agents [6, 7]. The membranes are usually cleaned with some chemicals, by back flushing with pure water or by permeation. They either break off the operation or incur costs related to chemical dosing and waste disposal. Photocatalysis has recently been applied in fouling removal of membranes and in the enhancement of permeate flux [8–14]. Some studies even claimed that UV/TiO_2, a photocatalysis process, could reach the self-cleaning effect [10, 11].

UV/TiO_2 can generate various free radicals, such as hydrated electron (Eaq^-), hydroxyl radical ($OH^\bullet$), and oxide radical ion ($O^{-\bullet}$), to oxidize stubborn organic matters [15]. Moreover, UV/TiO_2 may modify the superhydrophilicity of a membrane to increase the permeate flux [10, 16]. Kim et al. successfully fixed TiO_2 particles on the RO membrane in their study [8]. After UV radiation of TiO_2 for 4 hours, a reverse osmosis (RO) process killed the water-born microorganisms effectively and thereby reduced biofouling and increased the permeate flux. Yang et al. found that PSF/TiO_2 composite improved the hydrophilicity of the UF membrane and even reduced the fouling without UV radiation [9]. Madaeni and Ghaemi [10] and Rahimpour et al. [11] coated TiO_2 on RO and UF membranes, respectively. After UV radiation for 10–20 minutes, both were able to reduce the fouling, increase the permeate flux, and even attain the self-cleaning effect. Wu et al. produced the composite membrane of TiO_2 and PES [12]; they observed that the composite membrane had the reduction in fouling and an increase in permeate flux without UV radiation. However, the membrane pore became clogged with the increase of TiO_2 concentration. Syafei et al. even utilized the high-temperature durability of a ceramic membrane [13]; they successfully sintered TiO_2 particles on a ceramic membrane. Although they found that the composite membrane led to the reduction of humic matter, the permeate flux was not improved. Furthermore, Zhang et al. also found that a nanofiltration membrane made of nanoline TiO_2 under continuous UV radiation could reduce fouling, increase the permeate flux, and destroy the humic matter [14].

As described by the previous works, most processes could increase the permeate flux and even attain the self-cleaning effect. However, whether it could be applied to real wastewater is questionable and worthy of further study. This study applied an UF membrane coated with TiO_2 nanoparticles under UV irradiation to pretreat the secondary effluent from the wastewater of a TFT-LCD manufacturing plant and investigated the removal of fouling from ultrafiltration membranes in order to improve the recovery rate. We evaluated the affection of the three parameters, namely, concentration of TiO_2 nanoparticles, molecular weight cutoff (MWCO), and UV irradiation time. At the end of the experiments, the characteristic changes of dry membrane surface were observed.

2. Materials and Methods

2.1. Feed Water. In the experiments in this study, we randomly sampled the secondary effluent of the biological treatment system from a TFT-LCD manufacturing plant in Chunan Science Park in Taiwan. The influent flow to the biological treatment system contained little or no toxic organic waste, coming primarily from the production line and the sewerage wastewater. Before entering the biological treatment system, the fluoride-containing wastewater had been treated by chemical precipitation with $CaCl_2$ and coagulation sedimentation. Table 1 indicates that the water quality of the effluent was stable, showing little variation.

Table 1: Water quality of secondary effluent.

pH	6.74~7.28
Conductivity (mS/cm)	2.47~2.97
Turbidity (NTU)	1.57~2.02
TOC (mg/L)	2.16~2.58

2.2. Experimental Setup. Figure 1 shows the bench-scale UF and UV/TiO_2 system used in the experiments. The plate-and-frame module was made of acrylic plate and PES membrane. Two UV_{365} tubes with 18-W input were adopted to irradiate on the plate-and-frame module. PES membranes with 5 KD and 10 KD MWCO were used in the system. The membrane dimension was 7 cm (W) × 15 cm (L). TiO_2 (Degussa P-25, Germany) suspended solutions of 2 wt% to 10 wt% were prepared, and the membrane was then dipped in the TiO_2 solution for one hour. The membrane coated with TiO_2 was then taken out and rinsed with distilled water. Teflon tubing and stainless steel joints and valves were used throughout the system. Air was injected into a 20-liter feed water tank through a plate diffuser at the bottom of the tank to mix the water. A booster pump with 0.8 liter/minute capacity was employed to draw water from the feed water tank into the membrane module for the experiments.

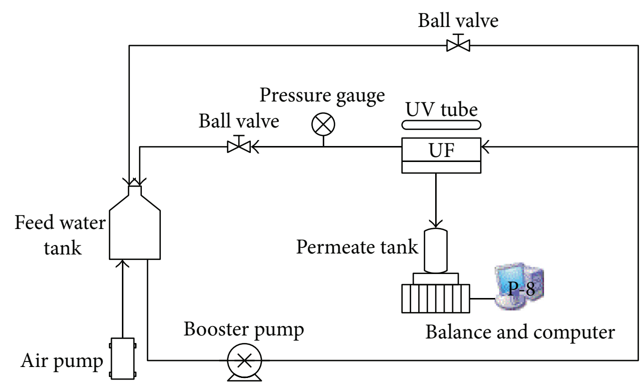
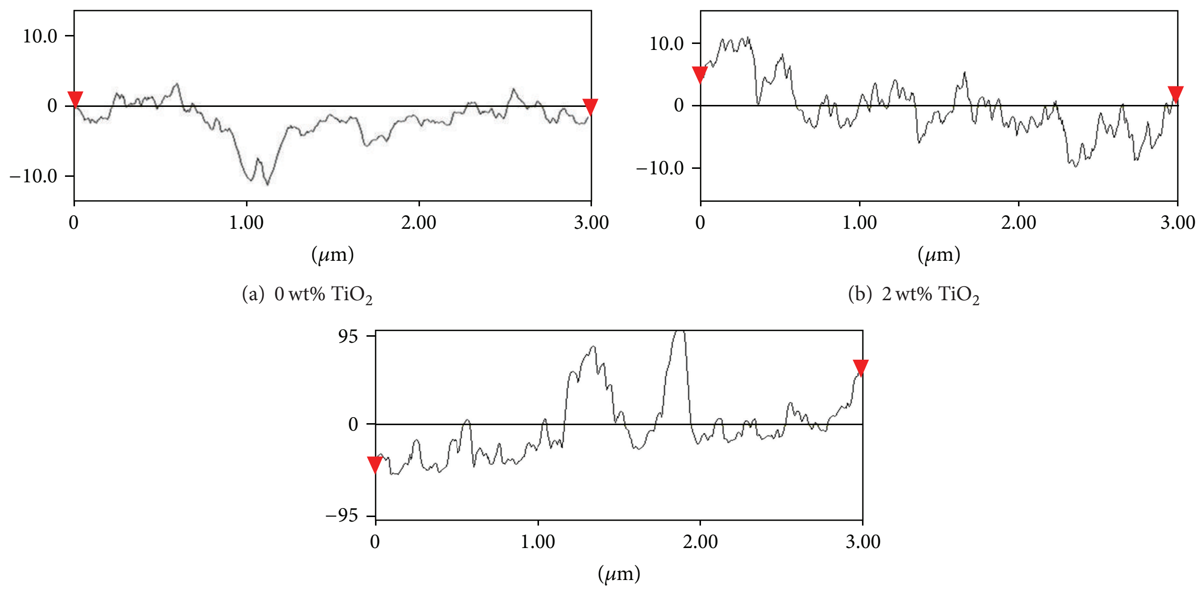


Figure 1: Diagram of the UF and UV/TiO_2 system.

2.3. Experimental Procedures

2.3.1. Pretreatment. Prior to the experiments, the new membrane was soaked in pure water overnight and then pretreated with pure water to achieve a more stable permeate flux. The water pressure was fixed at 300 KN/m^2, the water temperature was maintained at 25°C, and the velocity of the crossflow was about 0.20 m/s. The permeate flow was directly monitored by an electric balance. The system was kept running under these operating conditions for at least 9 hours. During the pretreatment, a more stable initial permeate flux (J_0) was achieved after 9 hours.

2.3.2. Membrane Property Test for Various TiO_2 Concentrations and UV Radiation. The test membranes were coated with TiO_2 of different concentrations. After the previous 9-hour pure water feed experiment, distilled water was then continuously pumped into the system. The water pressure during the experiment was still fixed at 300 KN/m^2, the water temperature was also maintained at 25°C, the velocity of the crossflow was 0.20 m/s, and the time for UV radiation was



(a) 0 wt% TiO_2 (b) 2 wt% TiO_2 (c) 10 wt% TiO_2

Figure 2: AFM analysis for different wt% of TiO_2 on the PES membrane.

4 hours. At the end of the experiment, microscopic observations of the dried membrane were made by using Fourier-transform infrared spectroscopy (FTIR-ATR, Thermo Nicolet Nexus-470), Contact Angle (Kruss DSA10), Atomic Force Microscopy (Digit Ins NanoScope SPM), and Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS, HITACHI S-800), respectively. Contact Angle was used to observe the hydrophilicity of the membrane surface, and Atomic Force Microscopy was used to measure the membrane surface roughness. FTIR-ATR and SEM-EDS were used to observe the appearance and the chemical composition of the membrane surface.

2.3.3. Ultrafiltration for Secondary Effluent. After the previous 9-hour pure water feed experiment, the secondary effluent was pumped into the system continuously. The water pressure during the experiments, the water temperature, the velocity of the crossflow, and the time for UV radiation were controlled as same as in the membrane property test. The permeate flow was also monitored directly by an electric balance and then stored in the permeate tank. The reject flow was recycled into the feed water tank. The experiment continued until the permeate flux (J) became more stable, which took about 4 hours. At the end of the experiment, microscopic observations of the dried membrane were made by using FTIR-ATR and SEM-EDS.

Additionally, in order to study the effects of different UV irradiation types on permeate flux, the experiment contained three different processes for the UF membranes (5 KD, 10% TiO_2). In the first process, prior to ultrafiltration, the membrane had been irradiated about 30 minutes. In the second process, the membrane was irradiated continuously after one hour of ultrafiltration. The third process was with continuous UV irradiation and ultrafiltration.

Table 2: Contact angle between deion water drop and the surface of the PES membrane.

	TiO_2 concentration (%)	Contact angle (°)
Without UV radiation	0	61
	5	56
	10	54
With UV radiation	0	61
	5	47
	10	44

2.4. Water Analysis. The quality of feed water and permeate was measured using Standard Methods for the Examination of Water and Wastewater before and after changing the operational mode, including the analysis of pH, conductivity, turbidity, and TOC measurements. Laser Particle Size Analyzer (ASYS HIAC ROYCO 8000A) was used to measure the size distribution of particles in the water.

3. Results and Discussion

3.1. Effects of TiO_2 Concentration and UV Radiation on Membrane Properties. Table 2 shows that the contact angle reduced with increasing TiO_2 concentration. Since the smaller the contact angle is, the greater the hydrophilicity becomes, therefore, the increase in hydrophilicity of UV-radiated membrane was greater than that of the nonradiated one, in agreement with the findings of Laugel et al. [16]. Furthermore, Figure 2 presents that with increasing TiO_2 concentration, membrane surface roughness also increases, which enhances the surface area for UV radiation. Increases in both hydrophilicity and UV radiation area of the membrane surface would affect the permeate flux.

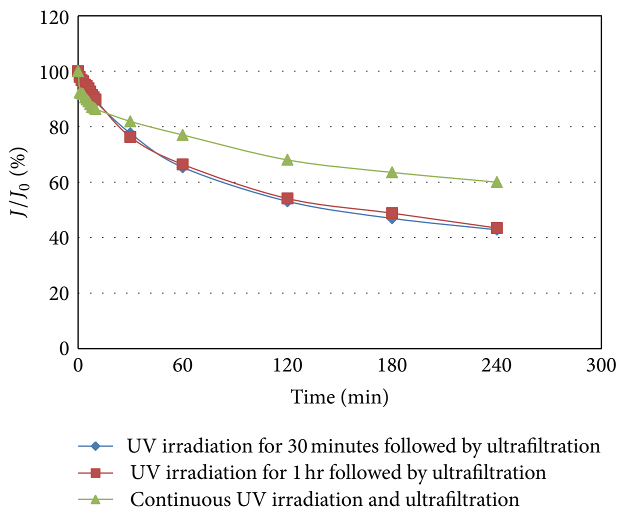


Figure 3: Effects of different UV irradiation types on permeate flux (5 KD, 10% TiO_2).

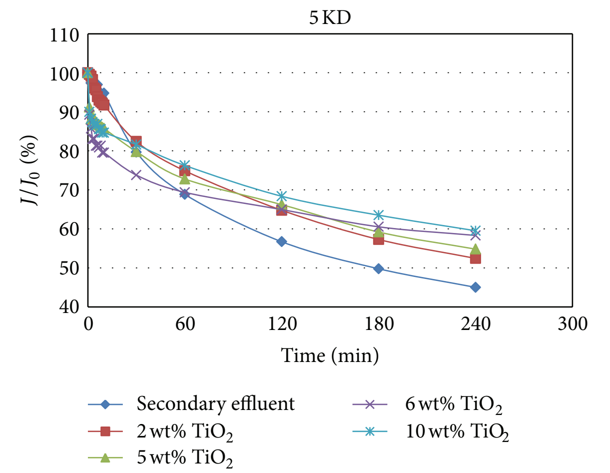


Figure 4: Effects of different TiO_2 concentration UV radiation on permeate flux during continuous UV radiation (5 KD).

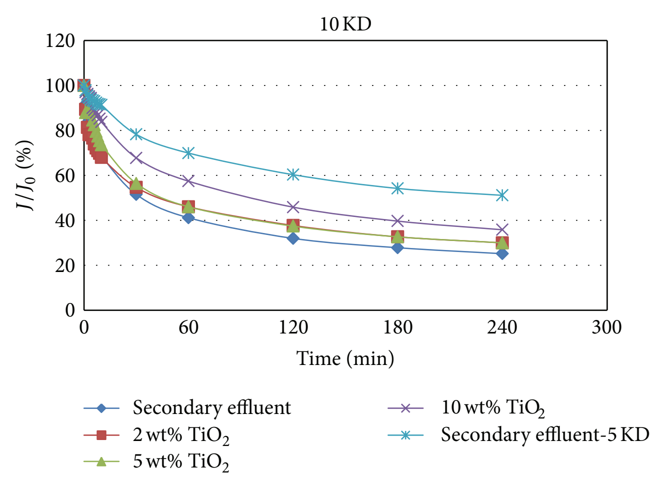


Figure 5: Effects of different TiO_2 concentration UV radiation on permeate flux during continuous UV radiation (10 KD).

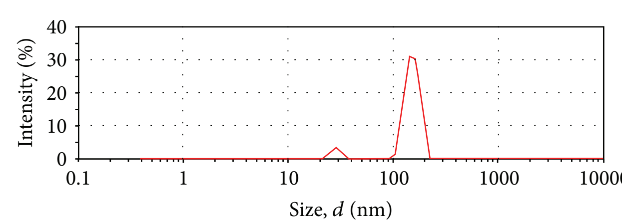
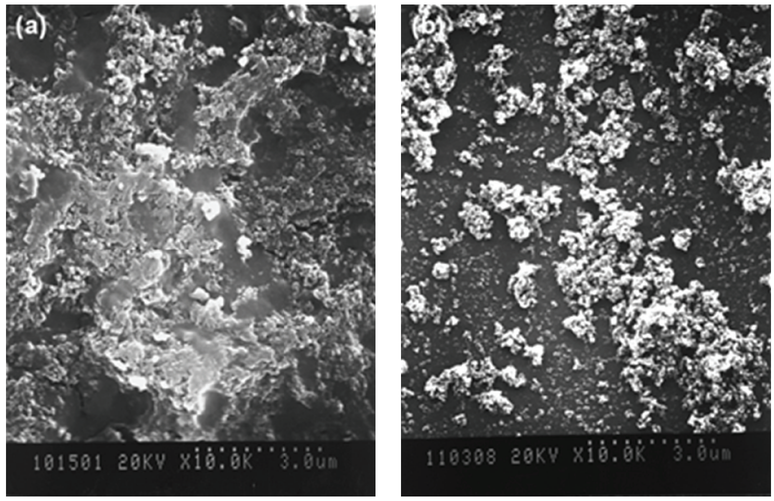


Figure 6: Size distribution of TFT-LCD effluent.

3.2. Effects of UV Irradiation and TiO_2 Concentration on Permeate Flux. Figure 3 shows the effects of different UV irradiation types on permeate flux. As can be seen, the initial permeate flux (J_0) was 145.2 L/m^2·hr for the 5 KD UF membrane in the pretreatment test. In the first process, prior to ultrafiltration, the membrane had been irradiated about 30 minutes. In the second process, the membrane was irradiated after one hour of ultrafiltration. Both permeates were less than that of the third process, with continuous UV irradiation and ultrafiltration. It was apparent that continuous UV irradiation not only increased the hydrophilicity of the UV-radiated membrane but also continuously destroyed the organic fouling on the membrane surface, thereby increasing the more permeate flux. Thus for effluent recovery, continuous UV irradiation was necessary during increasing the permeate flux.

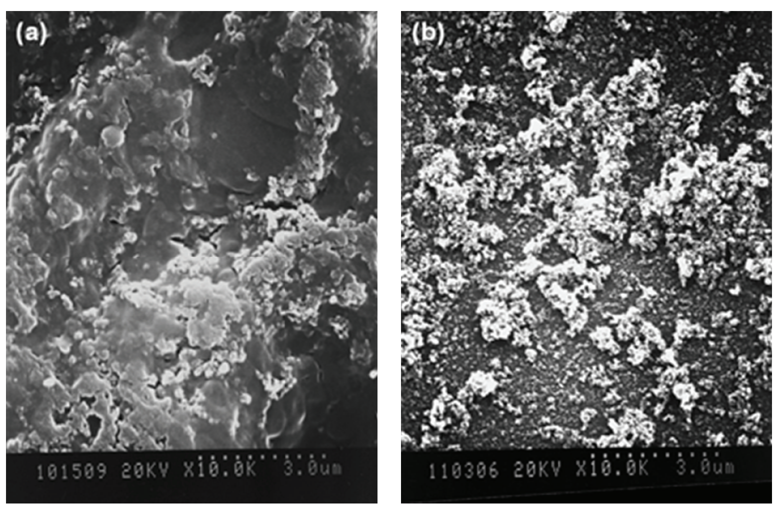
Figure 4 shows the effect of different TiO_2 concentrations on permeate flux during continuous UV irradiation. After 4 hours, the permeate flux (J/J_0) for 2%, 5%, 6%, and 10% TiO_2 rose to 52.4%, 54.85%, 58.35%, and 59.55%, respectively. This indicates that attaching TiO_2 on the 5 KD UF membrane had a good effect on the permeate flux rate. Moreover, the higher the TiO_2 concentration was, the better the effect was. As noted previously, the increase of permeation flux may be due to the increase of hydrophilicity and the membrane surface.

Figure 5 indicates that more TiO_2 concentration for 10 KD also improved the J/J_0 better than that without TiO_2 attached. Nevertheless, comparing J/J_0 with 5 KD, the J/J_0 for 10 KD without TiO_2 attached was 25.1% after 4 hours, which is less than the rate of 45% for 5 KD. Figure 6 indicates that the size distribution of TFT-LCD effluent primarily ranged in 20–40 nm and 100–200 nm. Because the size of water particles ranged in 20–40 nm which was near the pore size for 10 KD membrane, some water particles would pass through the pore of the membrane and deposit onto the inner membrane pore which could not be irradiated by UV light, thereby reducing the permeate flux. Some studies had also indicated that when the membrane pore size is near the size of water particle, the permeate flux is less [17, 18]. On the contrary, when these water particles would deposit mostly on the 5 KD membrane surface and form cake fouling that could easily be flushed out by crossflow, so that the permeate of the 5 KD membrane was larger than that of 10 KD membrane. It seemed that using UV/TiO_2 photocatalysis to remove the fouling of ultrafiltration for TFT-LCD effluent had less



(a) (b)

Figure 7: Surface of the UF membrane after ultrafiltration (5 KD, magnified 10000x), (a) without TiO_2 and (b) with 10 wt% TiO_2.



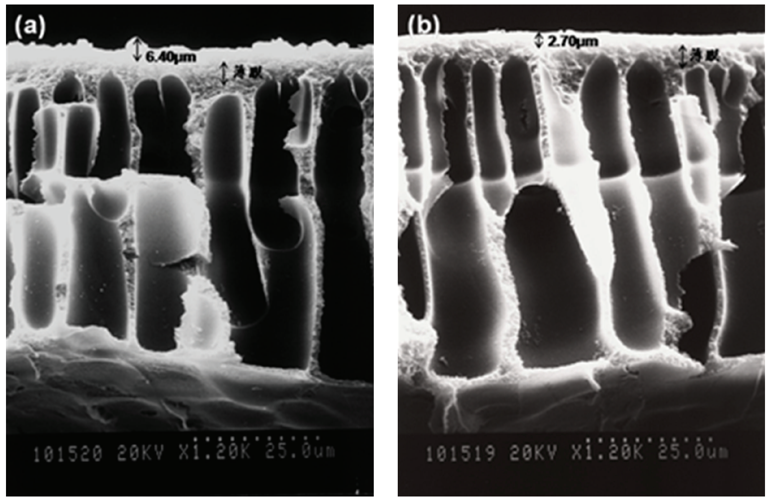
(a) (b)

Figure 8: Surface of the UF membrane after ultrafiltration (10 KD, magnified 10000x), (a) with 0 wt% TiO_2 and (b) with 10 wt% TiO_2.

effectiveness than that by ozonation [6], since ozonation can not only oxidize and destroy cake fouling on membrane but also oxidize particles that had been adsorbed onto the membrane inner pore, especially with organic matter.

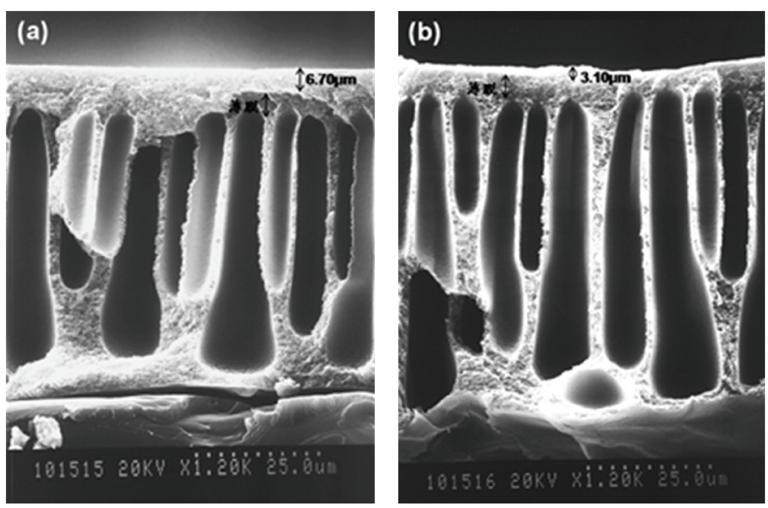
3.3. Results of SEM-EDS and FTIR-ATR Analyses. Figures 7 and 8 also present the SEM results of membrane surface. The layered stack of fouling was found during without TiO_2 coating, as shown in Figures 7(a) and 8(a), but little fouling was formed with glomeration on the membrane surface during with a 10 wt% of TiO_2 coating, as shown in Figures 7(b) and 8(b). This glomeration phenomenon may be caused by the surface absorption between the nano-TiO_2 particles and the water solution particles, which allows for TiO_2 exposure under continuous UV radiation. Figures 9(a) and 10(b) present the fouling depths of 6.40 μm without TiO_2 coating and 2.7 μm with 10% TiO_2 coating for 5 KD UF membranes, respectively. The UV/TiO_2 photocatalysis would destroy organic matter of the cake deposit into small organic matter by $OH^{\bullet}$ formation, causing the organic cake deposit on the membrane surface to become looser, also indicated by Zhang et al. [14].

This study used FTIR-ATR analysis to observe the chemical adsorption of TiO_2 on the membrane surface. The characteristic peak for new membrane was observed in the range of 3400–3600 cm^{-1}, as shown in Figure 11(a), that displays a weak O–H functional group on the PES membrane, also indicated by Rahimpour et al. [11]. The peak in 650–680 cm^{-1} was also observed in Figures 11(b) and 11(c), which is the characteristic of TiO_2 peaks, as indicated by Madaeni and Ghaemi [10], but the peak in 3400–3600 cm^{-1} was not apparent. Thus, it can be inferred that TiO_2 had coated on



(a) (b)

Figure 9: Profile of the UF membrane after ultrafiltration (5 KD, magnified 1200x), (a) with 0 wt% TiO_2 and (b) with 10 wt% TiO_2.



(a) (b)

Figure 10: Profile of the UF membrane after ultrafiltration (10 KD, magnified 1200x), (a) with 0 wt% TiO_2 and (b) with 10 wt% TiO_2.

the surface of the PES membrane. We have also found that the characteristic peak 650–680 cm^{-1} of titanium dioxide still exists on the membrane coated with Degussa P25 after filtration by Figure 11(c). However, the characteristic peak intensity is slightly weakened, so the partial peeling of titanium dioxide may occur probably.

3.4. Effects of TiO_2 Concentration and Continuous UV Radiation on Permeate Quality. Figures 12 and 13 present the permeate quality when treated with different TiO_2 concentrations. For the 5 KD membrane without TiO_2 coating (0 wt%), the removal rates ($1 - C/C_0$) of turbidity, TOC, and conductivity were 83.4%, 47.7%, and 25.5%; the removal rates for the 10 KD membranes without TiO_2 coating (0 wt%) were 80.1%, 48.0%, and 16.2%, respectively. The removal of turbidity was the greatest, followed by TOC and then by conductivity in all results. It is obvious that the removal function for UF was particle screening.

The UV/TiO_2 photocatalysis primarily destroyed the organic matter screened on the membrane surface, turning it into dissolved organic matter by $OH^{\bullet}$ reaction, as previously indicated by Zhang et al. [14]. Therefore, the dissolved matter such as TOC or conductivity was removed less with the increase of TiO_2 concentration.

4. Conclusion

This study was carried out within three parameters, namely, TiO_2 concentration, MWCO, and UV irradiation time. Among these parameters, MWCO affected the permeate flux mostly, because the size distribution of feed water particles was close to the pore size of the membrane, allowing it

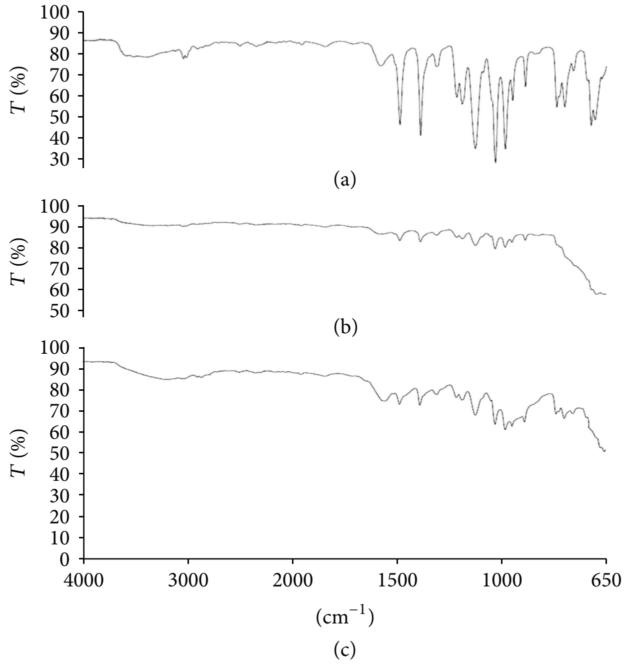


Figure 11: FTIR-ATR analysis for observing chemical adsorption of TiO_2 on the membrane surface: (a) new membrane without TiO_2 coating, (b) before ultrafiltration with TiO_2 coating, and (c) after ultrafiltration with TiO_2 coating.

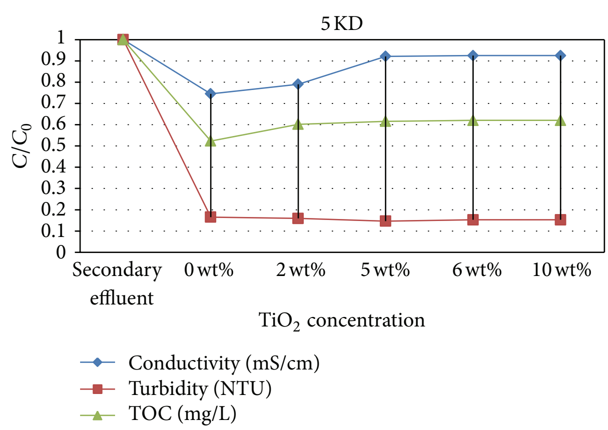


Figure 12: Permeate quality when treated with different TiO_2 concentrations (5 KD).

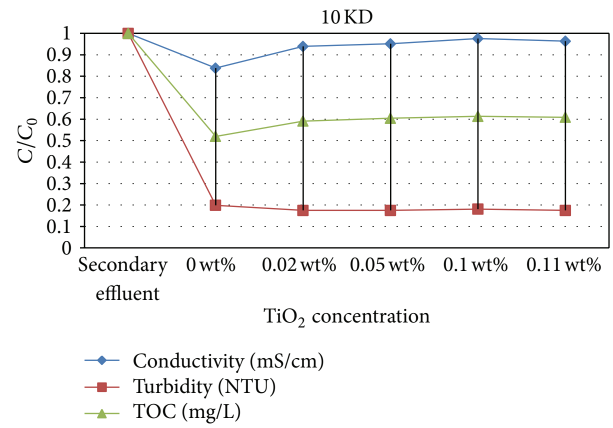


Figure 13: Permeate quality when treated with different TiO_2 concentrations (10 KD).

to pass through the pore of membrane and deposit onto the membrane pore, thereby reducing the permeate flux. Therefore, when selecting the MWCO of membrane, it is necessary to analyze the size distribution of feed water.

Photocatalysis increased the hydrophilicity and the UV radiation area of the membrane surface, leading to the increase in permeation flux. The UV/TiO_2 photocatalysis also destroyed organic matter of the cake deposit into small organic matter by $OH^{\bullet}$ formation, causing the organic cake deposit on the membrane surface to become looser. Since the photocatalysis changed the hydrophilicity, which made it more difficult for the cake deposit to adhere to the membrane surface, the cake deposit could be flushed away by crossflow more easily. It is apparent that continuous UV irradiation not only increases the hydrophilicity of the UV-radiated membrane but also continuously destroys the organic fouling on the membrane surface, thereby increasing the more permeate flux. Thus for effluent recovery, continuous UV irradiation is necessary during increasing the permeate flux.

Although discontinuous photocatalysis can increase membrane hydrophilicity, self-cleaning effect is not good for discontinuous UV irradiation in this study. Therefore, continuous UV irradiation is necessary to destroy the organic fouling on the membrane for self-cleaning effect.

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