Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2013, Article ID 796421, 6 pages
http://dx.doi.org/10.1155/2013/796421

Research Article

Combination of TiO_2-Film Photocatalysis and Ultrafiltration to Treat Wastewater

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Received 22 May 2013; Revised 29 August 2013; Accepted 4 September 2013

Academic Editor: Peter Robertson

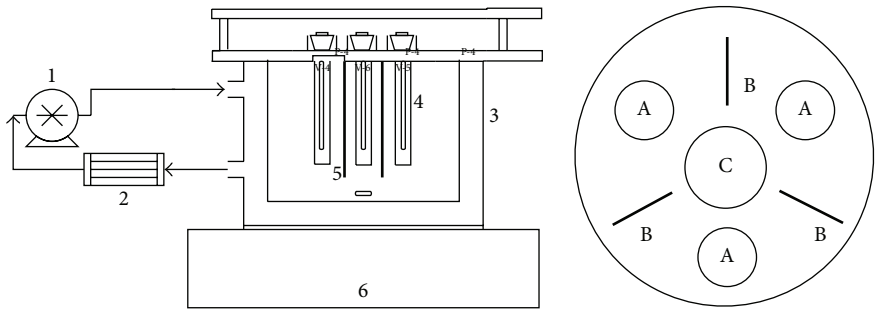
In this study, a combination of TiO_2-film photocatalysis reactor and ultrafiltration was used treat the secondary effluent from the manufacturing of thin film transistor-liquid crystal display (TFT-LCD). TiO_2 particles, as a photocatalyst, were immobilized on silica glass to form TiO_2-film by the sol-gel and dip coating methods. TiO_2-film photocatalysis was done within three parameters, including number of coating times of TiO_2-film, wavelengths of UV light source, and operating time. During ultrafiltration, the operating pressure and feed water temperature were controlled at 300 KN/m^2 and 25°C, respectively. It was found that TiO_2-film photocatalysis followed by ultrafiltration increased the removal of total organic carbon (TOC) to 47.13% and 49.94% for 5 KDa and 10 KDa membranes, respectively. It was also found that the process increased the permeate flux rate (ca 23%) for 10 KDa membrane after 6 hours of operation, since some larger organic matter had been broken into small organic matter and some small organic matter had been mineralized into CO_2 following TiO_2-film photocatalysis. Therefore, combining TiO_2-film photocatalysis reactor and ultrafiltration can improve organic wastewater quality and increase the permeate flux of ultrafiltration membrane, which may enhance the recycling and reuse of wastewater.

1. Introduction

TFT LCD manufacture is one of the booming high-tech industries in Taiwan in recent years. During the manufacturing process a large number of chemical solvents and water is needed to use, and a lot of wastewater will be produced. TFT-LCD manufacturing usually combines array, panel, and module processes. The wastewater of the TFT-LCD factory is divided into fluoride waste from rinsing, inorganic waste from etching, less toxic organic waste, and sewerage wastewater. The wastewater mostly came from the array process. The developer, stripper, and rinse solvents were used in the array process, so less toxic matter was produced in the wastewater [1]. The less toxic organic waste and the sewerage wastewater could be treated together by biological or secondary treatment system, but the fluoride waste would be pretreated before being introduced to the biological treatment system.

Water sources are insufficient in Taiwan, and it is difficult to obtain new ones because of environmental protests. Authorities have passed legislation compelling factory owners to increase the recovery rate of wastewater from the high-tech industry. To enhance the recovery rate of effluent from TFT-LCD factories, the suspended solids, colloid matter, and other trace elements need to be removed. Many methods have been studied and developed in Taiwan, of which reverse osmosis (RO) is one of the methods with the greatest potential due to its relatively higher removal rate, ease of set up, and minimal land requirements.

However, before RO treatment, other membrane treatments, for example, microfiltration (MF) or ultrafiltration (UF), are usually required. Otherwise, the RO membranes may be rapidly blocked by various foulings from the influent water [2, 3]. However, the UF or MF treatments have operational problems like concentration polarization and membrane fouling. Concentration polarization and membrane fouling decrease the permeate flux, the recovery rate, increase the operating cost, and shorten membrane life [4]. The former is induced by solute accumulation on the membrane. In



(1) Pump (2) Water bath with constant temperature (A) UV lamp in silica glass tube
(3) Reactor (4) UV lamp in silica glass tube (B) Sheet glass
(5) Sheet glass (6) Magnetic stirrer (C) Sampling hole
(Cross-sectional view) (Top view for reactor)

(a) (b)

Figure 1: Equipment for TiO_2-film photocatalysis.

a cross flow this accumulation normally decreases, because solutes can be removed by shear force [5], but membrane fouling is not so easily removed. There are many methods to prevent fouling, including pretreating the feed water and cleaning the membranes.

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 refractory organic matters in the wastewater [6, 7]. Earlier studies usually added titanium dioxide powder directly into the solution to form suspension reactor that has the advantage of a larger specific surface area. However, the small particles would increase turbidity significantly and easily gather a light shielding effect, so the addition of titanium dioxide concentration needs to be carefully controlled. Further, it will cause the follow-up problem such as separation and recovery of small suspension particles and increased overall processing costs [8–11]. Therefore, thin film reactor has been used to solve the problem occurred in the suspension reactor [12–15].

In this study, a combination of TiO_2-film photocatalysis reactor and ultrafiltration was used to treat TFT-LCD effluent. TiO_2 particles, as a photocatalyst, were immobilized on the silica glass to form TiO_2-film by the sol-gel method and dip coating method. The aim of the study is chiefly to treat the feed water (TFT-LCD effluent) by TiO_2-film photocatalysis to improve water quality or increase the permeate flux of the ultrafiltration membrane, which may enhance the recycling and reuse of wastewater.

2. Experimental

2.1. Feed Water. 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 toxic organic waste, coming primarily from the manufacturing process and the sewerage wastewater. Before entering the biological treatment system, the fluoride-containing wastewater had been treated by chemical ($CaCl_2$) dosing and coagulation sedimentation. The water quality of the effluent was relatively stable and showed little variation.

2.2. Preparation of TiO_2-Film. In a sol-gel method, titanium (IV) *n*-butioxde ($C_{16}H_{36}O_4Ti$) was used as an initiator, which was poured into ethyl alcohol to form a highly uniform TiO_2 gel solution, and then the merchandized TiO_2 powder (Degussa P-25, Germany) was dosed into the gel solution to form the coating solution [14]. During the preparation of the TiO_2-film, the coating solution was coated on both sides of the sheet glass by the dip coating method. The sheet glass was 20 cm (L) × 5 cm (W) × 0.3 cm (H). The numbers of coating times were 1, 2, 3, 5 and 7 for every batch test, respectively. The TiO_2-film was dried at room temperature for some time after dipping, and cured at 80°C in an oven for 30 minutes, and the first coating was completed. If wish to obtain multilayer film, we could repeat the above step of coating. Finally, the cured film was sintered at 450°C for 1 hour, the TiO_2 sol substrate on the glass surface would be more closely, and then the whole dip coating process of the titanium dioxide film was completed.

At the end of the experiment, microscopic observation of the TiO_2-film was made using Scanning Electron Microscopy (HITACHI S-800, Japan).

2.3. Experimental Setup. A two-liter reactor contains three UV lamps and three sheets of glass for TiO_2 coating, as shown in Figure 1. The selected wavelengths of UV light source in the reactor were 254 and 365 nm lamps, respectively. The water temperature in the reactor was constant controlled by a water bath with recirculating cooling water. A magnetic stirrer at the bottom of the reactor was used to completely mix the feed water.

Figure 2 shows the bench-scale UF system used in the experiments. The plate-and-frame module was made of acrylic plate and polyethersulfone (PES) membrane. PES membranes with 5 KD and 10 KD MWCO were used in the system. The membrane dimension was 7 cm (W) × 15 cm (L). Teflon tubing and stainless joints and valves were used

throughout the system. A booster pump with a 0.8 liter/minute capacity was employed to draw water from the feed water tank into the membrane module for the experiments.

2.4. Experimental Procedures

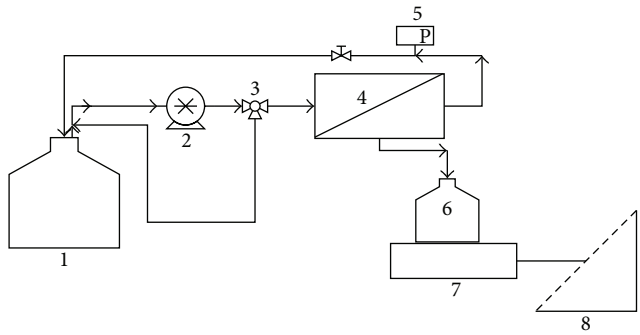
2.4.1. Treating Feed Water (TFT-LCD Effluent) by TiO_2-Film Photocatalysis. TiO_2-film photocatalysis was carried out with parameters, namely, coating times of TiO_2-film, wavelengths of UV light source, and irradiating periods. Two liters of feed water were put into the TiO_2-film photocatalysis reactor, as shown in Figure 1. The numbers of coating times were 3, 5 and 7 times for every batch test, respectively. The water temperature in the reactor was controlled at 25°C by water bath. The three lamps of UV_{365} or UV_{254} were adopted to irradiate the three sheets of glass with TiO_2 coating film. The UV lamps used in the study were Sparkie BLB-6W, and GLQ-8W, China. The average distance between UV lamps and TiO_2-films was 3 cm. The irradiating periods were 60, 120, 180, 240, and 360 minutes for every batch test. After every test, the treated water quality was measured.

2.4.2. Pretreatment for Ultrafiltration. 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 also fixed at 300 KN/m^2, the water temperature was maintained at 25°C, and the velocity of the cross flow was about 0.20 m/s. The permeate flux was directly monitored by an electric balance. The system was kept running under this operating condition for at least 9 hours. During the pretreatment, a more stable initial permeate flux (J_0) was achieved after 9 hours.

After the above ultrafiltration test for pure water, the feed water (TFT-LCD effluent) in the 10-liter tank was then drawn into ultrafiltration. The water pressure, temperature, and the velocity of the cross flow were the same as the above UF operation. The permeate flow was directly monitored by an electric balance. The reject flow was returned into the 10-liter tank. The system was kept running under this operating condition for at least 6 hours. The permeate flux for feed water without TiO_2-film photocatalysis was gotten in the test.

2.4.3. Combination of TiO_2-Film Photocatalysis and Ultrafiltration for Treating TFT-LCD Effluent. First, 10 liters of treated feed water were collected by TiO_2-film photocatalysis for every batch test and then followed by ultrafiltration.

After the above 9-hour pretreatment for pure water, the collected treated 10 liters feed water was pumped into the ultrafiltration system continuously in Figure 2. The water pressure during the experiments was still fixed at 300 KN/m^2, the water temperature was maintained at 25°C, and the velocity of the cross flow was 0.20 m/s. 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 became more stable, which took about 6 hours. The treated water quality of photocatalysis or ultrafiltration was also measured.



(1) Feed water tank
(2) Booster pump
(3) Ball valve
(4) UF
(5) Pressure gauge
(6) Permeate tank
(7) Balance
(8) Computer

Figure 2: Diagram of the UF system.

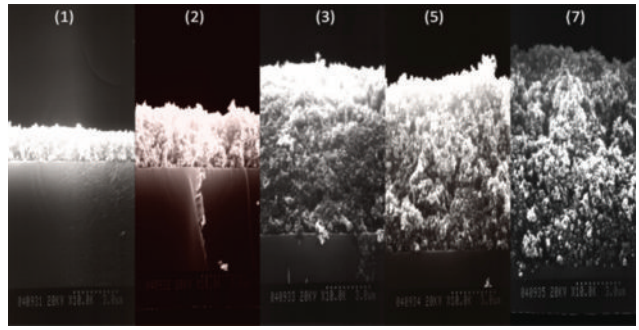


Figure 3: Corresponding film thicknesses after TiO_2 coating with 1, 2, 3, 5, and 7 times.

2.4.4. 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. The pH, conductivity, turbidity, and TOC measurements were analyzed. Laser Particle Size Analyzer (ASYS HIAC ROYCO 8000A) and Spectrophotometer (HITACH-U2001) were used to measure the size distribution of particles and organic matter spectrum in the feed and treated water, respectively.

3. Results and Discussion

3.1. Properties of TiO_2-Film Preparation. In the TiO_2-film preparation test, it was found the amount of TiO_2-film produced was higher with the increased coating times after the high temperature sintering. Figure 3 shows that the film thicknesses were 1.33, 2.00, 6.00, 7.33, and 8.00 μm, respectively, after the different coating times of TiO_2-film with 1, 2, 3, 5, and 7.

Figure 4 shows the XRD patterns of TiO_2 thin films in laboratory preparation. According to the database, the anatase phase of the strong diffraction peak is at 25.4°, 37.9°, and 48.2°, and the rutile phase of the strong diffraction peak is at 54.5°; the figure shows that the XRD diffraction

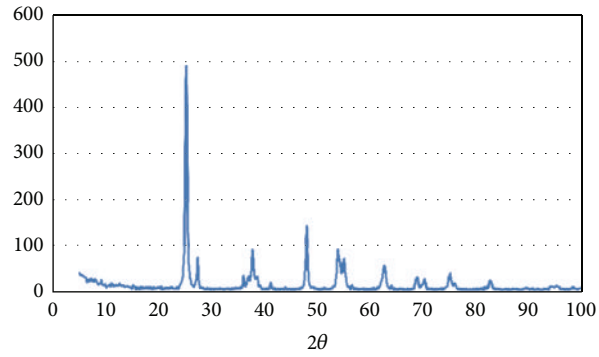


Figure 4: XRD patterns of TiO_2-films in laboratory preparation.

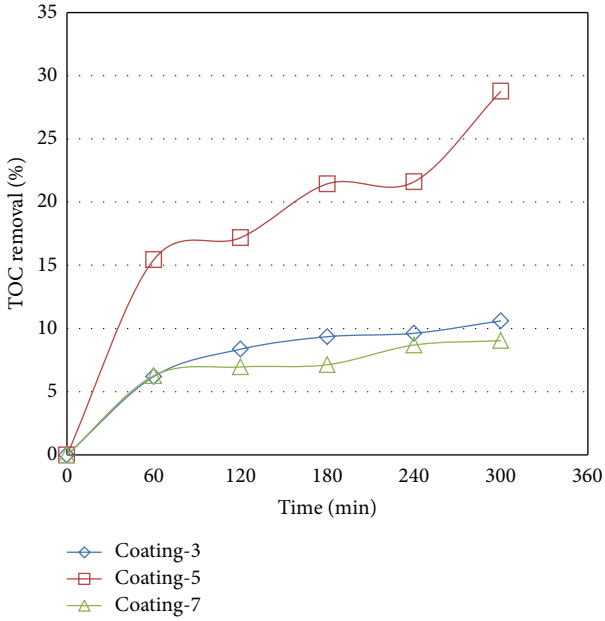


Figure 5: Corresponding TOC removals after photocatalysis with different TiO_2 coating times.

peaks for the anatase phase and rutile phase are all found. It indicates that the high temperature sintering process did not undermine the crystalline phase of the TiO_2 particles.

3.2. Effect of Different Coating Times of TiO_2-Film for Photocatalysis. Figure 5 shows the TOC removals of feed water rapidly increased during the first 60 minutes foreverynumber of coating times of TiO_2-films by photocatalysis (254 nm), but the removal gradually slowed after 60 minutes. The simple organic would be easily degradable to form CO_2 during the first 60 minutes, and the refractory organic would be hard to be mineralized [6, 7]. Further, Figure 5 also shows the removal for the 5-coating times of TiO_2-films was higher than that for the 3-coating times of TiO_2-films, due to the specific surface area of TiO_2-film would increase for higher coating times. However, the removals for 7-coating times were lower than that for 5-coating times, it may be the specific surface area of TiO_2-film would increase to an up-limit with more

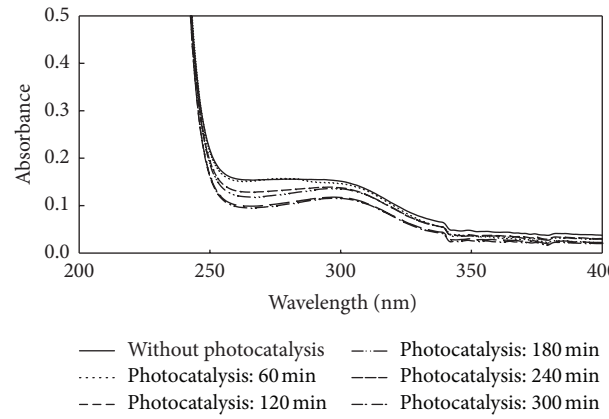


Figure 6: UV spectra of feed water during various irradiation periods for TiO_2-film photocatalysis (5 coating times).

coating times, and the UV light would not penetrate the lower layer of TiO_2 [11, 12]. Additionally, we also measured the UV light irradiances on TiO_2-films were 0.545 mW/cm^2 and 0.09 mW/cm^2 for UV_{254} and UV_{365} lamps by UV Intensity Meters (UVP, USA), respectively. Therefore, TOC removals were not apparent by photocatalysis (365 nm) in this study, maybe the irradiation strength of 365 nm was far less than that of 254 nm.

Figure 6 shows the UV spectra of feed water during various irradiation periods for TiO_2-film photocatalysis (5-coating times), the absorbance of 200–400 nm apparently decreased with the increased reaction time. The refractory organic matters in the feed water had been further decomposed, for example, the benzene or other aromatic ring compounds and compounds having a conjugated double bond with a strong absorption characteristics in the UV spectra [16]. They even had been mineralized into CO_2, therefore resulting in the increase of TOC removal after longer irradiation on TiO_2-film.

3.3. Effect of UF Permeate Flux Improved by TiO_2-Film Photocatalysis. This study chiefly uses photocatalytic reactors, which may upgrade organic effluent quality to improve ultrafiltration permeate flux. Figures 7 and 8 show the permeate flux of UF for feed water pretreated by TiO_2-film photocatalysis. For 5 KDa ultrafiltration, after 300 minutes operation the permeate flux for raw water increases from 36.92 to 39.47 l/m^2 hr for photocatalysis (5 times coating). The permeate flux rate for photocatalysis (5 times coating) was 7.0% higher than that without photocatalysis. However, for 10 KD ultrafiltration, after 300 minutes operation, the permeation flux increased from 41.38 to 50.93 l/m^2 hr for photocatalysis (5 times coating). The permeate flux rate for photocatalysis (5 times coating) was 23% higher than that without photocatalysis; therefore, TiO_2-film photocatalysis had improved the permeate flux better for 10 KDa UF than that for 5 KDa UF.

Further, Figure 9 shows that the particle size distribution appears in two ranges (i.e., 35–60 and 150–500 nm) for TFT-LCD secondary effluent. However, the size distribution did

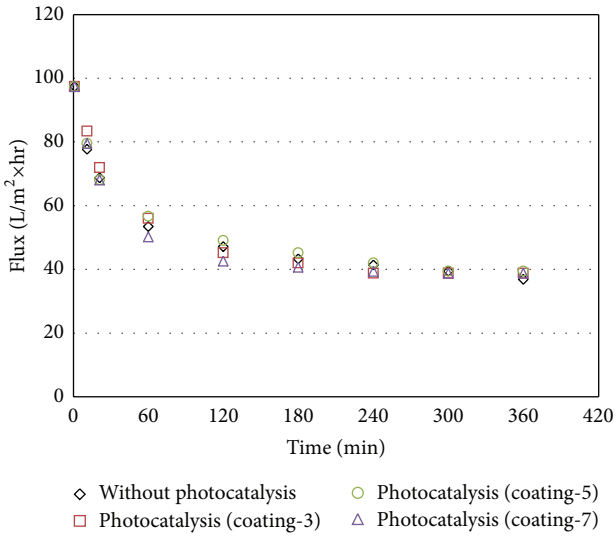


FIGURE 7: Permeate flux of UF for feed water pretreated by TiO_2-film photocatalysis (5 KDa).

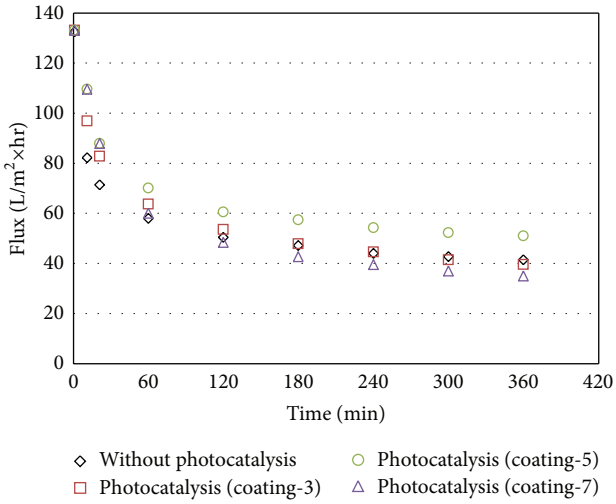


FIGURE 8: Permeate flux of UF for feed water pretreated by TiO_2-film photocatalysis (10 KDa).

not appear in the above ranges when feed water was treated by TiO_2-film photocatalysis (5 coating times), as shown in Figure 10. Instead, the range of 60–90 nm appeared. Clearly, some larger organic matter had been broken into the small organic matter, and some small organic matter had undergone demineralization following TiO_2-film photocatalysis. The size distribution range of 35–60 nm for TFT-LCD effluent is near the size range of 10 KDa UF that would clog in the membrane pores and lead to irreversible fouling, which could not be cleaned by cross flow [17, 18]. However, after TiO_2-film photocatalysis, this range of particles disappeared, resulting in better permeate improvement for 10 KDa UF.

3.4. Effect of UF Permeate Quality Improved by TiO_2-Film Photocatalysis. Table 1 indicates that the removal of dissolved

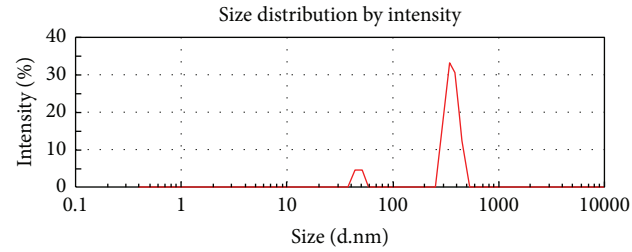


FIGURE 9: Particle size distribution for TFT-LCD secondary effluent.

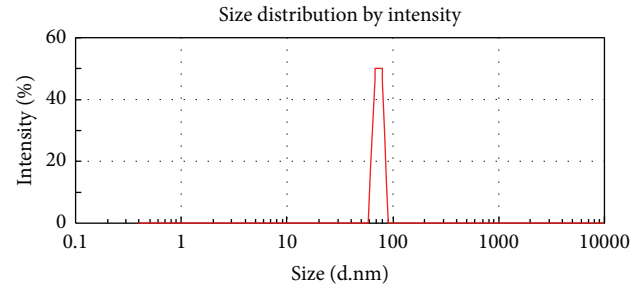


FIGURE 10: Particle size distribution for feed water treated by TiO_2-film photocatalysis (5 coating times).

matter, such as conductivity, was minimal after the single ultrafiltration, but the removal of turbidity was about 80.6%. The ultrafiltration had effectively decreased the turbidity associated with the suspended solids and colloids.

Further, the water sample was filtered by 0.45 μm membrane before the TOC analysis, so the TOC contained the colloid and dissolved organics. Following the single ultrafiltration, TOC removal in the permeate flow was 33.71%, indicating that ultrafiltration had effectively decreased the TOC associated with the colloids. However, the dissolved TOC would still need to decrease to enhance the recycling and reuse of wastewater. This study found that TiO_2-film photocatalysis followed by ultrafiltration increased total TOC removal to 49.94% for 10 KDa membranes, which would make it helpful for reverse osmosis treatment.

4. Conclusion

This study found that TiO_2-film photocatalysis improved the permeate flux by more for 10 KDa UF than that for 5 KDa UF. This was because some larger organic matter had broken into the small organic matter and some small organic matter had undergone demineralization following TiO_2-film photocatalysis. However, it depends on the particle size range in the water before and after TiO_2-film photocatalysis. It was also found TiO_2-film photocatalysis followed by ultrafiltration effectively increased total TOC removal. Therefore, the combination of TiO_2-film photocatalysis and ultrafiltration would pretreat the organic matter effectively and reduce the fouling on the reverse osmosis membrane to enhance the recycling and reuse of wastewater.

Table 1: Permeate quality after being treated by TiO_2-film photocatalysis (10 KDa).

	Raw water	UF		Coating-3 + UF		Coating-5 + UF		Coating-7 + UF	
pH	6.53	6.53	—	6.52	—	6.54	—	6.53	—
Conductance (mS/cm)	3.27	3.18	2.75%	3.20	2.14%	3.19	2.45%	3.22	1.53%
Turbidity (NTU)	1.96	0.38	80.61%	0.37	81.12%	0.34	82.65%	0.39	80.10%
TOC (mg/L)	15.9	10.6	33.71%	9.53	40.40%	8.00	49.94%	11.7	26.83%

UF: raw water treated by 10 KDa ultrafiltration.
Coating-3: raw water pretreated by photocatalysis (300 min, 3-coating times, 6 μm thickness); coating-5: raw water pretreated by photocatalysis (300 min, 5-coating times, 6.67 μm thickness); coating-7: raw water pretreated by photocatalysis (300 min, 7-coating times, 8 μm thickness).

Acknowledgment

The authors would like to thank the National Science Council of China, Taiwan, for financially supporting this research under Contract no. NSC 98-2622-E-239-001-CC2.

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