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Original Article

Surface modification of polyamide thin film composite membrane by coating of titanium dioxide nanoparticles

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ABSTRACT

In this paper, the coating of TiO_2 nanoparticles onto the surface of a polyamide thin film composite nanofiltration membrane has been studied. Changes in the properties and separation performance of the modified membranes were systematically characterized. The experimental results indicated that the membrane surface hydrophilicity was significantly improved by the presence of the coated TiO_2 nanoparticles with subsequent UV irradiation. The separation performance of the UV-irradiated TiO_2-coated membranes was improved with a great enhancement of flux and a very high retention for removal of residual dye in an aqueous feed solution. The antifouling property of the UV-irradiated TiO_2-coated membranes was enhanced with higher maintained flux ratios and lower irreversible fouling factors compared with an uncoated membrane.

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1. Introduction

During the last decades, interest in the use of membrane technology has emerged for wastewater treatments as well as for the production of drinking water [1]. Particularly, fouling is one of the main problems in any membrane separation process. Surface modification of membranes has been considered to be the most sustainable solution to reduce the fouling. Among various approaches, hydrophilization of membranes is a potential fouling mitigation method [2,3]. The idea is to introduce hydrophilic groups into a polymeric membrane surface, so that the overall membrane material becomes more hydrophilic and thus less prone to organic fouling. The polyamide thin film composite (TFC-PA) membranes have been widely used for water treatments due to their superior water flux, good resistance to pressure compaction, wide operating pH range, and good stability to biological attack; however, it has also significant drawbacks due to the membrane fouling [1,4].

Titanium dioxide (TiO_2) nano-sized particles are a popular photocatalysts. They attract much attention from both fundamental research and practical applications for the removal of contaminants from water because of the high photoactivity and chemical stability [5–9]. It is well known that TiO_2 would generate electrons and empty holes under ultra-violet (UV) irradiation [10]. There have been numerous studies about this material in recent years due to its innocuity, resistivity, photo catalytic and superhydrophilicity properties [3,5]. Two different schemes [11] can explain the self-assembly (Fig. 1a, b) behavior of TiO_2 on the surface of polymer containing COOH and the COOH groups. One way is to link TiO_2 with oxygen atoms via coordination to Ti^{4+} cations (Fig. 1a). The other way is to form a hydrogen bond between COOH groups and the hydroxyl group of TiO_2 (Fig. 1b).

Many experiments have been carried out for modifying the ultrafiltration (UF) and microfiltration (MF) membranes using TiO_2 nanoparticles [2,5–8,12–14]. Rahimpour et al. [7] successfully prepared two types of the modified polyethersulfone (PES) membranes via entrapping or coating TiO_2 nanoparticles along with UV irradiation. However, the separation performance and antifouling properties of the UV-irradiated TiO_2-coated membranes were higher than those of the UV-irradiated TiO_2-entrapped membranes. The optimum conditions for the preparation of TiO_2-coated membranes were determined when using 0.03 wt.% of a TiO_2 colloidal suspension, followed by 15 min UV irradiation at 160 W. Li et al. [12] successfully coated TiO_2 nanoparticles onto an ultrahigh molecular weight poly (styrene-alt-maleic anhydride)/poly (vinyldene fluoride) (SMA/PVDF) membrane surface. It was demonstrated that

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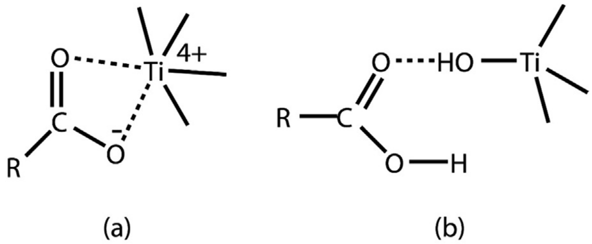

Fig. 1. Mechanism of self-assembly of TiO_2 nanoparticles [11].

TiO_2 particles were tightly absorbed on the surface of SMA/PVDF membranes and the amount of TiO_2 increased with the increase of −COOH groups hydrolyzed from SMA in membranes. The hybrid membranes exhibited extraordinary hydrophilicity, superior permeability and excellent fouling resistance in contrast with an original SMA/PVDF membrane. Madaeni et al. [10] coated TiO_2 nanoparticles and subsequently irradiated UV light onto the cellulose ultrafiltration membrane surface. The results indicated that the stable whey flux of the coated TiO_2 nanoparticle membrane was higher than that of the uncoated one. After an exposure of the membrane surface under the UV light, two phenomenon can be occurred: photo catalytic and ultrahydrophilicity, which lead to the decomposition and removal of the foulant and increase the membrane flux.

The coating of TiO_2 particles followed by UV radiation could improve membrane flux and the self-cleaning property increases with the longer UV irradiation time [8,9,15–19]. It is important to mention that TiO_2 nanoparticles have the ability to temporarily keep their photo-induced superhydrophilicity after switching off the UV light.

In this work, the surface of a TFC-PA NF membrane was modified by coating TiO_2 nanoparticles with a subsequent UV irradiation. Changes in the membrane surface characteristics were determined through the scanning electron microscope (SEM) images, time of flight secondary ion mass spectroscopy (Tof-SIMS) analysis, Fourier transform infrared spectroscope − attenuated total reflectance (FTIR−ATR) spectra, and water contact angle (WCA) measurements. The changes in the membrane separation performance were evaluated through water permeability, flux, and retention for removal of reactive red dye in an aqueous feed solution. The antifouling property of the membranes was determined through a maintained flux ratio and an irreversible fouling factor for filtration of the dye and protein feed solutions.

2. Experimental

2.1. Materials

A commercial TFC-PA membrane (Filmtec BW30) was used as the substrate material for the surface coating of TiO_2 nanoparticles. It consists of a topmost ultrathin polyamide active layer on a reinforced polysulfone (PSf) porous substrate and demonstrates up to 99.1% NaCl rejection with flux as high as 42.5 L/m^2h at a pressure of 5.5 MPa [20]. The membrane samples were cut to have a diameter of 47 mm and soaked in a 25 v/v % aqueous solution of isopropanol (99.9%, Sigma−Aldrich) for 60 min; next, they were carefully rinsed with deionized water, and then kept wet until they were used for surface coating. The commercial TiO_2 nanoparticles in aggregated form with primary particle size of 14 nm and anatase phase of 89.38% were used for the surface coating. Reactive red dye RR261 (China) and pure-grade bovine serum albumin (BSA) (Wako, Japan) were used for the preparation of aqueous feed solutions for membrane filtration tests.

2.2. Coating of TiO_2 nanoparticles onto membrane surface

The solutions of TiO_2 nanoparticles in suspension were prepared by ultrasonic method. The TFC-PA membrane substrate was dipped in the TiO_2 colloidal solution containing 10–80 ppm of TiO_2 nanoparticles. The membrane was then washed with deionized water and exposed to UV light (UV-B lamp, 300 nm, 60 W) for different time periods, from 15 s to 90 s. The coated TiO_2 membranes were kept wet in deionized water until they were used for characterization.

2.3. Membrane characterization

2.3.1. Morphology

The membrane surface morphology was observed through the scanning electron microscopy (SEM), using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800). The micrographs were taken in high vacuum conditions at 5 kV. The membrane samples were sputter coated with a 3 nm thick platinum layer prior to imaging.

2.3.2. Tof-SIMS analysis

The existence of TiO_2 nanoparticles on the surface of a TiO_2-coated TFC-PA membrane was also determined through time of flight secondary ion mass spectroscopy (ToF-SIMS), using MiniSIMS (SAI Scientific analysis instruments Ltd.). Gallium ions (Ga^+) with energy of about 6 keV were used as the primary ion beam for a nominal incident angle of 90° to the surface.

2.3.3. Functionality

The surface chemical functionality of the membranes was characterized by the attenuated total reflectance Fourier transform infrared spectroscopy (FTIR−ATR, Spectro100 Perkin Elmer) for a nominal incident angle of 45°, with 100 scans at a resolution of 4 cm^{-1}. All membrane samples were dried at 25 °C under vacuum before characterization.

2.3.4. Wettability

The wettability of the membrane surface was examined through the water contact angle measurements, using a goniometer (DMS012) equipped with a camera, which captured images of deionized water drops on the dried surfaces of the membranes at 25 °C. The contact angles were then calculated from the captured images. For each sample, three drops (3 μL) were placed at different positions on the membrane surface, and the average value of the contact angles was obtained.

2.3.5. Evaluation of the membrane filtration properties

The membrane filtration experiments were performed in a dead-end membrane filtration system, consisting of a stainless steel cylindrical cell with a volume of 300 cm^3 supplied by Osmonics (USA) and a stirrer connected to a nitrogen gas cylinder, which provided a working pressure through a membrane area of 13.2 cm^2. Filtration experiments were carried out at room temperature. The membrane was compacted by deionized water at 15 bar for 15 min before carrying out the filtration measurements. In all experiments, the membrane cell was carefully rinsed with deionized water before and after using. The water flux was determined by

$$J_W = [V_W/(A \times t)]\left(L\big/m^2.h\right)$$

where V_w is the deionized water volume obtained through a membrane area of A within a filtration time of t.

The normalized water flux ratio (J_w/J_{wo}) was used to evaluate changes in water permeability of the membranes resulting from the surface coating of TiO_2, where J_w and J_{wo} are the average water fluxes of the coated and uncoated membranes, respectively.

The retention (R) was determined by

$$R = \{[(C_0 - C)/C_0] \times 100\} \text{ (\%)}$$

where C_0 and C are the concentrations of the removal object (RR261 or BSA) in the feed and filtrate, respectively.

The permeate flux (J) was evaluated by

$$J = [V/(A \times t)]\left(L/m^2 \times h\right)$$

where V is a filtrate volume obtained through a membrane area of A within a separation time of t at the determined pressure driving force. The normalized flux ratio (J/J_o) was used to evaluate the changes in the membrane flux caused by the surface coating, where J and J_o are the average fluxes of the TiO_2-coated and uncoated membranes, respectively.

2.3.6. Evaluation of the membrane antifouling property

The antifouling property of the membranes was estimated through the maintained flux ratios (%) during filtration of the different feed solutions containing high fouling tendency compounds such as dyes (RR261) or proteins (BSA).

An irreversible fouling factor (FR_w) of the membranes was calculated by

$$FR_w = \{[(J_{w1} - J_{w2})/J_{w1}] \times 100\} \text{ (\%)}$$

where J_{w1} and J_{w2} are the deionized water fluxes of the membranes before and after using them for the filtration of the feed solutions, respectively. The antifouling properties of the membranes improved with higher maintained flux ratios and lower irreversible fouling factors.

3. Results and discussion

3.1. Membrane characterization

3.1.1. SEM images

The SEM images of the TFC-PA and TFC-PA/TiO_2-coated membranes were shown in Fig. 2. The results indicated that the TiO_2 nanoparticles were deposited onto the surface of the TFC-PA membrane. The density of TiO_2 on the surface increased with higher TiO_2 concentration in the colloidal solution used for coating. In our experiments, the aggregated TiO_2 nanoparticles were easily broken to form secondary particles of few tens to few hundreds of nanometers under a sonication process. The TiO_2 nanoparticles were deposited onto the membrane surface, where they were formation of hydrogen bonds between TiO_2 nanoparticles and the membrane surface.

3.1.2. FTIR–ATR spectra

The FTIR–ATR spectra of uncoated and TiO_2-coated TFC-PA membranes were shown in Fig. 3. The spectrum of the (a)

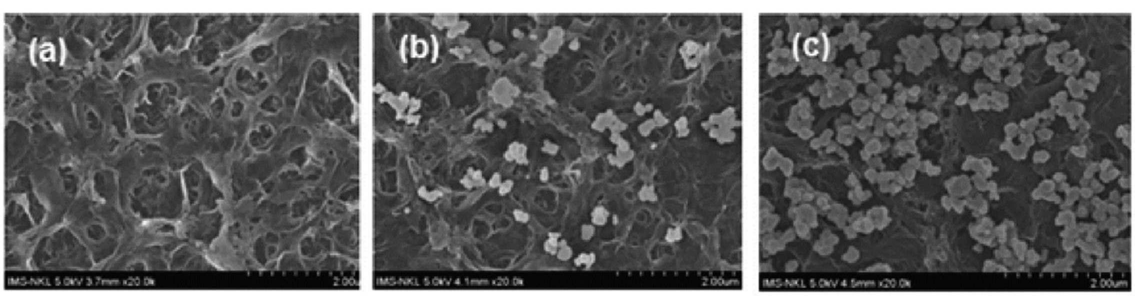

Fig. 2. SEM images of (a) uncoated and TiO_2-coated membranes using (b) 15 ppm and (c) 80 ppm TiO_2 coating solutions.

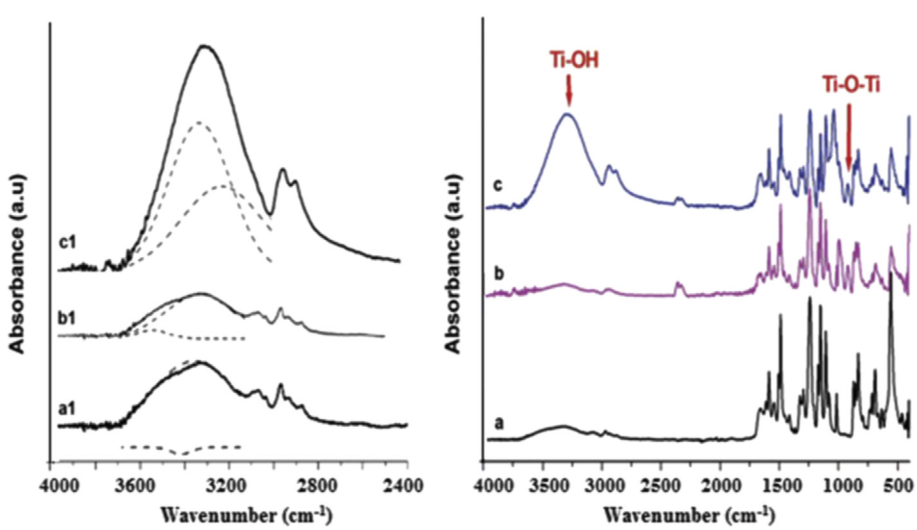

Fig. 3. FTIR–ATR spectra of uncoated (a, a1), TiO_2-coated (b, b1) and TiO_2-coated membrane with UV irradiation (c, c1).

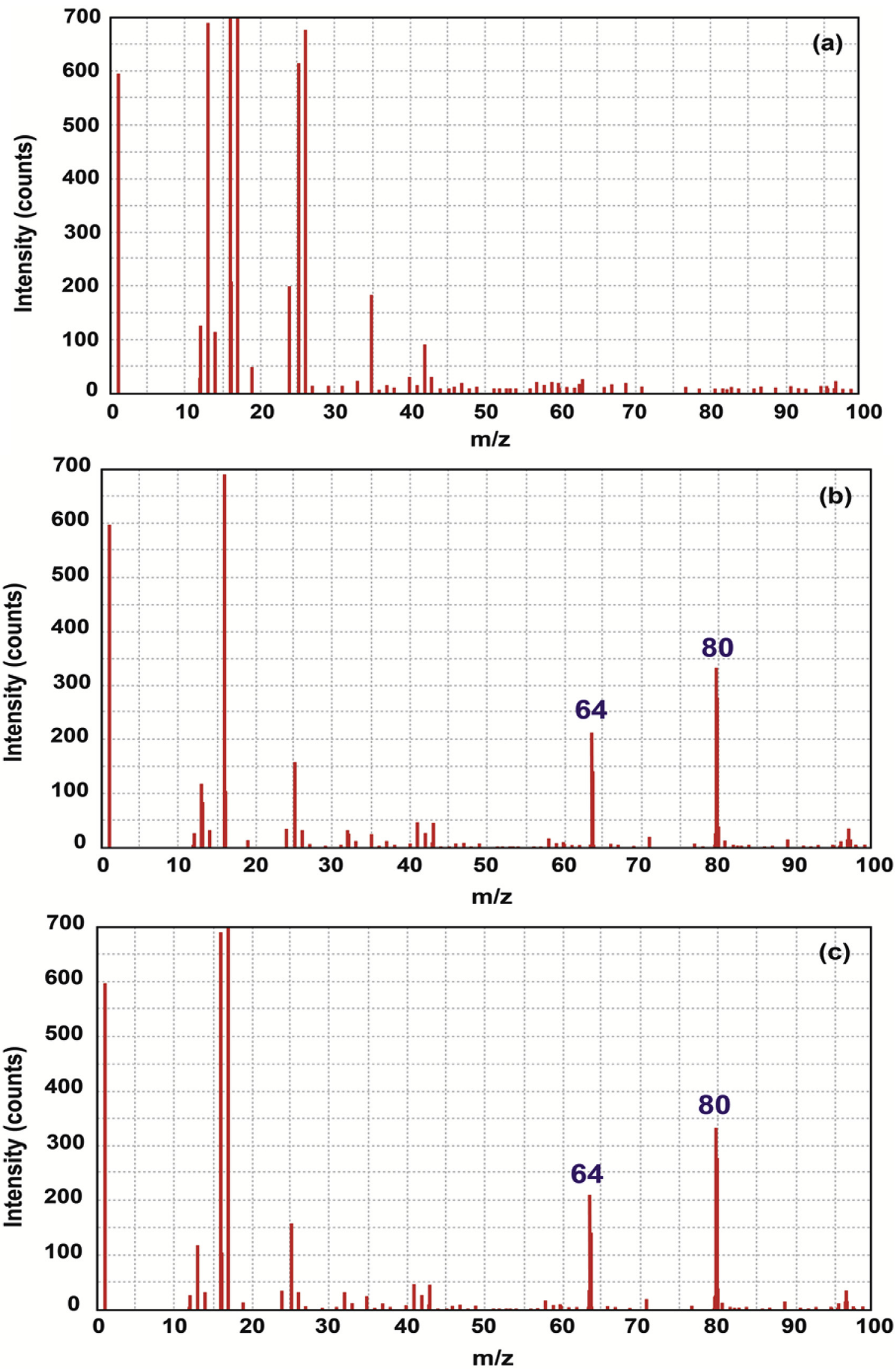

Fig. 4. MiniSIM's mass spectroscopy of (a) uncoated and TiO_2-coated membranes using (b) 15 ppm and (c) 80 ppm TiO_2 coating solutions.

uncoated membrane revealed characterized absorptions of N—H (3340 cm^{-1}), C=O (1640 cm^{-1}), C=C (1400 – 1600 cm^{-1}) and C—N (1080 – 1360 cm^{-1}). The spectrum of the TiO_2-coated membrane surface (b) without and (c) with UV light exhibited a new peak at approximately 953 cm^{-1}, which was attributed to the stretching vibration of Ti—O—Ti band [21], indicating the successful incorporation of TiO_2 particles onto the membrane surface. For the TiO_2-coated membrane followed by UV irradiation (c), the increase of the absorption intensity around 3300 cm^{-1} almost coincided with the absorption of NH groups of the uncoated polyamide surface; this may be ascribed to the absorption of O—H groups. Further analysis of the peak confirmed the presence of two absorptions of Ti—OH at 3319 cm^{-1} and NH at 3217 cm^{-1} on the TiO_2-coated membrane surface with UV light exposure. The presence of OH bonds in the TiO_2-coated membrane followed by UV irradiation could lead to the superhydrophylicity of the modified membranes. For the TiO_2-coated membrane without exposure under UV light, the peak at 3300 cm^{-1} was similar to the uncoated one.

3.1.3. Tof-SIMS analysis

The presence of TiO_2 nanoparticles on the TiO_2-coated membrane surface was further confirmed by mass spectroscopy obtained from the ToF-SIMS analysis. The results (Fig. 4) showed the appearance of the new signals (m/z = 64 and m/z = 80), which could be due to the Ti—O and O—Ti—O species splitted from the TiO_2-coated membrane surfaces.

3.1.4. Contact angle measurements

The WCA measurements shown in the Fig. 5 revealed that the hydrophilicity of the membrane surface remarkably improved after

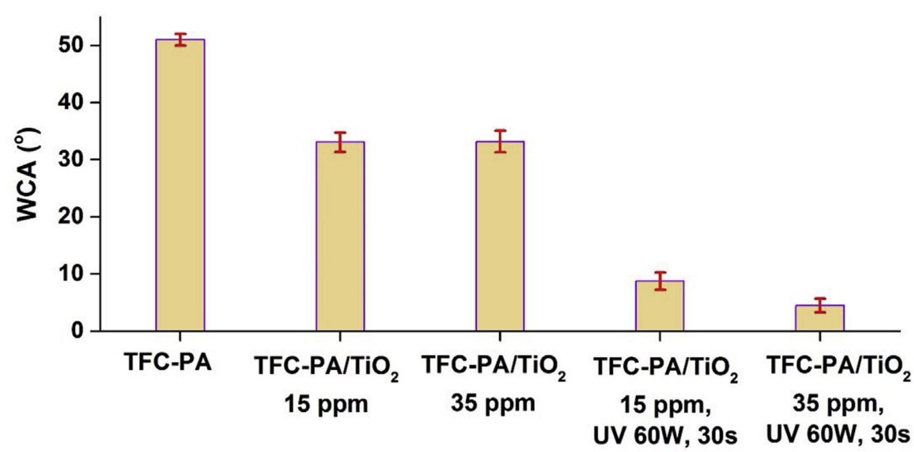

Fig. 5. Water contact angles of the uncoated and TiO_2-coated membranes.

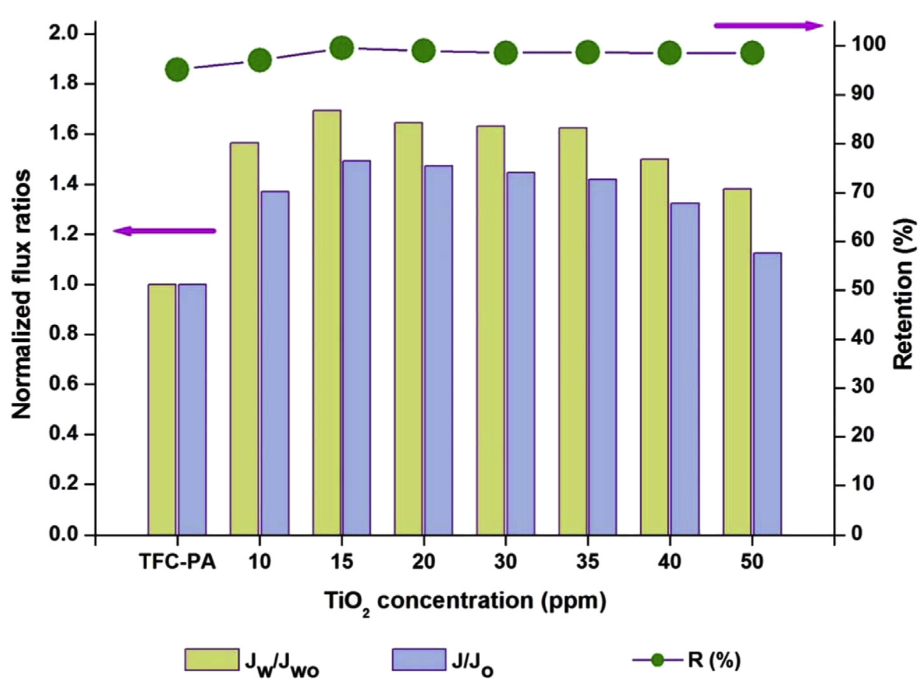

Fig. 6. Influence of TiO_2 concentration on membrane separation performance.

coating of TiO_2, as indicated by highly reduced WCA values. The TiO_2-coated membranes with subsequent UV irradiation showed a much lower WCA, thus the membranes are expected to be more hydrophilic.

3.2. Effect of the TiO_2 concentration on the coated membrane separation performance

In this experiment, the different TiO_2 colloidal solutions (10–50 ppm) were used for the surface coating. The membranes were immersed into the TiO_2 solutions for 30 min, then they were carefully washed by deionized water and exposed to UV light for 30 s. The filtration tests, using an aqueous feed solution containing 30 ppm reactive red 261 dye (RR261), were carried out. The effect of the TiO_2 concentration on the coating solution of the TiO_2-coated membranes separation performance was shown in Fig. 6.

The results indicated that the fluxes of the TiO_2-coated membranes were highly improved compared to the uncoated one. For a concentration range of TiO_2 from 10 to 15 ppm, the flux significantly increased, but started to decrease at a TiO_2 concentration of 20 ppm. The dye retention of membranes was slightly increased (97 – 99%) compared to the uncoated one (~95%). The decrease of membrane flux at higher TiO_2 concentrations could be due to the increased TiO_2 density incorporated on the membrane surface, thus increasing the mass resistance through the membrane.

3.3. Effect of the UV irradiation time on the TiO_2-coated membrane separation performance

In this experiment, the TiO_2-coated membranes (using 15 ppm TiO_2 coating solution) were subsequently exposed to the UV light

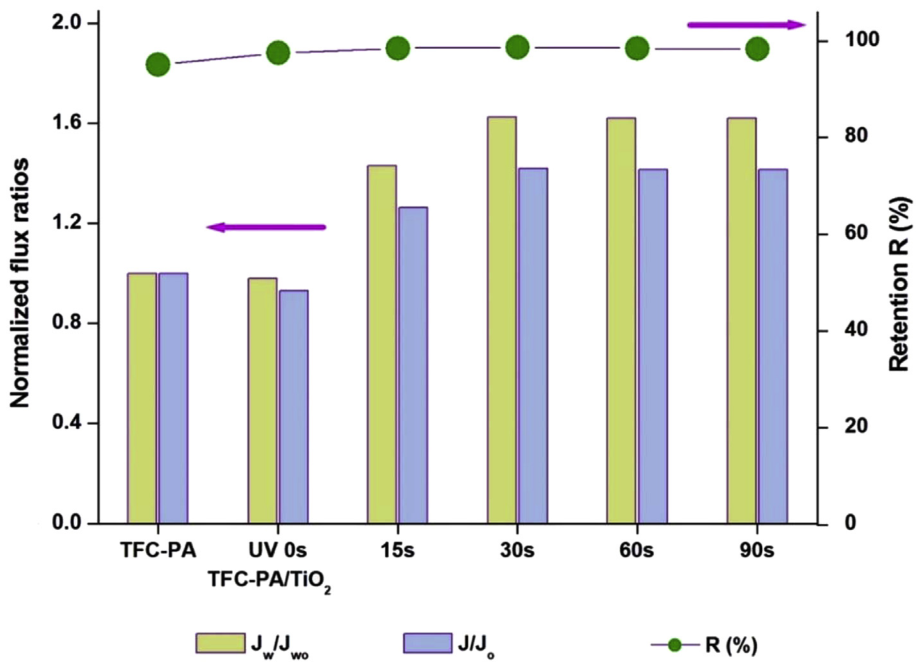

Fig. 7. Influence of the UV irradiation time on the membrane performance.

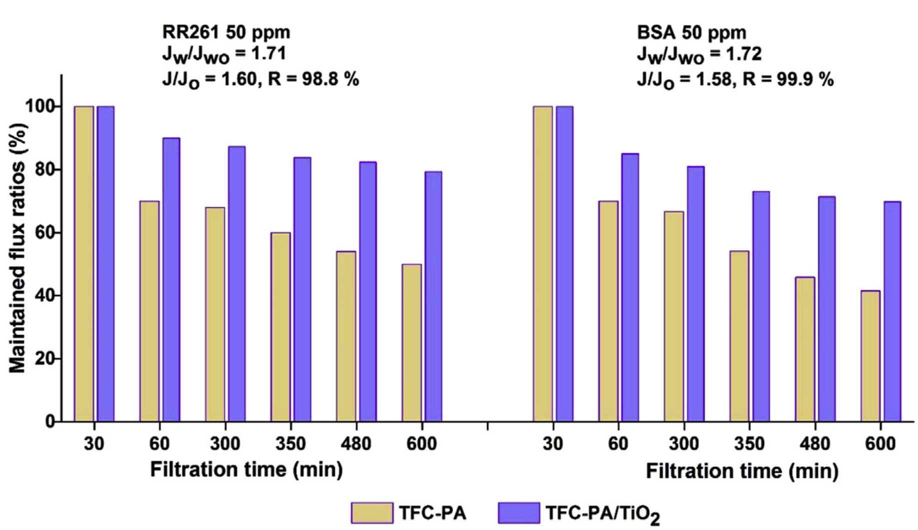

Fig. 8. Maintained flux ratios of the membranes.

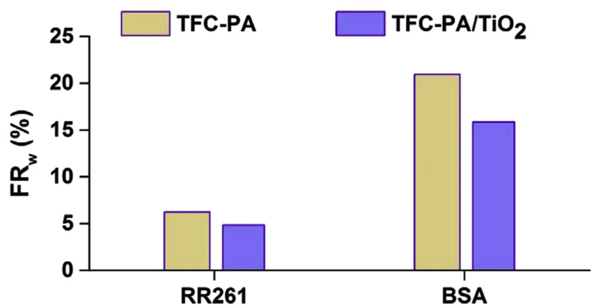

Fig. 9. Irreversible fouling factors of uncoated and coated membranes.

for 15, 30, 60 and 90 s. The fluxes of the UV exposed TiO_2-coated membranes were determined and compared to the uncoated and the non-UV exposed TiO_2-coated membranes.

The experimental results (Fig. 7) showed that the flux of the TiO_2-coated membrane followed by UV irradiation was strongly improved when compared to the uncoated and non-UV exposed TiO_2-coated ones. The fluxes of the UV exposed TiO_2-coated membranes increased and almost was stable for longer UV irratiation times of 30, 60 and 90 s. This is because the UV irradiation increased the hydrophilicity of the membrane surface, thus a layer of water is chemically adsorbed on the membrane surface. When such a surface comes into contact with water, it can absorb further layers of water through hydrogen bonds and Van der Waals forces, leading to the formation of a water layer on the surface that causes a high level of wettability [15].

3.4. Antifouling property

The maintained flux ratio and the irreversible fouling factor of the uncoated and the UV exposed TiO_2-coated membranes were determined and represented in Figs. 8 and 9. The filtration experiments were carried out for aqueous feed solutions containing 50 ppm RR261 dye or 50 ppm BSA, respectively. Fig. 8 showed a comparison of the maintained flux ratios between the uncoated and TiO_2-coated membranes with subsequent UV irradiation. As shown in the figure, the fluxes of the uncoated and the UV exposed TiO_2-coated membranes gradually decreased during filtration as a result of the membrane fouling. However, the degree of the flux decline differed with the two membranes. The flux decline of the UV exposed TiO_2-coated membranes was much less than that of the uncoated one, resulting in a higher flux maintenance during filtration. For example, after 60 min of filtration, the maintained flux ratios of the uncoated membrane for filtration of RR261 and BSA feed solutions was 70%, while that of the UV irradiated TiO_2-coated membranes were 90 and 85%, respectively. After 300 min of filtration, the maintained flux ratios of the uncoated membrane for filtration of RR261 and BSA feed solutions were reduced to 68.0 and 66.7%; while the fluxes of the UV irradiated TiO_2-coated membrane were maintained at 87.23 and 80.95%. After 600 min, the maintained flux ratios of both membranes were further reduced; however, the UV exposed TiO_2-coated membrane still showed a higher flux maintenance, indicating the improved fouling resistance of the TiO_2-coated membrane with subsequent exposure to UV light irradiation.

In addition, the evaluations of the normalized flux (J/J_o) and the retention (R) of RR261 dye and BSA revealed that the separation performance of the UV irradiated TiO_2-coated membrane has been kept well for the prolonged usage. After 10 h of filtration, the retentions for RR261 and BSA were maintained at 98.8 and 99.9%, respectively. Importantly, the flux of the UV irradiated TiO_2-coated membranes was highly improved compared with that of the uncoated one, with the fluxes increasing approximately 1.6 times for filtration of RR261 and BSA feed solutions.

The comparison in the irreversible fouling factors between the uncoated and the UV irradiated TiO_2-coated membranes was given in the Fig. 9, which indicated that the UV irradiated TiO_2-coated membranes had lower irreversible fouling factors than the uncoated one.

The obtained experimental results revealed that the antifouling property of the TFC-PA membrane was clearly improved after coating of TiO_2 nanoparticles onto the membrane surface with subsequent UV irradiation. The improvement of the membrane fouling resistance was mainly due to the enhanced surface hydrophilicity of the UV irradiated TiO_2-coated membrane.

4. Conclusion

The experiment results indicate the successful coating of TiO_2 nanoparticles onto the surface of a polyamide thin film composite membrane. The water contact angle measurements demonstrate the significantly improved membrane surface hydrophilicity of the TiO_2-coated membranes with subsequent UV irradiation. The separation properties of these membranes are clearly improved with a much better flux and a great retention for the removal of reactive dye in an aqueous feed solution. The UV irradiated TiO_2-coated TFC-PA membranes also demonstrate the significant enhancement of the antifouling property, with the higher maintained flux ratios and the lower irreversible fouling factors compared to the uncoated TFC-PA membrane.

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