Preparation of Polyethersulfone Ultrafiltration Membrane Surface Coated With TiO$_2$ Nanoparticles and Irradiated Under UV Light

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**Abstract.** This paper focuses on performance of polyethersulfone (PES) ultrafiltration membrane coated with titanium dioxide (TiO$_2$) nanoparticles and irradiated with UV light. The flat sheet membrane was prepared via phase inversion method, with two types of membrane; TiO$_2$ coated PES membrane and UV irradiated TiO$_2$ coated PES membrane. TiO$_2$ suspension with concentration of 0.01, 0.03 and 0.05 wt.% were prepared and coated on the PES surface via dip coating. Membrane was immersed in all suspension for 15 minutes and 30 minutes. Then, prepared coated membranes were irradiated by 184 Watts UV lamp for 15 minutes. The performance of membranes was examined by permeation of humic acid. The morphology of membranes was analyzed by scanning electron microscopy (SEM). It was revealed that the pure water flux and humic acid permeation of UV irradiated TiO$_2$ coated membrane was higher than TiO$_2$ coated membrane. It can be concluded that TiO$_2$ coated with 0.03 wt.% of suspension, 30 minutes and 15 minutes UV irradiation with 184 Watt light were determined as the optimum conditions for preparation ultrafiltration PES membrane.

**Introduction**

Generally, polyethersulfone (PES) is one of the polymeric materials, which has high mechanical, thermal and chemical resistances, easy processing and environmental endurance. However, its poor antifouling properties affect its application and usage life [1-2]. In previous study, researchers have investigated incorporation of TiO$_2$ into polyethersulfone membranes. There are two main approaches techniques for producing nanocomposite TiO$_2$ PES membranes: blending the TiO$_2$ nanoparticles in the membrane solution [3-5] and coating the nanoparticles on the surface of the prepared membrane [2, 6-7]. Titanium dioxide (TiO$_2$) has been focus of numerous studies in recent years due to its photocatalytic and superhydrophilicity effects, stable chemical property, innocuity and low cost. Besides, TiO$_2$ nanoparticles also can degrade chemicals especially organic compounds successfully with UV light. Based on previous studies, Kim et al. [8] prepares hybrid thin film composite (TFC) membrane by self-assembly of the TiO$_2$ nanoparticles through interaction with the COOH functional groups. The hybrid TFC membrane was found that dramatic photobactericidal effect on *E. coli* under UV light illumination. Kawaguchi et al. [9] study on hollow fiber membrane with TiO$_2$ particles by the immersion precipitation method, the effect of TiO$_2$ particles is one of the useful techniques to prevent the membrane fouling. Other researchers, Bae et al. [10] were prepared two types of TiO$_2$ immobilized ultrafiltration membranes, TiO$_2$ entrapped and deposited membranes. TiO$_2$ entrapped membrane showed lower flux decline compared to neat membrane and TiO$_2$ deposited membrane exhibited greater fouling mitigation effect compared to TiO$_2$ entrapped membrane. In this research, the influences of concentration of TiO$_2$ nanoparticles, immersion time and irradiation in producing coated polyethersulfone membrane were studied.
Experimental

**Membrane Preparation.** Polyethersulfone was used as the base polymer, dried with temperature 60˚C for 24 hours in a drying oven before use. N-methyl-2-pyrrolidione (NMP) was used as solvent, polyethylene glycol was used as pore forming in the casting solution and distilled water used as the non-solvent in the coagulation bath. Neat polyethersulfone membrane was prepared using phase inversion method. The TiO$_2$ coated membrane was prepared by dipping (PTL-MM01 Dip Coater) the neat membrane in different concentrations of TiO$_2$ nanoparticles (0.01, 0.03 and 0.05 wt.%) with speed 50 mm/second. Membranes were immersed in TiO$_2$ suspensions for various periods (15 and 30 minutes). TiO$_2$ suspensions were prepared by adding different concentration of TiO$_2$ in distilled water and then stirred before use. Lastly, membranes were washed with distilled water and illuminated by 184 Watt UV lamp for 15 minutes.

**Membrane Characterization.** Scanning Electron Microscopy (SEM) was used to examine the coated flat sheet membrane surface. The membranes were cut into pieces of small sizes and coated gold with before testing.

**Membrane Performance.** The permeation and rejection of all membranes were measured by an ultrafiltration cross flow test at 3 bars. The pure water flux (PWF) and rejection experiments were using distilled water and humic acid respectively. PWF and rejection values were calculated using following equation (1) and (2):

\[
PWF = \frac{Q}{A \times \Delta t} \quad (1)
\]

\[
R(\%) = [1 - (C_p/C_f)] \times 100 \quad (2)
\]

PWF in (L/m$^2$h), where Q is volume of permeate (L), A is membrane surface area (m$^2$) and $\Delta t$ is permeation time (h). Where R (%) is rejection percentage, $C_p$ is concentration permeates and $C_f$ is concentration feed.

Result and Discussion

**Pure water flux performance**

![Fig. 1: Pure water flux permeation for (a) TiO$_2$ coated and (b) UV irradiated TiO$_2$ coated of PES membrane](image)

Based on the results in Fig. 1, indicated that the pure water flux (PWF) performance of PES membrane with UV irradiated and TiO$_2$ coated is higher compared to TiO$_2$ coated on membrane surface. Fig.1 (a) shows the TiO$_2$ coated results, PWF behavior has increased as TiO$_2$ suspension increased from 0.01 to 0.03 wt.%. The flux of coated membrane with 0.05 wt.% of TiO$_2$ nanoparticles is decreased compared to the membrane coated with 0.03 wt.% of TiO$_2$. This is due to the blockage of some membrane pores by TiO$_2$ nanoparticles at higher concentrations. This finding has similarity with studies of A. Rahimpour et al. [6]. The 30 minutes immersion (23.23 L/m$^2$h) of
membrane in 0.03 wt.% of TiO\(_2\) suspension showed the excellence performance compared to 15 minutes immersion (18.43 L/m\(^2\)h). The extended period of membrane immersion in TiO\(_2\) suspension will increased formation TiO\(_2\) nanoparticles in membrane surface. The influence of UV irradiation on pure water flux of PES membrane is shown in Fig.1 (b). All TiO\(_2\) coated membranes were exposed to 184 Watt light at 15 minutes. The membranes immersed in 0.03 wt.% TiO\(_2\) suspension for 30 min and irradiated with UV for 15 minutes exhibited the highest flux performance (24.75 L/m\(^2\)h) compared to 15 minutes immersion (21.76 L/m\(^2\)h). The higher flux of UV irradiated TiO\(_2\) coated PES membrane can be due to TiO\(_2\) nanoparticles use their capability in decomposition and destroying the impurities especially organic compounds by producing strong oxidant reagents. Thus, the photo-induced hydrophilicity of TiO\(_2\) nanoparticles irradiated by UV light on the membrane surface and further detail explanations are described elsewhere [11-12].

**Humic acid rejection**

![Fig. 2: Humic acid permeation for (a) TiO\(_2\) coated and (b) UV irradiated TiO\(_2\) coated of PES membrane](image)

Fig. 2: Humic acid permeation for (a) TiO\(_2\) coated and (b) UV irradiated TiO\(_2\) coated of PES membrane

![Fig. 3: Rejection results for (a) TiO\(_2\) coated and (b) UV irradiated TiO\(_2\) coated of PES membrane](image)

Fig. 3: Rejection results for (a) TiO\(_2\) coated and (b) UV irradiated TiO\(_2\) coated of PES membrane

The permeation of humic acid for TiO\(_2\) coated and UV irradiated TiO\(_2\) coated of PES membrane is clearly presented in Fig. 2. Based on humic acid permeation, permeate flux of UV irradiated TiO\(_2\) coated with 30 minutes immersion exhibited highest performance compared to TiO\(_2\) coated. This is due to the hydrophilicity and photocatalytic properties of TiO\(_2\) nanoparticles radiated on membrane surface by UV light. TiO\(_2\) nanoparticles can decompose and destroy the contaminations and impurities especially organic compounds [6]. Fig. 3 shows humic acid rejection results for TiO\(_2\) coated and UV irradiated TiO\(_2\) coated of PES membrane. It was found that humic acid rejection performance between TiO\(_2\) coated and UV irradiated TiO\(_2\) coated are not significantly different, the range for both condition are 99.2% - 99.9%.
Morphology

Fig. 4 shows the SEM images of TiO\(_2\) coated with different concentration of TiO\(_2\) nanoparticles on PES membrane surface. It can be observed that TiO\(_2\) nanoparticles are uniformly distributed on the membrane surface of PES membrane for 0.01 wt.%, 0.03 wt.% and 0.05 wt.% of TiO\(_2\) concentration. However, some particles form large aggregates on 0.05 wt.% TiO\(_2\) coated surface as shown in Fig. 4 (b). This is due to presence of OH bonds in the membrane structure is the main factor for arrangement TiO\(_2\) nanoparticles on the membrane surface. The membrane coating was accomplished by self-assembly of TiO\(_2\) nanoparticles and the polymer with OH bonds [6].

Conclusion

In the present research, TiO\(_2\) nanoparticles were coated on the ultrafiltration PES membrane surface and irradiated by UV light. The pure water flux and humic acid permeation of UV irradiated TiO\(_2\) coated membrane was higher performance compared to TiO\(_2\) coated membrane. The enhancement of flux was due to TiO\(_2\) nanoparticles use their potential in decomposition and destroying the impurities and photo-induced hydrophilicity when exposed by UV light on the membrane surface. The optimum conditions for preparation TiO\(_2\) coated membrane were determined as 0.03 wt.% TiO\(_2\) of suspension, 30 minutes and 15 minutes UV irradiation with 184 Watt light.

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