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Membrane Performance: TiO_2 Nanoparticles Coated on Polysulfone (PSf) Ultrafiltration Membrane Surfaces

Siti Hawa Mohamad[a*], Hasan Zuhudi Abdullah[b], Maizlinda Izwana Idris[b], Zawati Harun[a]

[a]*Advanced Materials and Manufacturing Centre (AMMC), Universiti Tun Hussein Onn Malaysia, Batu Pahat 86400, Johor, Malaysia*
[b]*Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, Batu Pahat 86400, Johor, Malaysia*

*Corresponding author: cthawamd@gmail.com

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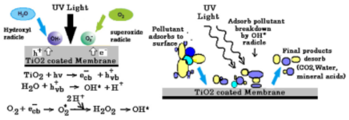
Graphical abstract



Abstract

This study focuses on the modification polysulfone (PSf) ultrafiltration membrane surfaces via coated and irradiated with titanium dioxide (TiO_2) nanoparticles with UV lights respectively. Basically, the flat sheet membrane was prepared using phase inversion technique with three conditions: (i) uncoated PSf membrane, (ii) coated PSf membrane with TiO_2 and (iii) PSf membrane coated with TiO_2 irradiated to UV. The coating process was carried out using dipping method into TiO_2 nanoparticles suspension at different concentrations (0.01, 0.03 and 0.05 wt.%). Membrane was immersed in all suspension for 15 and 30 minutes. Then, coated membranes were exposured under 184 Watts UV lamp at two different durations, 15 and 30 minutes. The performance of membranes was evaluated in terms of pure water flux (PWF) and humic acid (HA) rejection. The morphology of membranes was characterized using scanning electron microscopy (SEM). Analysis of the result revealed that 15 minutes immersion of membrane in TiO_2 suspension showed a better performance in term permeation and rejection of compared to 30 min immersion. This is due to the pore plugging as time of immersion increased. Therefore, the coated membranes with 0.03 wt.% of TiO_2 nanoparticles at 15 minutes immersion and 15 minutes exposure of UV light irradiation were determined as an ideal performance of rejection and permeation compared to the other.

Keywords: Polysulfone; TiO_2 nanoaprticles; UV irradiation

■1.0 INTRODUCTION

Polysulfone (PSf) membranes have been widely used as ultrafiltration (UF) membranes in many industrial fields for their low cost, superior film forming ability, good mechanical and anti-compaction properties, strong chemical and thermal stabilities and outstanding acidic and alkaline resistance. However, their hydrophobic nature results in severe membrane fouling and decline of flux has been a barrier for their application of water treatment[1]. Recently many studies have been focused on the preparation of membrane with TiO_2 entrapped which can offer several advantages like excellent self cleaning or antifouling, bactericidal and photoactive properties based on UV/ TiO_2 photocatalytic mechanism as compared to membrane modified by other methods. The theory of photocatalytic mechanism and process are shown on Figure 1. Among semiconductors TiO_2 has gained and attention because of its stability, cheapness and commercial availability, excellent photocatalytic, antibacterial and self cleaning ultra hydrophilic properties by absorbing UV rays[2-3]. Therefore, membrane fouling can be prevented by incorporating TiO_2 nanoparticles over polymeric membrane surface. In fact, titanium dioxide (TiO_2) has been extensively utilized in recent years to improve the permeability and antifouling properties of membrane due to photocatalytic and superhydrophilicity effects[4-6]. TiO_2 nanoparticles effectively degrade chemicals especially organic compounds with UV light. Based on previous studies, Kim *et al.*[7] 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. Other researchers, Bae *et al.*[5] 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.

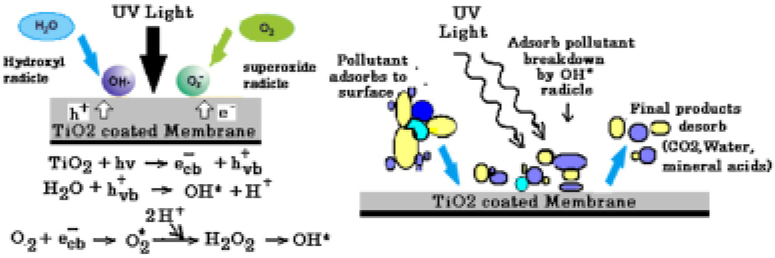


Figure 1 Photocatalytic mechanism and process

■2.0 EXPERIMENTAL

2.1 Materials

Polymer solution was prepared using polysulfone (UDEL P1700) as membrane material. The solvent N, N, methyl pyrrolidone (NMP) and additive polyethylene glycol (PEG 400) were supplied by Merck and Qrec. Nanosized anatase TiO_2 (Degussa P25, particle size: 21 nm) was purchased from Degussa. Distilled water was used as non-solvent throughout the studies. Humic acid supplied by Sigma Aldrich was used as the solution for membrane solute rejection.

2.2 Membrane Preparation

Polysulfone was used as a base polymer, dried at temperature of 60˚C for 24 hours in drying oven. N-menthyl-2-pyrrolidione (NMP) was used as solvent, polyethylene glycol (10 wt.%) was used as a pore forming in the casting solution. Polysulfone membrane was prepared using phase inversion method. The casting solution was cast using casting knife with range thickness 100-120µm and immersed into a coagulation bath containing distilled water as a non-solvent[8-10]. The TiO_2 coated membrane was prepared by dipping (PTL-MM01 Dip Coater) the prepared polysulfone 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 different durations (15 and 30 minutes). TiO_2 suspensions were prepared by adding different concentration of TiO_2 in distilled water and then sonicated by probe (Sonic Dismembrator FB-50) to improve the dispersion stability of TiO_2 nanoparticles. Finally, membranes were washed with distilled water and illuminated by 184 Watt UV lamp for 15 and 30 minutes.

2.3 Characterizations

The morphologies of coated flat sheet membrane surface were examined using Scanning Electron Microscopy (SEM) model JOEL JSM-6380LA. The membranes were cut into pieces of small sizes and coated with thin gold layer before scanning for producing electric conductivity[6,11].

2.4 Membrane Performance

The permeation and rejection of the membranes were measured by an ultrafiltration cross flow test at 3 bars. The pure water flux (PWF) and rejection experiments were used distilled water and humic acid respectively. Coated membranes were prepared with size 5.5 cm in diameter[12]. The solute concentrations of feed and permeate (C_f and C_p) were evaluated using UV-Vis spectrometer at a wavelength of 254nm[13-14]. PWF and rejection values were calculated using following Equation (1) and (2):

$$PWF = Q/(A \times \Delta t) \quad (1)$$

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

where Q is volume of permeate (L), A is membrane surface area (m^2), Δt is permeation time (h), R (%) is rejection percentage, C_p is concentration permeates and C_f is concentration feed.

■3.0 RESULTS AND DISCUSSION

3.1 Pure Water Flux

The result of pure water flux of coated TiO_2 nanoparticles on membrane surface is present in Figure 2. The TiO_2 concentration coated on membrane surface are increased from 0.01 to 0.05 wt.%. Analysis show that, PWF behavior has increased as suspension increased from 0.01 to 0.03 wt.% and then decreased at 0.05 wt.%. This is due to blockage of some membrane pore by TiO_2 nanoparticles at higher concentrations. As reported by similar results by A. Rahimpour *et al.*[6], flux for coated membrane with 0.05 wt.% of TiO_2 nanoparticles is slightly less compared to the membrane coated with 0.03 wt.% TiO_2. They also reported that the extended time of membrane immersion in TiO_2 suspensions caused pore plugging. As demostrates in this work, membrane coated with 0.03 wt.% of TiO_2 nanoparticles, 15 min immersion time and 15 min UV irradiation period exhibits high performance (129.04 L/m^2h). This is due to the hydrophilicity and photocatalytic properties of TiO_2 nanoparticles irradiated on polysulfone membrane surface by UV exposure. This situation also agreed by others researchers TiO_2 nanoparticles exhibited superhydrophilicity when they are exposed to UV light[15].

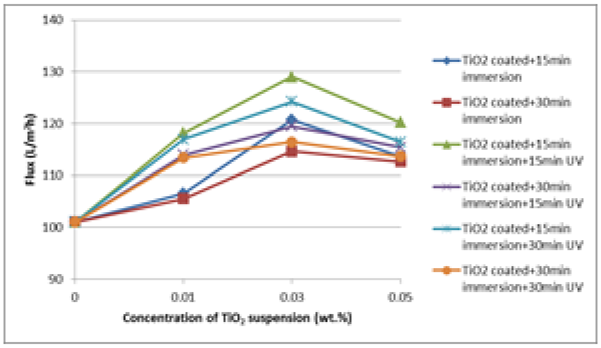


Figure 2 Pure water flux (PWF) with different of concentration of TiO_2, immersion time and irradiation period

3.2 Humic Acid Rejection

The permeation of humic acid for PSf membrane coated with different TiO_2 concentration, immersion time and irradiation period clearly presented in Figure 3. In the case of TiO_2 concentration, the low concentration (0.01 wt.%) of TiO_2 nanoparticles leads to low coverage of the membrane surface resulting in lower hydrophilicity and photocatalytic ability compared to the coated membrane of 0.03 wt.% of TiO_2. Membrane with coated of 0.05 wt.%, show slight decreased in flux due to blockage of pore by TiO_2 nanoparticles at higher concentration of the solution. This results is similar with previous findings as reported by Rahimpour *et al*.[6,15-16]. At 15 min immersion of membrane in TiO_2 suspensions showed higher permeate of humic acid compared to 30 min, due to pore plugging when immersion time of TiO_2 suspension was extended. The influence of UV irradiation period on flux behavior show that the flux of humic acid decreased by increasing irradiation period. This is due to formation of many radicals and aggregats on membrane surface after exposed to UV. Longer period of UV exposure will create the absence of hydrophilicity or hydrophobic monomers. The reaction between these recombined OH radicals, results in peroxide groups on the membrane surface[17-18]. Thus, permeate flux of 0.03 wt.% of TiO_2 coated with 15 min immersion and 15 min UV irradiated showed better performance compared to others condition. In addition, by coupling coating TiO_2 nanoparticles and UV irradiation can improve in antifouling properties of membrane surface. As described in the previous section, TiO_2 nanoparticles has the capability in decomposition and destroying the contaminations and impurities especially organic compounds by producing strong oxidant reagents[6]. TiO_2 nanoparticles exhibit superhydrophilicity property when they are exposed to UV light. However, if TiO_2 nanoparticles on the membrane surface without UV irradiation it will create fouling by blocking the fluid passage[15]. Figure 4 presents humic acid rejection result for polysulfone membrane coated with different parameter of TiO_2 nanoparticles concentration, immersion time and irradiation period. It was found that humic acid rejection performance between TiO_2 nanoparticles coated and TiO_2 nanoparticles with UV irradiated are slightly similar, the range of rejection for this studies are 98.70 to 99.07%.

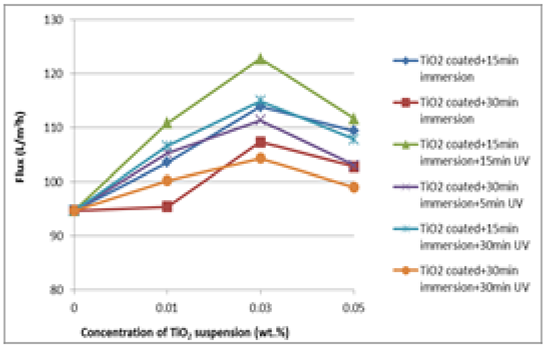


Figure 3 Humic acid permeation with different of concentration of TiO_2 suspensions, immersion time and irradiation period

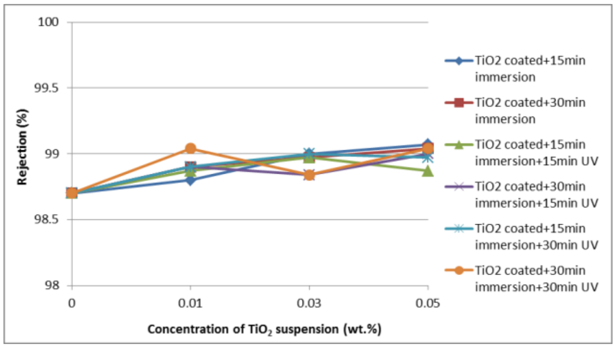


Figure 4 Humic acid rejection with different of concentration of TiO_2 suspensions, immersion time and irradiation period

3.3 Morphology

The SEM micrographs of PSf membrane coated with TiO_2 nanoparticles (0.01, 0.03 and 0.05 wt.%) by different immersion duration are presented in Figure 5. Based on observation, TiO_2 nanoparticles were not uniformly distributed on the surface membrane except for 0.03 wt.% TiO_2 nanoparticles and 15 min immersion time. However, some particles create a larger clusters. The presence of –OH gropus on the membrane surface and increase the sites for self-assembly of TiO_2 nanoparticles and is the strong factor for consistent adhesion of TiO_2 nanoparticles on the memberane surface[19] as shown previously in section 3.1 and 3.2 .

■4.0 CONCLUSION

In this present work, TiO_2 nanoparticles were coated on ultrafiltration polysulfone membrane surface and irradiated to UV light with different parameters. The pure water flux and humic acid permeation of TiO_2 nanoparticles coated and irradiated to UV showed higher performance compared to TiO_2 nanoparticles coated membrane without UV irradiation. The flux enhancement also was caused by increment of the hydrophilicity due to reaction of TiO_2 nanoparticles on the membrane surface when irradiated by UV light. The optimum conditions for preparation TiO_2 coated membrane were determined as 0.03 wt.% TiO_2 of suspension, 15 minutes immersion and 15 minutes UV irradiation with 184 Watt light.

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