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

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. 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 photocatalytic 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. 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. 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.
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 TiO₂ (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-methyl-2-pyrrolidone (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. The TiO₂ coated membrane was prepared by dipping (PTL-MM01 Dip Coater) the prepared polysulfone membrane in different concentrations of TiO₂ nanoparticles (0.01, 0.03 and 0.05 wt.%) with speed 50 mm/second. Membranes were immersed in TiO₂ suspensions for different durations (15 and 30 minutes). TiO₂ suspensions were prepared by adding different concentration of TiO₂ in distilled water and then sonicated by probe (Sonic Dismembrator FB-50) to improve the dispersion stability of TiO₂ 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.

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. The solute concentrations of feed and permeate (Cₐ and Cₚ) were evaluated using UV-Vis spectrometer at a wavelength of 254nm. PWF and rejection values were calculated using following Equation (1) and (2):

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

\[ R(\%) = \left[ 1 - \left( \frac{C_p}{C_f} \right) \right] \times 100 \]  

where Q is volume of permeate (L), A is membrane surface area (m²), Δt is permeation time (h), R (%) is rejection percentage, Cₚ is concentration permeates and Cₐ is concentration feed.

3.0 RESULTS AND DISCUSSION

3.1 Pure Water Flux

The result of pure water flux of coated TiO₂ nanoparticles on membrane surface is present in Figure 2. The TiO₂ 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 TiO₂ nanoparticles at higher concentrations. As reported by similar results by A. Rahimpour et al., flux for coated membrane with 0.05 wt.% of TiO₂ nanoparticles is slightly less compared to the membrane coated with 0.03 wt.% TiO₂. They also reported that the extended time of membrane immersion in TiO₂ suspensions caused pore plugging. As demonstrates in this work, membrane coated with 0.03 wt.% of TiO₂ nanoparticles, 15 min immersion time and 15 min UV irradiation period exhibits high performance (129.04 L/m²h). This is due to the hydrophilicity and photocatalytic properties of TiO₂ nanoparticles irradiated on polysulfone membrane surface by UV exposure. This situation also agreed by others researchers TiO₂ nanoparticles exhibited superhydrophilicity when they are exposed to UV light. 

![Figure 2 Pure water flux (PWF) with different of concentration of TiO₂, immersion time and irradiation period](image-url)
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. 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 aggregates 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. 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. 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. Figure 4 presents humic acid rejection result for polysulphone 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%.

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 groups 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 membrane surface as shown previously in section 3.1 and 3.2.

4.0 CONCLUSION

In this present work, TiO$_2$ nanoparticles were coated on ultrafiltration polysulphone 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.

Acknowledgement

The authors would like to thank to Ministry of High Education Malaysia, Postgraduate Incentive Research Grant (GIPS) and Universiti Tun Hussein Onn Malaysia for their Long Term Research Grant Scheme (LRGS vot A022) for support in providing the grant implement “High Performance of Polymeric Materials” project.

References