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RESEARCH ARTICLE

The influence of Fe doped TiO_2 as inorganic additive on the properties of polysulfone ultrafitration membrane

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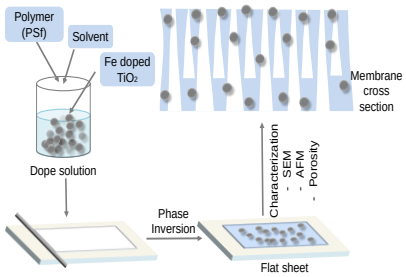
Graphical Abstract



Abstract

Recent development of utrafiltration (UF) technology for the mixed matrix polymeric membranes plays an important role to improve membrane properties. In this paper, the effects of inorganic additives prepared by green synthesis route towards polysulfone (PSf) membrane performance at different concentrations of Fe-TiO_2 (1.0wt%, 3.0wt% and 5.0wt%) have been investigated. The blended membranes were fabricated via phase inversion using PSf as based polymer, N-metyl-2-pyrrolidone (NMP) as solvent, distilled water as a non-solvent, polyethylene glycol (PEG) as pore performing agent and Fe doped TiO_2 nanomaterial as inorganic additive. The characterization and morphology of the polysulfone mixed matrix membranes were analyzed via scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle and porosity. The performances of the membrane were evaluated in terms of pure water flux (distilled water) and rejection (humic acid) by using membrane permeation testing unit. The results of microscopic images revealed that the membranes incorporated with Fe doped TiO_2 have the asymmetric structure while the number and length of finger-like pores at top layer slightly increased from 3.0 wt% to 5.0 wt%, indicating the effect of hydrophilicity. Furthermore, the increasing of Fe-TiO_2 percentages also increased the porosity of membrane, as well as rejection percentages and hydrophilicity of membrane.

Keywords: Fe doped titanium dioxide, PSf membrane, polymeric mixed-matrix membrane, membrane technology

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INTRODUCTION

Recent advancement has been focusing on the development of ultrafiltration (UF) polymeric mixed matrix membrane by incorporating inorganic nanomaterials such as titanium dioxide, silica oxide, zinc oxide and silver oxide into the polymeric membranes to improve its structure, performance, mechanical and thermal strength as well as chemical stability. Incorporating inorganic nanomaterials can increase the hydrophilicity of polymeric based membrane that usually made from hydrophobic polymers such as polysulfone (PSf) and polyethersulfone (PES) (Rahimpour, 2010) which highly exposed to the fouling problem (Freeman, 2012). Thus developing the mixed matrix membranes is one way to overcome this phenomena since by adding certain additive with desired properties can be used to tailored and controlled the properties and characteristic of the fabricated membrane.

There are various types of organic and inorganic additives that have been used widely to enhance membrane performance. TiO_2 particles is one of the most common additives that preferred been used to gain photocatalyst effect in treating wastewater problem. Besides, TiO_2 has been proven to be the most suitable for environmental applications (Liu *et al.*, 2011) among various oxide photocatalyts for its biological and chemical inertness, strong oxidizing power, cost effectiveness, and long-term stability against photo and chemical corrosions (Xiang *et al.*, 2011). The implementation of phocatalytic treatment has several advantages, such as no waste solids disposal, no energy consumption, utilization of sunlight or near UV light for irradiation which provides the lower and cheaper treatment cost, and no involvement of chemical process.

Moreover, functional properties of TiO_2 can be improved by a small amount of doping and elements such as Fe, Al, Cr, Zr and Ca that are frequently used as dopants (Tonejc *et al.*, 2001). In fact, there is much interest in Fe doped TiO_2 since the radius of Fe^{3+} is similar to that of Ti^{4+}, and Fe^{3+} may easily be incorporated within the crystal lattice of TiO_2 (Matsumoto *et al.*, 2001; Chambers *et al.*, 2001). In this work, the focus was on the addition of the Fe doped TiO_2. Fe doped TiO_2 additives would help to increase the hydrophilic properties of the membrane for the purpose to increase the performance of photocatalytic activity.

As reported by many researchers, the addition of hydrophilic inorganic materials is not only able to create and change hydrophilicity property of membrane, but also able to alter its microstructure (Koseoglu-imer, 2012; Yuliwati and Ismail, 2011). Hydrophilicity effect from additive tends to shorten the demixing time and make the membrane structure more porous (Rahimpour, 2010; Razmjou *et al.*, 2011). However, it is believed that the addition of higher amount of inorganic materials is likely to block membrane pore structure which creates greater resistance for water molecules. Furthermore, agglomeration of inorganic additives may not be completely avoided and is likely to reduce mechanical properties of membranes.

In this paper, polysufone/Fe doped TiO_2 (PSf/Fe-TiO_2) membranes were prepared via phase inversion method by blending the PSf dope solution with Fe-TiO_2 powder. The doped TiO_2 was characterized by X-ray diffraction (XRD) while the membrane properties were characterized by scanning electron microscope (SEM), atomic force microscope (AFM) and porosity. The membrane hydrophilicities were examined by contact angle measurement. In addition, the performance of membrane was investigated with respect to water permeation and humic acid rejection. The present work aimed to study the effects of Fe-TiO_2 as inorganic additive on the properties of PSf membrane. This work would be valuable for the practical application of Fe-TiO_2 in the field of photocatalysis under uv/visible light irradiation.

EXPERIMENTAL

Materials

Polysulfone (PSf) (UDEL P1700) supplied by BG Oil Chemical was used as base material for membrane, N-methyl-2- pyrrolidone (NMP) from MERCK was used as solvent and Fe doped TiO_2 in powder was used as inorganic additive in casting solution. Distilled water was used as non-solvent to induce phase inversion process. Humic acids (HA) purchased from Sigma-Aldrich was used as solute rejection evaluation.

Synthesis of Fe doped TiO_2 nanoparticles

Fe doped titanium dioxide (Fe-TiO_2) powder was obtained by using green route synthesized from *lawsonia inermis* leaf extract that act as reducing agent. 50 ml of filtered *lawsonia inermis* leaf extract and 5 ml titanium (IV) butoxide were dissolved. The solution was completely dissolved in aquoues extract with heat treatment at 50˚C. After 1 hour, 1 g of $FeNO_3$ was added and the solution was stirred for 4 hours. The solution was placed in the oven for the drying purpose. Basically the solution needed about 48 hours to dry and form a powder. After the solution was completely dried, the powder was collected. The sample was then collected by centrifugation, washed repeatedly with deionized water, dried for 12 hours at 80°C and then calcined at 300°C for 4 hours.

Membrane fabrication

The effect of the weight percentage (wt%) of Fe-TiO_2 was investigated by preparing dope solutions as presented in Table 1. The flat sheet membranes were prepared using the composition at 18 g PSf 82 g NMP and 10 g PEG with stirring for 4 h. Then, Fe-TiO_2 at different concentrations was subsequently added with continuous stirring and heating at 60℃ until the solution was completely homogenous. At first, PSf pellets were dried in an oven at 40˚C for 1 hour prior to use. The casting solutions were then prepared by dissolving PSf followed by Fe-TiO_2 powder into NMP according to formulations presented in Table 1. The NMP solvent was mechanically stirred at 60˚C with a speed of around 450 rpm. It was followed by adding PSf pellets into NMP and the mixture was continued to stir for 4 hours to achieve homogenous solution. Fe-TiO_2 powder was then added slowly into solution and the stirring process was continued for another 10 min. The solutions were transferred into a dry clean bottle before putting into an ultrasonic bath for air bubble removal. The dope solution was then casted onto a clean glass plate using film knife with gap of 120 µm before immersing into a coagulation bath containing only pure water. At last, the flat sheet membranes were dried for 24 hours before testing.

Table 1 Dope formulation in membrane fabrication.

No	PSf (g)	NMP (g)	PEG (g)	Fe-TiO2 (wt %)
1	18	82	10	1.0
2	18	82	10	3.0
3	18	82	10	5.0

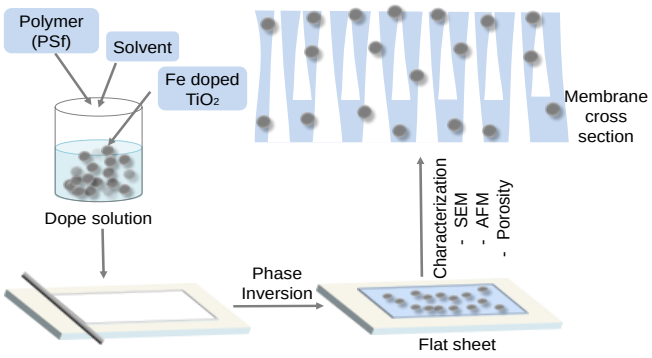

Fig. 1 Schematic diagram for preparation of PSf/Fe-TiO_2 mebrane.

Membrane characterization

X-ray diffraction (XRD)

Compatibility of PSf/Fe-TiO_2 was investigated with PANanalytical's instrument Cu Kα radiation (λ=0.1540 nm). The scanning rate was fixed at 0.02˚/s and 2θ range from 10˚ to 80˚. The analysis was important to investigate the changes on membrane properties upon the addition of Fe-TiO_2. The XRD data could also be used to identify whether the added additive was in crystalline or amorphous state.

Scanning electron microscopy (SEM)

The cross-sectional structures of membranes were observed using SEM (JEOL JSM6380LA). The samples were prepared by breaking the films into small piece in liquid nitrogen. Samples films were then sputtered with gold to 150 nanometers in thickness (Yunus *et al.*, 2014; Harun *et al.*, 2013) before subjecting to SEM. The image samples were viewed at an accelerating voltage of 10 kV.

Atomic force microscopy (AFM)

The topology of membrane top surface was characterized using AFM. Each membrane sample was cut into small pieces using sharp razor stainless steel blade, followed by fixing the sample onto magnetic disk using double-sided adhesive tape. A tapping mode AFM in air was used to take the micrograph. The measurement was performed under ambient atmospheric conditions. At least three scans were conducted for each sample to yield average result. Membrane roughness values and its standard deviation were then determined based on 5µm² scanning area.

Membrane hydrophilicity and porosity

To determine membrane porosity, the membranes were cut in a square shape in the 2cm x 2cm area. Then, membranes were immersed into distilled water at 25˚C for 24 hours. Membrane in wet state was weighted in electronic balance after wiping carefully the surfaces with the clean tissue, w_w.This wet membrane was then dried in an oven at 60˚C for 24 hours. The membrane was re-weighted in dried state, w_d. Membrane porosity was calculated using the following equation.

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$$\varepsilon = \frac{w_w - w_d}{\rho_w \times v} \quad (1)$$

where ρ_w is density of pure water at room temperature (g/cm³) and v is the volume of membrane in wet state (cm³) (Basri *et al.*, 2012; Wongchitphimon *et al.*, 2011).

Membrane performance evaluation

The performance of filtration of PSf/Fe-TiO_2 UF membrane was evaluated by UF cross flow filtration method with respect to pure water permeation flux (PWP) and solute rejection (SR). All the experiments were performed at ambient temperature. The flat sheet membrane was cut into a circular geometry before placing it in membrane permeation testing unit. The tested area for experiment was approximately 2.0 x 10^{-3} cm². Prior to any measurement, the membrane was pre-pressurized at 4 bar with distilled water for 10 min. For each membrane sample, at least three measurements were taken to obtain average value. The pure water flux was calculated using Eq (3).

$$PWF = \frac{Q}{A \,.\, \Delta t} \quad (3)$$

where Q is the volume permeate (L) PWP = J_w in unit (L/m²h), A is membrane surface area m² and Δt is permeation time (h).

Meanwhile, the rejection test was performed using 0.2 g/L humic acid (HA) aqueous solution as feed and the membrane rejection efficiency was determined using formula as Eq. (4).

$$R(\%) = \left[1 - \left(\frac{C_p}{C_f}\right)\right] x\, 100 \quad (4)$$

Where C_p is solute concentration in permeate stream and C_f is solute concentration in feed stream.

In order to study the effect of fouling on PSf/ Fe-TiO_2 membrane, the membranes were subjected to a cross-flow filtration experiment (Yunus *et al.*, 2014). To compare flux decline among the membranes prepared, relative fluxes were defined as the relation of the permeate flux to the pure water flux of the respective membrane as expressed in Eq. (5).

$$RF = \frac{J}{J_o} \quad (5)$$

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD)

The synthesized Fe doped TiO_2 (Fe-TiO_2) powder was characterized by using X-Ray Diffraction (XRD). XRD Bruker D8 Advance was used to carry out the Fe-TiO_2 characterization process. Fig. 2 shows the XRD pattern for the powder synthesized from the *lawsonia inermis* leaf extract using the green route method. Based on the result, the synthesized Fe-TiO_2 was composed of anatase as the predominant phase.

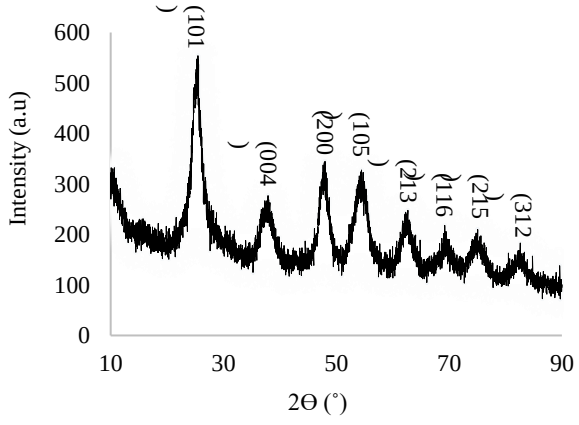

Fig. 2 XRD pattern of Fe-TiO_2.

The XRD pattern of Fe doped TiO_2 has crystalline characteristic peaks at 2Θ of 25.28˚, 37.80˚, 48.05˚, 53.89˚, 62.12˚, 68.76˚, 75.03˚, and 83.15, corresponding to (101), (004), (200), (105), (213), (116), (215) and (312) lattice planes (JCPDS No 21-1272) and similar to the peaks of Fe-TiO_2 from previous researchers with a slight shift (Yang *et al.*, 2007; Mohammed *et al.*, 2016; Naeem and Ouyang, 2010; Sood *et al.*, 2015). This shift and dispersion peak variation of Fe-TiO_2 might be owing to the interfacial interactions between Fe-TiO_2 nanoparticles and amorphous structure of polymers membrane which was in good agreement with the macropores foaming of membrane in SEM analysis (Wang *et al.*, 2017).

Scanning Electron Microscopy (SEM)

In order to understand the effects of Fe-TiO_2 on the PSf membrane morphology, the cross-sectional structure for membranes was observed by SEM and the results are presented in Fig. 3. It is observed that all membranes exhibited asymmetric structure that consisted of dense top layer supported by microporous bottom layer. The top layer acts as separating layer while bottom layer provides mechanical strength to membrane during filtration process. Comparison among these membranes, it is observed that the membrane structure was altered upon addition of inorganic additive that presented at different concentrations. By increasing the concentration of additive, the spongy pore structures at the wall fingerlike and bottom layer were also increased, indicating the existence of hydrophilicity effect. The dense layer also became thinner. These results supported previous research by Nasrollahi *et al.*, (2018) where the structure of their fabricated membrane samples almost showed a high similarity but when additive (CZN) with higher value of concentration was added to the casting solution, the structure slightly changed and increased the membrane porosity.

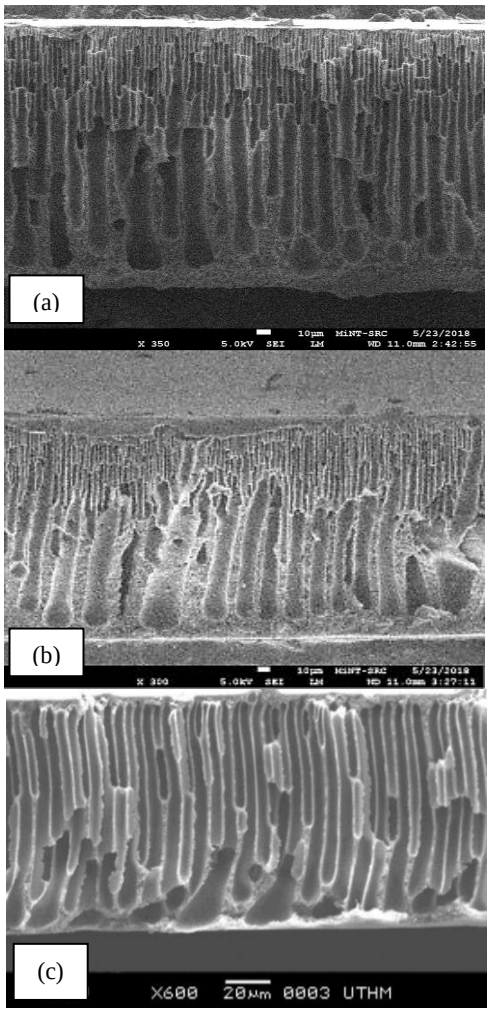

Fig. 3 SEM images of (a) PSf/Fe-TiO_2 (3.0wt%) and (b) PSf/Fe-TiO_2 (5.0wt%) (c) PSf/Fe-TiO_2 (0.0wt%) as control membrane.

The cross sectional image results in Fig. 3 reveals that PSf/ Fe-TiO_2 membrane experienced the extended finger-like structure from top to the bottom layer especially at higher concentration. This membrane also came with thinner dense layer and also larger porosity at higher loading of Fe-TiO_2 due to the hydrophilicity effect. In general, the formation of membrane has strongly linked to solubility and diffusivity of solvent (Ma *et al.*, 2012). At higher concentration with strong effect of hydrophilicity NMP will diffuse easily from dope solution into water which causes instantaneous PSf to be solidified leading to formation of more porous structure.

Atomic Force microscopy (AFM)

Fig. 4 presents the 3D AFM images of the prepared membranes. The high peaks indicated as bright region nodules in the AFM images, while the pores were labelled as dark area. As shown, nodular-like structure was established on the membrane top surface. Based on data presented in Table 2, PSf/Fe-TiO_2 (5.0 wt %) membrane showed the highest roughness value with mean roughness parameter obtained was 22.97 nm, following by PSf/Fe-TiO_2 (3.0 wt %) and PSf/Fe-TiO_2 (1.0 wt %) with Ra values of 16.01 nm and 12.68 nm, respectively. As the percentage concentration of the hydrophilic Fe-TiO_2 nanoparticles was increased, the agglomeration and sedimentation of the additive at the surface would take place, thus increasing the surface roughness. Overall, it was found that all the PSf/ Fe-TiO_2 membranes have more dark regions on the surface compared to the bare PSf membrane. Higher surface roughness will provide more surface area that assists the permeation mechanism (Goodyer and Bunge, 2012).

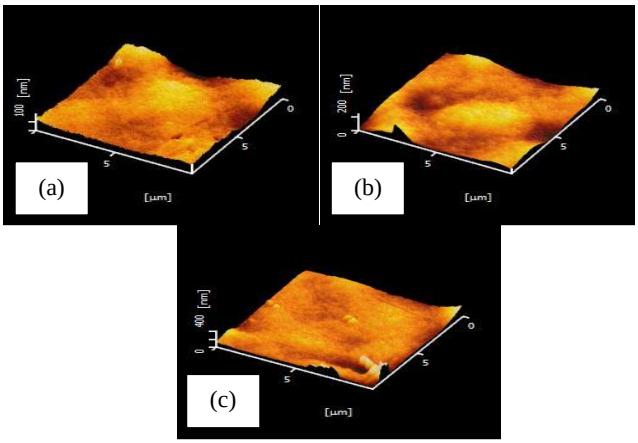

Fig. 4 AFM images of PSF membrane effect by Fe-TiO_2 a) Ra: 12.68 nm [PSf/Fe-TiO_2 (1.0 wt %)] b) Ra: 16.01 nm [PSf/Fe-TiO_2 (3.0 wt %)] c) Ra: 22.97 nm [PSf/Fe-TiO_2 (5.0 wt %)]

Table 2 Surface roughness of the PSf/Fe-TiO_2 mixed matrix membrane.

Membrane sample	Surface roughness, Ra (nm)
PSf/Fe-TiO2 (1.0 wt%)	12.68
PSf/Fe-TiO2 (3.0 wt%)	16.01
PSf/Fe-TiO2 (5.0 wt%)	22.97

However, experimental studies also revealed that higher concentration of particles also would block and able to restrain the permeate flow and thus, producing contradictory results in which flux did not always increase with surface roughness enhancement. In fact, higher surface roughness provides more surface area for foulant attachments compare to a smooth surface (Woo *et al.*, 2015; Bildyukevich *et al.*, 2017). Thus addition of additive particles into membrane structure always need to be controlled to ensure the effect of additive will not sacrifice the performance of membrane.

Membrane hydrophilicity and porosity

Fig. 5 compares the water contact angle of the prepared membranes. Results indicate that all mixed matric membranes with Fe-TiO_2 concentration have relatively lower contact angle compared to the bare PSf membrane, suggesting the improvement of surface hydrophilicity. Addition of lower concentration of Fe-TiO_2 (up to 1 wt %) has enhanced the membrane hydrophilicity. This was in line with the SEM and AFM results which indicated that the addition of Fe-TiO_2 would possess more finger-like and porous structure. However, with further increasing of Fe-TiO_2 concentration, the hydrophilicity of membrane was negatively affected, owing to the possible agglomeration of Fe-TiO_2 particles. This agglomeration will reduced hydrophilicity effect that can be associated to the slightly changes of contact angle value at higher concentration of additive particles. In fact, the agglomeration is also able to lessen the pore formation ability (see AFM analysis) as well as block the pores (as viscosity was increased as more Fe-TiO_2 was added). These two factors indirectly will affect membrane water flux.

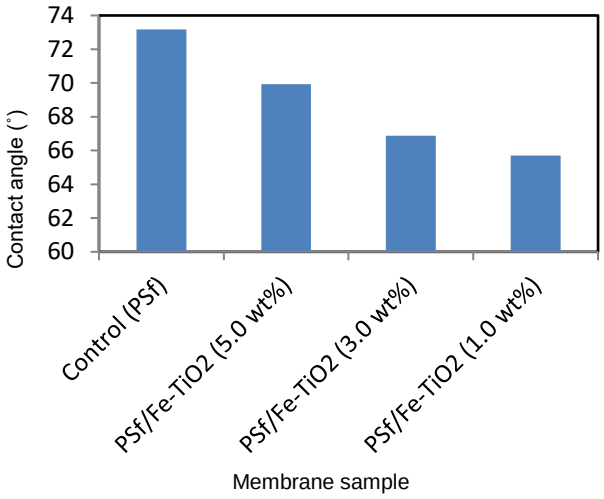

Fig. 5 Contact angle of membrane sample at different concentrations (wt%) of Fe-TiO_2.

Table 3 Porosity of the PSf/Fe-TiO_2 mixed matrix membrane.

Membrane sample	Porosity
Control PSf without Fe-TiO_2	0.0329
PSf/Fe-TiO2 (1.0 wt%)	0.0344
PSf/Fe-TiO2 (3.0 wt%)	0.0357
PSf/Fe-TiO2 (5.0 wt%)	0.0369

The porosity values of the fabricated PSf membrane incorporated with and without Fe-TiO_2 are shown in Table 3. It is shown that all PSf/ Fe-TiO_2 membranes were tend to have higher porosity values than that of bare PSf membrane and this was in agreement with the SEM analysis. As discussed in previous sections, the addition of 3 wt% Fe-TiO_2 in PSf membrane was able to create more finger-like and bigger macrovoid pores at top surface and bottom layer, which contributing to higher porosity value. Nonetheless, when Fe-TiO_2 concentration was increased from 1 to 5 wt%, the top dense layer became thicker and less finger-like structure was developed, which resulting in the reduction of membrane porosity as shown by SEM images. The concentration of Fe-TiO_2 is the main factor that affects the porosity of the membranes. When the concentration of Fe-TiO_2 was increased towards the maximum at 5.0 wt%, the porosity of the membrane was also increased due to the hydrophilic nature of Fe-TiO_2 that responsible for the fast exchange between solvent and non-solvent during phase inversion process which leading to the extended porosity and the changes in macrovoids structure. These results were in line with the increase of hydrophilicity properties that indicated hydrophilicity as the main contributor to the increased finger-like structure and macrovoid formation at top, sub-layer and bottom layer. In addition, a more porous membrane will influence its hydrophilicity

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which then leads to the fast inflow and out-flow of solvent during phase inversion (Basri *et al.*, 2012).

Addition of Fe-TiO_2 might also reduce the mean pore radius compared to the bare PSf membrane. The formation of smallest mean pore radius was given by the membrane blended with 1 wt % of Fe-TiO_2 that has smaller finger-like pore and thin surface layer. This result was in line with the previous discussion and other related works (Yuliwati *et al.*, 2011) that showed hydrophilic effect could alter the asymmetric membrane structure by generating smaller pore. However, by increasing Fe-TiO_2 concentration, hydrophilicity effect of Fe-TiO_2 was reduced due to the increase of dope viscosity. Increased dope viscosity will slightly slow down the demixing process that created by the delayed demixing mechanism that leads to the formation of a slightly thicker and bigger finger-like structure during membrane precipitation (Ma *et al.*, 2012).

Water permeability and rejection test

The membrane performance was examined in terms of water permeability and solute rejection. Table 4 shows the performance for all the PSf membranes prepared. The results demonstrated that water permeability was increased as Fe-TiO_2 concentration was increased. This improvement can be attributed by the improvement of finger-like structure and macrovoid morphology as observed by SEM images and also by the increase of hydrophilic characteristic obtained from contact angle measurement.

Table 4 The membrane performance.

Membrane sample	Permeation (L/m^{2}h)	Rejection (%)
PSF/Fe-TiO2 (1.0 wt%)	204.19	66.2
PSF/Fe-TiO2 (3.0 wt%)	319.72	71.52
PSF/Fe-TiO2 (5.0 wt%)	325.67	70.81

In order to explore the fouling resistance of PSf/Fe-TiO_2 membrane, filtration experiments were conducted using humic acid as a model organic foulant in aqueous solution. The 0.2 g/L of humic acid was selected in this test. Results showed that the addition of Fe-TiO_2 could enhance the fouling resistance considerably. This phenomenon is due to the increase of PSf/Fe-TiO_2 membrane hydrophilicity which reduces the adsorption of organic molecules onto the membrane. Table 4 also shows the humic acid rejection of the membranes prepared. It was found that the humic acid rejection was increased with increasing of Fe-TiO_2 content from 1 to 3 wt%. However, the humic acid rejection was only slightly decreased as Fe-TiO_2 concentration was increased from 3 to 5 wt%. The increase and reduction of rejection values are most likely due to the reduction and increment of mean pore size, respectively. In general, the mean pore radius has also contributed to the decrease of humic acid rejection as larger pore size will allow more humic acid to pass through the membrane. The results also suggested that an optimum concentration of 3 wt% addition has increased the relative flux and improved other properties and rejection as well, but further increasing Fe-TiO_2 concentration would not improve flux and membrane performance and properties.

CONCLUSION

In this work, asymmetric PSf/Fe-TiO_2 membranes were prepared via phase inversion method by using immersion precipitation technique. The effects of Fe-TiO_2 concentration (1, 3 and 5 wt%) on the properties of PSf membrane were investigated. Based on the results obtained, it was revealed that the presence of Fe-TiO_2 in the PSf membrane could enhance the membrane performance with respect to water permeation and humic acid rejection. Nonetheless, the use of relatively high concentration of Fe-TiO_2 (1 - 5 wt%) might reduce membrane permeability and hydrophilicity. The morphology of all fabricated membranes indicated the similar asymmetric structure with dense top surface and finger-like macrovoid at the sub-layer. The growth of more finger-like structures and macrovoids at the top and bottom layers could be clearly seen at low concentration of Fe-TiO_2. The change in the structure also resulted in smaller contact angle, but increase in porosity and surface roughness values. It was also found that further increasing of Fe-TiO_2 content would slightly reduce membrane performance and properties. Observation of the results also revealed that higher concentration of additive did not only reduce hydrophilicity effect but it also slightly affected demixing process as well as blocked the permeation flow and reduced the membrane performance.

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REFERENCES

Basri, H., Ismail, A. F., Aziz, M. 2011. Polyethersulfone (PES)–silver composite UF membrane: Effect of silver loading and PVP molecular weight on membrane morphology and antibacterial activity. *Desalination*, *273*(1), 72–80.

Basri, H., Ismail, A. F., Aziz, M. 2012. Microstructure and anti-adhesion properties of PES/TAP/Ag hybrid ultrafiltration membrane. *Desalination*. *287*, 71–77.

Bildyukevich, A. V., Plisko, T. V., Liubimova, A. S., Volkov, V. V, Ususky, V. V. 2017. Hydrophilization of polysulfone hollow fibre membranes via addition of polyvinylpyrrolidone to the bore fluid. *Journal of Membrane Science*, *524*, 537-549.

Chambers, S. A., Thevuthasan, S., Farrow, R. F. C., Marks, R. F., Thiele, J. U., Folks, L., Samant, M. G., Kellock, A. J., Ruzycki , N., Ederer, D. L., Diebold, U. 2001. Epitaxial growth and properties of ferromagnetic co-doped TiO_2 anatase. *Applied Physic Letters*, *79*, 3467–3469.

Freeman, B. 2012. Introduction to membrane science and technology. By Heinrich Strathmann. *Angewandte Chemie Internatial Edition*, *51*(38), 9485–9485.

Goodyer, C. E., Bunge, A. L. 2012. Mass transfer through membranes with surface roughness. *Journal of Membrane Science*, *409-410*, 127-136.

Harun, Z., Shohur, M. F., Yunos, Z., Jamalludin, M. R., Ismail A. F. 2013. The effect of crystalline rice husk silica on polysulfone membrane for wastewater treatment. *Applied Mechanic and Materials*, *328*, 798–801.

Kim, I., Yun, H., Lee, K. 2002. Preparation of asymmetric polyacrylonitrile membrane with small pore size by phase inversion and post-treatment process. *Journal of Membrane Science*, *199*(1-2), 75–84.

Koseoglu-imer, D. Y. 2012. The production of polysulfone (PS) membrane with silver nanoparticles (AgNP): Physical properties, filtration performances, and biofouling resistances of membranes. *Journal of Membrane Science*, 428, 620–628.

Liu, S. W., Yu, J. G., Jaroniec, M. 2011. Anatase TiO2 with dominant high-energy {001} facets: synthesis, properties, and applications. *Chemistry of Materials*, *23*(18), 4085– 4093.

Ma, Y., Shi, F., Wang, Z., Wu, M., Ma, J., Gao, C. 2012. Preparation and characterization of PSf/clay nanocomposite membranes with PEG 400 as a pore forming additive. *Desalination*, *286*, 131–137.

Matsumoto, Y., Murakami, M., Shono, T., Hasegawa, T., Fukumura, T., Kawasaki, M., Ahmet, P., Chikyow, T., Koshihara, S. Y., Koinuma, H. 2001. Room-temperature ferromagnetism in transparent transition metal-doped titanium dioxide. *Science*, *291*(5505), 854–856.

Mohamed, M. A., Salleh, W. N. W., Jaafar, J., Ismail, A. F., Mutalib, M. A., Sani, N. A. A., Asri, S. E. A. M., Ong, C. S. 2016. Physicochemical characteristic of regenerated cellulose/N-doped TiO2 nanocomposite membrane fabricated from recycled newspaper with photocatalytic activity under UV and visible light irradiation. *Chemical Engineering Journal*, *284*, 202–215.

Naeem, K., Ouyang, F. 2010. Preparation of Fe^{3+}-doped TiO_2 nanoparticles and its photocatalytic activity under UV light. *Physica B*, *405*(1), 221-226.

Nasrollahi, N., Vatanpour, V., Aber, S., Mahmoodi, N. 2018. Preparation and characterization of a novel polyethersulfone (PES) ultrafiltration membrane modified with a CuO/ZnO nanocomposite to improve permeability and antifouling properties. *Separation and Purification Technology*, *192*, 369-382.

Rahimpour, A., Madaeni, S. S., Mansourpanah, Y. 2010. Fabrication of polyethersulfone (PES) membranes with nano-porous surface using potassium perchlorate (KClO4) as an additive in the casting solution. *Desalination*, *258*(1-3), 79–86.

Razmjou, A., Mansouri, J., Chen, V. 2011. The effects of mechanical and chemical modification of TiO2 nanoparticles on the surface chemistry,

structure and fouling performance of PES ultrafiltration membranes. *Journal of Membrane Science*, *378*(1-2), 73–84.

Sood, S., Umar, A., Mehta, S. K., Kansal, S. K. 2015. Highly effective Fe-doped TiO2 nanoparticles photocatalysts for visible- light driven photocatalytic degradation of toxic organic compounds. *Journal of Colloid and Interface Science*, 450, 213–223.

Thirumavalavan, M., Huang, K.-L., and Lee, J.-F. 2013. Preparation and morphology studies of nano zinc oxide obtained using native and modified chitosans. *Materials (Basel)*, *6*(9), 4198–4212.

Tonejc, A. M., Djerdi, I., Tonejc, A. 2001. Evidence from HRTEM image processing, XRD and EDS on nanocrystalline iron-doped titanium oxide powders. *Material Science and Engineering: B*, *85*(1), 55–63.

Tu, Y. F., Huang, S. Y., Sang, J. P., Zou, X. W. 2010. Preparation of Fe-doped TiO2 nanotube arrays and their photocatalytic activities under visible light. *Materials Research Bulletin*, *45*(2), 224–229.

Wang, Q., Yang, C., Zhang, G., Hu, L., Wang, P. 2017. Photocatalytic Fe doped TiO2/PSF composite UF membranes: Characterization and performance on BPA removal under visible-light irradiation. *Chemical Engineering Journal*, *319*, 39–47

Wongchitphimon, S., Wang, R., Jiraratananon, R., Shi, L., Heng, C. 2011. Effect of polyethylene glycol (PEG) as an additive on the fabrication of polyvinylidene fluoride-co-hexafluropropylene (PVDF-HFP) asymmetric microporous hollow fiber membranes. *Journal of Membrane Science*, *369*(1-2), 329–338.

Woo, S. H., Park, J., Min, B. R. 2015. Relationship between permeate flux and surface roughness of membranes with similar water contact angle values. *Separation and purification technology*, *146*, 187-191.

Xiang, Q. J., Yu, J. G., and Wong, P. K. 2011. Quantitative characterization of hydroxyl radicals produced by various photocatalysts. *Journal of Colloid and Interface Science*, *357*(1), 163–167.

Yang, Y., Zhang, H., Wang, P., Zheng, Q., Li, J. 2007. The influence of nano-sized TiO2 fillers on the morphologies and properties of PSF UF membrane. *Journal of Membrane Science*, *288*(1-2), 231–238.

Yuliwati, E., Ismail, A. F. 2011. Effect of additives concentration on the surface properties and performance of PVDF ultrafiltration membranes for refinery produced waste- water treatment. *Desalination*, *273*(1), 226–234.

Yunos, M. Z., Harun, Z., Basri,, H., Ismail, A. F. 2014. Studies on fouling by natural organic matter (NOM) on polysulfone membranes: Effect of polyethylene glycol (PEG). *Desalination*, *333*(1), 36–44.

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